THE CHEMICAL AND PHYSICAL PROPERTIES OF HYDROGEN PEROXIDE — NITRIC ACID SOLUTIONS

A Thesis

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by

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DIAGRAMS AND GRAPHS

INTRODUCTION

The work to be described in the following pages may be conveniently divided into two parts, the first section dealing with various chemical reactions resulting from the action of hydrogen peroxide — nitric acid mixtures on organic compounds and identification of the products obtained, the second with physical measurements of hydrogen peroxide mixtures, principally of refractive index. The latter part is somewhat preliminary in nature, the ultimate aim being to obtain a means of determining the structure of hydrogen peroxide and the various peracids which are formed by its action upon different acids, both organic and inorganic.

The refractive index measurements were undertaken owing to several accidents experienced by the author and also due to his marked sensitivity to several organic compounds which were investigated. Thus in some instances, products were obtained which could not be further identified.

PART 1

HISTORICAL

Hydrogen peroxide has been employed most extensively as an oxidizing agent, ever since its discovery by Thénard in 1818. It was but a short time before its oxidizing properties were fully appreciated, and numerous investigators seized upon it and proceeded to react it with every conceivable type of compound. Apparently there was no attempt made in this connection to consider experimental conditions such as concentration, medium, temperature, etc. The advantages of hydrogen peroxide were soon recognized, for its action is comparatively mild, the reaction is easily controlled, and water is the sole reaction product after oxidation has occurred. It was but a natural result, therefore, that a voluminous mass of literature accumulated, a literature which it has been practically impossible to classify. It has been likewise impossible to apply any of these data in a manner that might lead to a possible mechanism for this reaction of oxidation. Furthermore, with conditions as they existed, the mode of action of hydrogen peroxide could not be correlated with that of other oxidizing agents, such as potassium permanganate.

Both hydrogen peroxide and potassium permanganate have been widely used in neutral, acid and alkaline media, the manner of oxidation often being governed by the condition of the medium. As a rule, hydrogen peroxide is relatively unsatisfactory in the presence of alkali owing to its ready decomposition. In an attempt to clarify these data, to make some kind of comparison between hydrogen peroxide and potassium permanganate as oxidizing agents, and to correlate the different experimental conditions, Hatcher and co-workers (1) carried out a large number of experiments. Organic acids were employed, the progression being from the simple to the more complex acids, both mono- and dicarboxylic. Great care was observed as to temperature, concentration, and the absence of catalysts of any description. To this latter end, scrupulously clean vessels and carefully purified acids were used, the hydrogen peroxide being distilled free from all inhibitors. Ultimately it was possible to arrive at a number of useful and important conclusions. Resulting from these experiments was the determination of a mechanism for oxidation; practically all cases studied involving organic acids and hydrogen peroxide, except for one or two instances, showed that the rates of reaction most closely approximated the requirements for the monomolecular equation.

So well has this work been accomplished that there remains but little more to do in this direction, except perhaps to investigate the higher and more substituted acids. In the formulation of the mechanism of the reaction, it was observed that a complex between acid and hydrogen peroxide was formed, which then decomposed according to the condition of the medium. It was believed at first that this complex was either an addition product of acid and peroxide (which later broke down more slowly to form a peracid) or the peracid itself. Further investigation proved the former to be the case.

Peracids, with which this thesis is mainly concerned, have long been known, but it is only within comparatively recent years that their use as oxidizing agents has really been appreciated. To-day, certain peracids are being employed more and more frequently in oxidation processes, producing excellent results.

In 1864, Brodie (2) reported the preparation of peracids from the hydrolysis of organic peroxides. This may be represented by:

$$(CH_3CO)_2O_2 + HOH \longrightarrow CH_3COOH + CH_3COOOH \qquad (1)$$

Some time after, Baeyer and Villiger (3) observed

the formation of peracetic acid which resulted from the action between Caro's acid and acetic acid.

$$CH_3COOH + H_2SO_5 \longrightarrow CH_3COOOH + H_2SO_4 \qquad (2)$$

Following Brodie's work to a certain degree, Clover and Richmond (4) hydrolyzed organic peroxides and obtained peracids. In this instance, further study of the reaction was made and these authors came to the conclusion that the peracid when formed, hydrolyzed slowly to acid and hydrogen peroxide.

$$CH_3COOOH + HOH \longrightarrow CH_3COOH + H_2O_2 \qquad (3)$$

Clover and Richmond stressed the fact that they regarded this last reaction as being irreversible.

In a subsequent communication, Clover and Houghton (5) were able to present a method for the determination of hydrogen peroxide, peracid and organic acid in the presence of each other. It remained for D'Ans and Friedrich (6) and Hatcher and co-workers (1) to show that the action between acid and peroxide to peracid and water is reversible.

Up to this time, peracids, chiefly peracetic acid, had been obtained by (a) the hydrolysis of organic peroxides, and (b) the action of Caro's acid upon organic acids; methods, such as the treatment of the anhydride or acid with hydrogen peroxide had not yet been attempted.

D'Ans and Friedrich (6) added a further contribution to this work when they perceived the formation of peracetic acid from acetic acid and hydrogen peroxide.

$$CH_3COOH + H_2O_2 \longrightarrow CH_3COOOH + H_2O \qquad (4)$$

Good yields were obtained also from the interaction of acetyl chloride and concentrated hydrogen peroxide.

$$CH_3COCl + H_2O_2 \longrightarrow CH_3COOOH + HCl \qquad (5)$$

D'Ans and Frey (7) extended this method of preparation somewhat to include the higher fatty acids, and succeeded in identifying the peracids of formic, acetic, propionic and butyric acids. In these instances, however, a small amount of sulphuric acid was used as a catalyst. Performic acid was produced very quickly and in good yield, but it hydrolyzed rapidly. The other peracids formed more slowly and were not so readily hydrolyzed.

Although varying concentrations of acid were used, and the solutions allowed to stand for different lengths of time, the percentage of peracid formed was approximately the same for a particular acid. This fact again showed that there was a reversible reaction possible, contrary to the statements of Clover and Richmond.

As has been already mentioned, Clover and Richmond were able to develop a method for the determination of

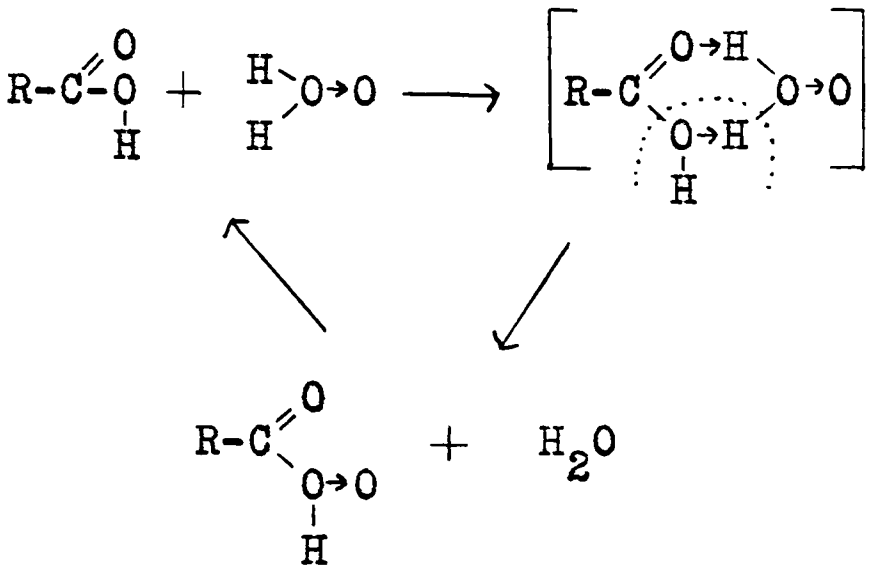
peracid, in the presence of the other components. This procedure was further developed by Hatcher and others (1) to give conclusive evidence for the existence of performic, peracetic, perpropionic, perbutyric, perglycollic, perlactic and perisobutyric acids, formed from the respective acids and hydrogen peroxide in the course of oxidation.

With accurate and correlated information concerning the monocarboxylic acids on hand, the next step was to observe the behaviour of the dicarboxylic acids. Hatcher and Mueller (8) attacked this problem and were, after a short interval, able to place the results that had arisen from this investigation in line with those already obtained.

At about the same time as the work of straight oxidation with hydrogen peroxide was being carried out, conductivity measurements were made on carefully prepared solutions of these acids in hydrogen peroxide. It was observed that the electrical resistance of these solutions increased so that in time they assumed constant values. Thus was it learned that the peracid formed between the components, hydrogen peroxide and acid, was quite un-ionized. Hatcher and Powell (9) postulated the following reaction to take place:

$$HX + H_2O_2 \longrightarrow (HX.H_2O_2) \longrightarrow HOX + H_2O \qquad (6)$$

First there is formed an un-ionized addition complex which more slowly breaks down to form the peracid, also un-ionized. In the case of a simple acid, a 6-membered chelate ring may be formed:



(7)

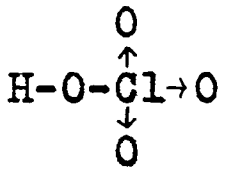
Although, as mentioned above, peracids have long been known, and some use was made of them as oxidizing agents, not a great deal was done with them. It is only fairly recently that they were again taken up and employed successfully as reagents. N. Prilezhaev (10) did indeed carry out a few oxidations with perbenzoic acid and found it to be a good reagent for the oxidation of double bonds in hydrocarbons. In all his communications, Prilezhaev refers to the peracid as a peroxide. Böeseken (11) has submitted a long series of papers in recent years, using both peracetic and perbenzoic acids for the oxidation of double bonds in all types of compounds. More recently, phthalic monoperacid (12) has been successfully employed for this purpose.

Closely associated with the peracid formation described above, is the well-known phenomenon of autoxidation of certain aldehydes to form peracids. Benzaldehyde behaves in this manner and was first observed by Baeyer and Villiger (13) and later by Wieland (14), and has since been the classical example to describe this reaction. In the past, however, insufficient attention has been paid to such behaviour on the part of aliphatic aldehydes. Baeyer and Villiger (15) observed the formation of a complex between hydrogen peroxide and acetaldehyde; this reaction was further investigated by Wieland (16). This latter author (17) also found that complexes were formed between hydrogen peroxide and formaldehyde, which appeared to possess peracid properties. More recently, Hatcher, Steacie and Howland (18) investigated the high temperature oxidation of acetaldehyde and found a complex to be formed which possessed properties characteristic of a peracid. They suggested the following reaction to take place:

$$CH_3CHO + O_2 \rightleftharpoons (CH_3CHO.O_2) \qquad (8)$$

Up to this point, the development has concerned only the organic peracids. Peracids also exist in the inorganic field, and have been widely used as oxidizing agents.

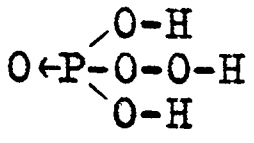
Perchloric acid contains more oxygen than any of the other oxychlor acids, hypochlorous, chlorous and chloric. It is an oxidizing agent, although less active than chloric, but is considerably more stable. Actually it is not a per-acid in the true sense of the word. It is fully ionized in aqueous solution, and even preserves its ionization in non-aqueous solvents. In ether, for example, it is dissociated one hundred times more than hydrochloric acid, and may well be called the strongest of known acids. Its structure is usually given as:



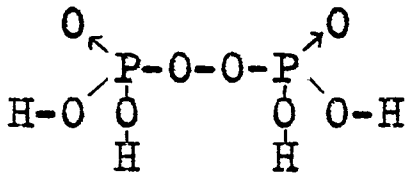
In the case of phosphoric acid, there are two per-acids; permonophosphoric acid, which is quite definitely known, and perdiphosphoric acid, which has been reported. Both have been obtained, like persulphuric acid, by electrolytic methods. The former may also be prepared by the interaction of phosphorus pentoxide and hydrogen peroxide:

$$P_2O_5 + 2H_2O_2 + H_2O \longrightarrow 2H_3PO_5 \qquad (9)$$

Permonophosphoric acid is said to resemble Caro's acid somewhat. The formulae for these acids have been proposed as follows:



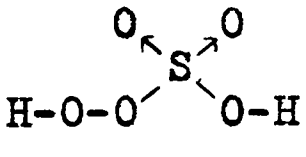
Permonophosphoric acid



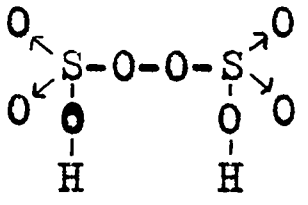
Perdiphosphoric acid

and are purely conjectural.

In the case of sulphuric acid, there are also two peracids, perdisulphuric and permonosulphuric acids. Both are strong oxidizing agents, the former being the more stable. Potassium perdisulphate, for example, is a very stable salt, whereas no salt of permonosulphuric acid has yet been prepared pure. Permonosulphuric acid, better known as Caro's acid, is a true peracid, and liberates iodine from potassium iodide immediately. Perdisulphuric acid, on the other hand, reacts but slowly in a manner similar to hydrogen peroxide itself. The structures usually assigned to these acids are:



Caro's acid



Perdisulphuric acid

Berthelot (19) obtained a compound from oxygen and sulphur trioxide under slight pressure and exposed

to the silent electric discharge, which he claimed to be sulphur heptoxide (S_2O_7). This supposed sulphur heptoxide, when passed into water, resulted in a solution which Berthelot observed to oxidize potassium iodide immediately with the formation of free iodine. The reaction might proceed in the following manner:

$$S_2O_7 + 2H_2O \longrightarrow H_2SO_5 + H_2SO_4 \qquad (10)$$

As an intermediate, perdisulphuric acid may be formed:

$$S_2O_7 + H_2O \longrightarrow H_2S_2O_8 \qquad (11)$$

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4 \qquad (12)$$

Berthelot (20) also observed the formation of a strongly oxidizing acid from sulphuric acid and hydrogen peroxide.

Caro, (21) in 1898, obtained a similar oxidizing solution from cold concentrated sulphuric acid and ammonium perdisulphate. There appears to be a curious reaction of hydrolysis in this instance:

$$HO_3SOOSO_3H + H_2O \longrightarrow HO_3SOOH + H_2SO_4 \qquad (13)$$

The reaction was investigated by Baeyer and Villiger (22) who stated that it was apparently a monomolecular reaction if a large excess of concentrated sulphuric acid be used.

These workers were responsible for calling permonosulphuric acid "Caro's acid".

Arhle (23) was able to prepare Caro's acid in a pure condition by treating concentrated sulphuric acid with sulphur trioxide.

D'Ans and Friedrich (24) employed hydrogen peroxide and chlorsulphonic acid.

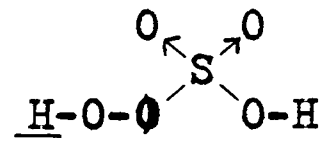
$$HO_3SCl + HOOH \longrightarrow HO_3SOOH + HCl \qquad (14)$$

This reaction may be considered to be a sulphonation of hydrogen peroxide. Extending this, they prepared perdisulphuric acid from Caro's acid and chlorsulphonic acid.

$$HO_3SOOH + ClSO_3H \longrightarrow HO_3SOOSO_3H + HCl \qquad (15)$$

Examination of equations (14) and (15) will show that half the amount of chlorsulphonic acid required for the production of perdisulphuric acid is necessary for the preparation of Caro's acid.

Analysis showed permonosulphuric acid to be H_2SO_5. Several attempts have been made to determine the structure, and it has been generally accepted, although not positively proved, as follows:



S. Price (25) carried out several experiments in an attempt to prove this structure, but his evidence is not conclusive, as he himself admits. Wilstätter and Hauenstein (26) succeeded in preparing and isolating the potassium-benzoyl derivative of Caro's acid, ($KOSO_2OOCOC_6H_5$), after careful work, and came to the conclusion that the above must be the structure.

The acid has been shown to be monobasic, i.e., the hydrogen atom underlined in the above formula is considered to be un-ionized. It would be predicted from this evidence that the conductivity of such a solution would be less than that of sulphuric acid itself, or even that of perdisulphuric acid. Caro's acid has been employed as an oxidizing agent in many instances, and has been thus used successfully.

A peracid of nitric acid has been reported and various investigators professed to have obtained it, and have studied some of its reactions. Pernitric acid has been given the empirical formula HNO_4.

Raschig (27) claimed to have prepared pernitric acid by the oxidation of nitrous acid with 3% hydrogen peroxide. According to his observations, the peracid is slowly hydrolyzed.

$$HNO_2 + H_2O_2 \longrightarrow HNO_4 + H_2O \qquad (16)$$

$$HNO_4 + H_2O \longrightarrow HNO_3 + H_2O_2 \qquad (17)$$

nitric acid being one of the products of this hydrolysis.

E. Pineura Alvarez (28) reported that he had been able to obtain the persalts of nitric acid, as well as of phosphoric, arsenic, tungstic, phosphotungstic acids. According to this worker, these salts are readily formed by the action of sodium peroxide on the alkali salts of these acids. These reactions were carried out in alcoholic solution.

$$KNO_3 + Na_2O_2 + H_2O \longrightarrow KNO_4 + 2NaOH \qquad (18)$$

$$KNO_4 + H_2O \longrightarrow KNO_3 + H_2O + O \qquad (19)$$

When dissolved in water, hydrolysis of the pernitrate occurred to give back the original nitrate.

In 1912, Jannasch (29) stated that in poison cases, treatment of the material with nitric acid, followed by hydrogen peroxide and nitric acid evaporation permitted of further investigation without trouble. Here, 15-20% hydrogen peroxide was used. 30% material was avoided for fear of explosions; even then the instability of such mixtures was realized.

Trifonov (30) claimed to have prepared pernitric

acid from hydrogen peroxide and acidified alkali nitrates in those concentrations advised by Raschig; these apparently gave the best yields. He suggested the following reaction to take place:

$$2HNO_2 + 3H_2O_2 \longrightarrow (n-1)H_2O + N_2O_6 \cdot nH_2O + 3H_2O \qquad (20)$$

Pollack (31) prepared the acid from nitrous acid and hydrogen peroxide; he proposed the following series of equations which would favour its formation:

$$(a)\quad xHNO_2 + mH_2O_2 \longrightarrow axHNO_4 + m'H_2O \qquad (21)$$

$$(b)\quad ayHNO_4 + nH_2O \longrightarrow yHNO_3 + n'H_2O_2 \qquad (22)$$

$$(c)\quad yHNO_3 + n'H_2O_2 \longrightarrow ayHNO_4 + nH_2O \qquad (23)$$

(a) is almost instantaneous, (b) goes quickly at first but slows down as (c) begins, i.e., an equilibrium results.

Gleu and Hubold (32) recently investigated the action of hydrogen peroxide upon nitrous acid, and their conclusions were that oxidation of the nitrous acid resulted in the production of pernitrous acid. This latter acid contained one active oxygen atom per molecule of nitrous acid. The peracid was formulated as:

H-O-O-N=O

isomeric with nitric acid; the formula, moreover, is quite reminiscent of Brühl's proposal as a possibility for the structure of nitric acid.

According to Friend (33) pure hydrogen peroxide and nitrogen pentoxide at low temperatures yield a substance exhibiting the properties of a peracid:

$$H_2O_2 + N_2O_5 \longrightarrow HNO_4 + HNO_3 \qquad (24)$$

In connection with their work on hydrogen peroxide, Hatcher and MacLaughlan (34) proceeded to investigate the conductivity of nitric acid in the above medium. Apparently little work had been done in this direction regarding nitric acid, i.e., measurement of its conductivity in media other than water. Hydrogen peroxide was selected for the following reasons: (a) the possible formation of pernitric acid, (b) the authors' interest in hydrogen peroxide and (c) the conductivity of peroxide is similar to that of water.

Conductivity measurements soon indicated an increase in the electrical resistance of the system nitric acid—hydrogen peroxide, very similar to the behaviour of the organic acids as discovered by Hatcher and Powell (9). Owing to the explosive nature of concentrated solutions of nitric acid and hydrogen peroxide, dilute solutions only

could be employed. From the behaviour of the conductivity, it is possible that pernitric acid is formed; it is equally possible that an un-ionized complex forms immediately, which more slowly may hydrolyze to yield the peracid. Experiments were also carried out with sulphuric acid; these yielded the same result. In this latter instance, it is definitely known that Caro's acid is formed, although in its preparation concentrated acid and peroxide are employed.

Considerable space has been allotted to a discussion of pernitric acid, since mixtures of hydrogen peroxide and nitric acid have been used somewhat extensively in this work. The reagent is relatively easily prepared, and quite explosive when concentrated. It was deemed desirable to investigate its action upon various organic compounds, and to observe its behaviour as an oxidizing agent. This work constitutes the first section of this thesis, dealing with the various chemical reactions encountered, and the identification of the products obtained. Those concentrations of hydrogen peroxide and nitric acid were employed which would not yield an explosive mixture, either immediately or after a short period of induction. Hatcher and MacLaughlan (34) plotted the lower limits of "instantaneous" and "any reaction whatever" of mixtures of nitric acid and hydrogen

peroxide. It was found impossible to have the nitric acid much more than 50% of the total weight, and it is the concentration of acid rather than of peroxide which is the controlling factor. Accordingly, the mixtures employed were of such concentrations that the nitric acid was always less than 50%, except for one or two cases, wherein, as expected, explosions resulted.

SIMPLE KETONES

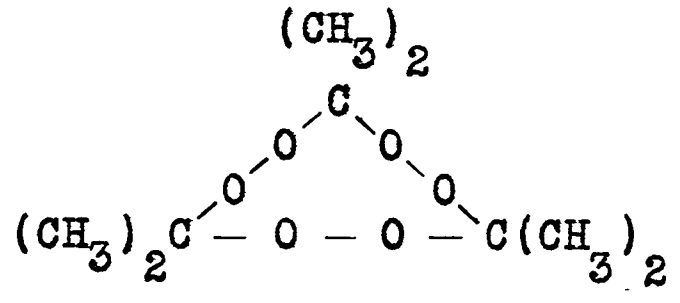
ACETONE

INTRODUCTION

The C.P. nitric acid of commerce and the 27-28% hydrogen peroxide used in the following reactions were of such concentrations that there might be no danger of an explosive mixture being formed. In the succeeding pages, this acid mixture will be referred to as "P.N. acid", since there is as yet no real justification to term it pernitric acid.

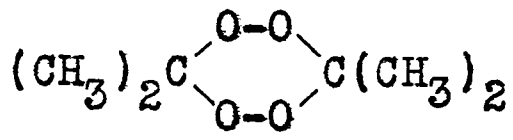
Reaction with acetone was such as to cause the immediate formation of a white amorphous substance, which proved to be violently explosive. Wolffenstein (35) in relation to his work on hydrogen peroxide, oxidized coniine in acetone solution and stated that the peroxide had no effect upon the medium. However, using higher concentrations of hydrogen peroxide (36), he observed the precipitation of a small amount of white, crystalline material. This occurred during a period of several weeks. Ultimately he was able to obtain a sufficient quantity of the substance for analysis. The outcome of his work was

the postulation of a new compound, tri-cyclo-acetone-peroxide, which he promptly patented, and formulated as follows:



Several weeks, and even months, were required to obtain but a small amount of this peroxide from the action of acetone and hydrogen peroxide alone. Wolffenstein observed that the yields were somewhat improved by the addition of a small amount of phosphoric acid, which may be considered to be a catalyst.

Baeyer and Villiger (37) carried out many experiments with a then new reagent, Caro's acid. In the course of their work, they subjected acetone to its action and straightway obtained a white crystalline material in considerable quantity. Investigation showed it to be very similar to Wolffenstein's product; it was explosive, but the melting point was higher than the former peroxide. Adopting Wolffenstein's proposal they termed it di-cyclo-acetone-peroxide, giving an analogous formula:



This peroxide the authors stated to be a specific reaction product of Caro's acid. Baeyer and Villiger were also able to prepare Wolffenstein's peroxide from acetone by the action of a 10% hydrogen peroxide solution saturated with potassium acid sulphate. Further investigation showed that hydrogen peroxide and sulphuric acid yielded di-cyclo-acetone-peroxide; the conclusion reached was that the two reagents named form Caro's acid, a preparation already pointed out.

Proceeding along a somewhat similar line of endeavour, Pastureau (38) obtained di-cyclo-acetone-peroxide from a reaction between acetone, dilute 2-3% hydrogen peroxide and a large excess of concentrated sulphuric acid, all being kept well cooled.

Wolffenstein's tri-cyclo-acetone-peroxide had a melting point of 97°C.; Baeyer and Villiger's di-cyclo-acetone-peroxide melted at 131-132°C.; with potassium acid sulphate and hydrogen peroxide they obtained a product melting at 94-95°C.; Pastureau always obtained a peroxide melting at 131.5°C.

EXPERIMENTAL

The reaction between concentrated nitric acid and 27.5% aqueous hydrogen peroxide is quite exothermic; when the two are mixed, considerable heat is evolved, the resulting temperatures being 30°C. and even 40°C. Both the acid mixture and the acetone were cooled to about 10°C. or lower before being brought together. When these reacted, again there was considerable heat evolved, the resulting temperature being noted in most cases. Upon addition of the P.N. acid to the acetone, a mass of white amorphous material was immediately precipitated. This was filtered off at once, washed well with water and spread out to dry. It was found that even after considerable exposure to the air, there remained a fair amount of water occluded in the material.

An acetone peroxide melting from 128-132°C. before purification was obtained in the experiments included in Series 1. Softening a few degrees below 128°C. was observed, before actual melting took place. The material was dissolved in ether, in which it is extremely soluble, and recovered by partial evaporation of the solvent. The crystalline peroxide did not show much improvement in melting point, i.e., not much, if any, purification had resulted from this

treatment. Recrystallization from ethyl acetate was found to yield a fine, white crystalline product, melting at 131-132°C. In several cases, the evolution of a few bubbles of gas was observed as the material melted, but this occurrence did not appear to alter the melting point in any way, as was evidenced by remelting the original sample.

SERIES 1

7.96 Grams - 0.137 Moles Acetone

Test	Gms. H_2O_2	Moles H_2O_2	Gms. HNO_3	Moles HNO_3	Temp.
1.	0.79	0.024	2.98	0.047	35°C.
2.	2.64	0.077	9.94	0.160	40-41
3.	3.96	0.116	14.91	0.236	38
4.	3.96	0.116	19.88	0.315	50-51
5.	5.28	0.155	19.88	0.315	33
6.	3.96	0.116	24.85	0.394	33
7.	8.05	0.237	23.86	0.379	42
	2.39 Grams - 0.041 Moles Acetone				
8.	0.823	0.025	4.86	0.076	-
	15.92 Grams - 0.274 Moles Acetone				
9.	8.05	0.237	31.81	0.505	48
10.	19.80	0.582	14.91	0.236	43

A second series of experiments was made, using different proportions of hydrogen peroxide and nitric acid from those used in the first series. Here, a material was obtained which was treated in the same manner as before, and recrystallized from ethyl acetate. A peroxide melting at 95-97°C. was obtained, i.e., the tri-cyclo-acetone-peroxide originally prepared by Wolffenstein.

SERIES 2

7.96 Grams - 0.137 Moles Acetone

Test	Gms. H_2O_2	Moles H_2O_2	Gms. HNO_3	Moles HNO_3	Temp.
1.	2.64	0.077	4.97	0.079	30°C.
2.	3.96	0.116	4.97	0.079	41
3.	3.96	0.116	9.94	0.160	41
4.	8.05	0.237	7.95	0.126	44
5.	8.05	0.237	15.90	0.252	44
	2.39 Grams - 0.041 Moles Acetone				
6.	0.791	0.024	2.98	0.047	-
7.	2.64	0.077	4.97	0.079	-
	15.92 Grams - 0.274 Moles Acetone				
8.	8.05	0.237	7.95	0.126	48
9.	8.05	0.237	15.90	0.252	48
	19.90 Grams - 0.343 Moles Acetone				
10.	0.791	0.024	2.98	0.047	-

From consideration of the above two series, it is apparent that variation in the quantities of acetone, hydrogen peroxide and nitric acid will yield both modifications of acetone peroxide. Where the nitric acid is about three times the amount of the hydrogen peroxide, the higher melting peroxide is produced; where it is less than this, the lower melting product is the result.

One further experiment was carried out involving the same concentrations as in Test 1 of Series 2, viz.:

7.96 grams acetone	0.137 moles
2.64 grams hydrogen peroxide	0.077 moles
4.97 grams nitric acid	0.079 moles.

In this instance, however, no cooling of the reagents was effected. Upon adding the acid mixture to the acetone, the temperature rose rapidly to 50°C., accompanied by the formation of acetone peroxide on the sides of the vessel. The solution assumed a paste-like consistency, the temperature rising to 60°C. during this period. At this point, bubbles of oxygen were evolved, and after three to five minutes, the temperature had risen to 80°C. Boiling occurred shortly after. The flask was thereupon placed in an ice-salt mixture which effectively arrested further action, and the peroxide recovered. After recrystallization from ethyl acetate the melting point was 131-132°C. It is to be observed, therefore, that too high a temperature is to

be avoided if the lower melting modification of acetone peroxide is desired.

Another experiment, which produced disastrous results, was conducted, the following quantities being employed:

7.96 grams acetone	0.137 moles
3.96 grams hydrogen peroxide	0.116 moles
24.85 grams nitric acid	0.394 moles.

Here, the acetone only was cooled to 0°C. When the P.N. acid was added, the temperature rose rapidly to 40°C., and then more slowly to 60°C. Evolution of oxygen began, accompanied by a more rapid increase in temperature. The solution turned light brown at this point, due to the production of oxides of nitrogen. When the temperature reached 90°C., the vessel was surrounded with an ice-salt mixture, which, however, failed to arrest the reaction. The solution boiled up rapidly and exploded, with the evolution of dark brown fumes. The material which had been formed was so scattered as to be beyond recovery. This behaviour was rather expected for here the concentration of the nitric acid with respect to the hydrogen peroxide, was well above the limiting concentration of 50%, as outlined by Hatcher and MacLaughlan (34).

PROPERTIES OF ACETONE PEROXIDE

By variation of the amounts of hydrogen peroxide and nitric acid, both modifications of acetone peroxide may be obtained, one melting at 131-132°C., the other melting at 95-97°C. Both forms exhibited a fine, white, amorphous appearance, and crystallized from ethyl acetate in transparent rhombohedral crystals. These peroxides are quite insoluble in water, dilute acids and bases, but they slowly hydrolyze, in the presence of sulphuric acid, back to acetone and hydrogen peroxide. In water, or in the presence of acid, hydrolysis is evidenced by the liberation of iodine from potassium iodide solution. They are readily soluble in the common organic solvents, such as ethyl acetate, alcohol, ether, petroleum ether and benzene. They explode violently under impact, when introduced into the Bunsen flame, and when mixed with concentrated sulphuric acid, the lower melting modification being considerably more explosive.

The mother liquor from a crystallization from ethyl acetate had been allowed to stand for some time, when evaporation took place to produce several relatively large transparent crystals of the peroxide melting at 95-97°C.

One of these crystals, when introduced into the Bunsen flame, exploded with extreme violence, accompanied by a loud report. These crystals are so sensitive that slight rubbing of some material which had crept up the sides of a Pyrex beaker, resulted in a violent explosion which quite deafened the investigator for a considerable period, and from which he has not yet wholly recovered. The beaker was utterly shattered and the bench top somewhat gouged out. One cannot be cautioned too much to exercise the greatest of care when handling this peroxide. In the Bunsen flame, the amorphous material flares up and explodes, with the production of little or no smoke. Both forms are quite volatile and can be sublimed successfully at 70°C.

Molecular weight determinations were made by the cryoscopic method, employing the ordinary Beckmann apparatus, and benzene as the solvent.

Acetone peroxide melting at 95-97°C.:

0.2625 grams material dissolved in 17.5022 grams benzene produced a freezing point depression of 0.355°.

$\left[(CH_3)_2CO_2\right]_3$ Found - 216 Calc. - 222

Acetone peroxide melting at 131-132°C.:

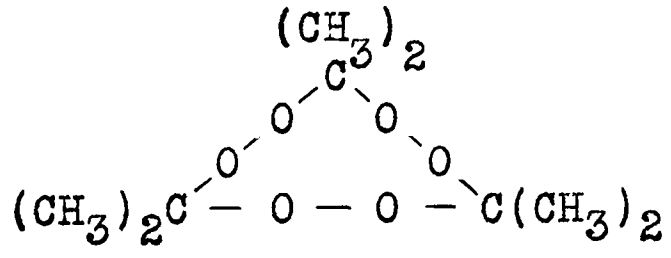
0.2160 grams material dissolved in 17.5022 grams benzene produced a freezing point depression of 0.445°.

$\left[(CH_3)_2CO_2\right]_2$ Found - 142 Calc. - 148

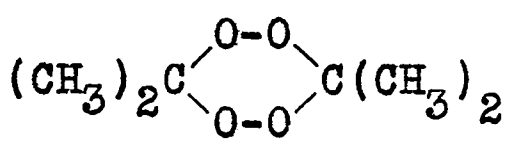
Because of the explosive nature of these peroxides, no combustion analyses were attempted; indeed, the molecular weight determinations render them unnecessary.

H. Lecoq (39) prepared an acetone peroxide and obtained the trimolecular modification; the method of preparation was that essentially outlined by Wolffenstein. This author claimed to have observed that the peroxide depolymerized to the monoperoxide. Cryoscopic measurements were carried out and over a period of time, a series of decreasing values for the molecular weight were observed. In no case during the progress of this work was this phenomenon observed.

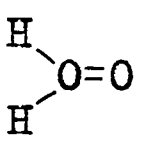
Wolffenstein (36) when he first prepared what he termed tricyclo-acetone peroxide, postulated a 9-membered carbon and oxygen ring as follows:



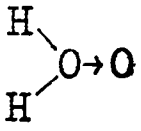
and indeed, such a formula would well indicate its instability. Baeyer and Villiger,(37) when they obtained the dimolecular modification, borrowed this idea, and stated the structure to be:



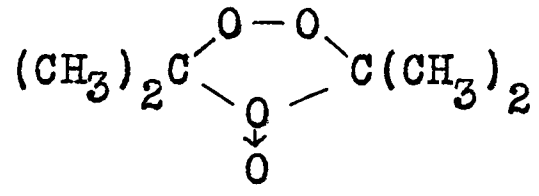
Considering the fact that hydrogen peroxide may have the structure as proposed by Kingzett in 1884, involving a quadrivalent oxygen atom:



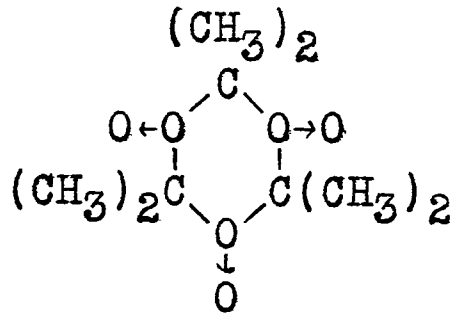
or, as it is written to-day, possessing a co-ordinate covalent bond between oxygen:



the possibility of the structure of the dimolecular modification of acetone peroxide should not be disregarded:



and a possible 6-membered ring for the trimolecular modification:



These may be capable of relatively easy formation, but being loaded up with oxygen, would tend to be quite unstable.

OTHER SIMPLE KETONES

Baeyer and Villiger (40) during the progress of their work on the oxidation of acetone with Caro's acid, had occasion to subject other simple ketones to the action of the reagent. As in the case of acetone, peroxides were produced, all of which were quite explosive. In these instances, however, oils, rather than solids were obtained.

Methyl-ethyl ketone and di-ethyl ketone were both treated with P.N. acid, the following quantities being employed:

8.0 grams ketone
15.86 grams hydrogen peroxide
39.76 grams nitric acid.

The ketones were at room temperature, the acid mixture

being cooled to about 10°C. before adding. A slight rise in temperature was observed as reaction proceeded but was not particularly noted in these experiments. After standing at room temperature for a short interval, an oily layer separated out on top of the acid solution. The peroxide was removed, taken up with ether, washed free from acid with sodium bicarbonate solution and water until neutral. Drying was effected over anhydrous sodium sulphate, and the peroxide recovered by evaporation of the ether solvent.

PROPERTIES OF METHYL-ETHYL AND DI-ETHYL KETONE PEROXIDES

With these higher ketones, somewhat heavy oils were obtained rather than solids. The oils were colourless and possessed a not unpleasant aromatic odour. They are extremely sensitive to shock, exploding when introduced into the Bunsen flame and when sharply struck. They are heavier than and insoluble in water, but are quite soluble in the organic solvents, ether, ethyl acetate, benzene and acetone. Although insoluble in water, the peroxides hydrolyze slowly, iodine being liberated from a dilute solution of potassium iodide.

Approximately 8.0 grams di-isopropyl ketone were

treated with the same quantity of P.N. acid as above. None of the constituents was cooled and no excessive temperature rise was observed after mixing. No reaction was apparent, even after standing for three months and more. It would appear in this case that the isopropyl groups so protect the carbonyl group that peroxide formation is impossible, the reagent not being strong enough either to force entry or to break up the molecule. Baeyer and Villiger (40) reported that they obtained the peroxide of di-n-propyl ketone; it is thus apparent that reaction can and does occur with the isomer.

ACETOPHENONE - BENZOPHENONE

Since the simple aliphatic ketones give rise to explosive peroxides, it was thought that perhaps ketones containing an aromatic nucleus next to the carbonyl group might give a similar result. It was considered, however, that the presence of the benzene ring might possibly hinder or slow down any reaction in which the carbonyl group might be involved.

Pastureau (41) asserted that the action of hydrogen peroxide upon acetophenone gives rise to acetophenone alcohol ($C_6H_5COCH_2OH$), and that such aryl ketones in general do not result in explosive peroxides. Beyond several statements to this effect, he does not appear to have done much more work upon the problem.

EXPERIMENTAL

10 grams acetophenone were added to P.N. acid, consisting of 30 cc. of 25% hydrogen peroxide and 25 cc. of 70% nitric acid, which latter had been cooled down to room temperature, 20°C. No rise in temperature was observed after mixing, the ketone forming an oily layer on top of the acid solution. The reaction mixture was left standing for five days, with occasional shaking; at the end of this time the

ketone layer had become quite dark in colour. This was separated from the acid and washed. It showed no change in properties. Apparently the acetophenone had not reacted to any perceptible extent.

The acid solution during this interval had turned a light yellow, and was allowed to stand for a further four days. It would seem that some of the acetophenone had dissolved, for, at the end of this period, a fluffy material had separated out, admixed with some yellow, gummy substance. The whole was removed and found to be insoluble in water. It was discovered, however, that upon taking up with methyl alcohol, the yellow gum dissolved, to leave a relatively white, amorphous material, which was filtered, washed and dried in the air.

A second trial was made, employing the same quantity of acetophenone, but a larger amount of P.N. acid (70 cc. of 28% hydrogen peroxide and 30 cc. of 70% nitric acid). The same behaviour was observed, and after standing at room temperature for seven days, with occasional shaking, there separated out an orange, gummy material. This was removed, washed well with water, and allowed to dry. After standing for several months, the material showed itself to be definitely crystalline, quite orange in colour, but still sticky in consistency.

Owing to the author's hypersensitivity towards compounds of the acetophenone type, further work on the identification of the products mentioned above had to be abandoned.

BENZOPHENONE

It might be expected that, since acetophenone reacts so quietly with P.N. acid, benzophenone, by virtue of the two phenyl groups present, would be even less inclined to react.

A small amount of benzophenone, about 8-10 grams, was dissolved in glacial acetic acid. To this was added the P.N. acid, cooled to 20°C., and consisting of 60 cc. of 25% hydrogen peroxide and 40 cc. of 70% nitric acid. Sufficient acetic acid was used to prevent the precipitation of the ketone after the addition of the oxidizing reagent. After the elapse of about 24 hours, the solution had become quite yellow in colour. At this point it was poured into water, which straightway turned milky; shortly after, some solid matter separated out. The material was augmented in quantity by partial neutralization with sodium carbonate. Purification of the compound showed it to be unchanged benzophenone. A mixed melting point with a known sample

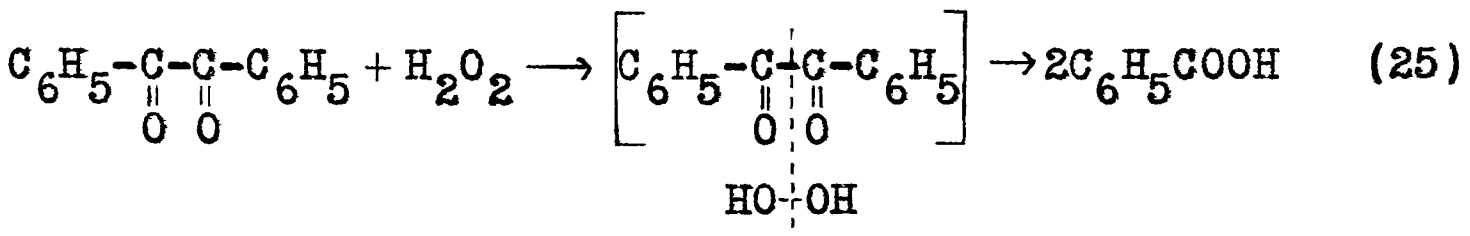
gave no depression. (M. Pt. 49-50°C.). Several other experiments yielded the same result. Apparently there is no reaction with benzophenone, which is quite in accordance with the general sluggishness of the carbonyl group in this compound.

BENZIL AND BENZOIN

BENZIL

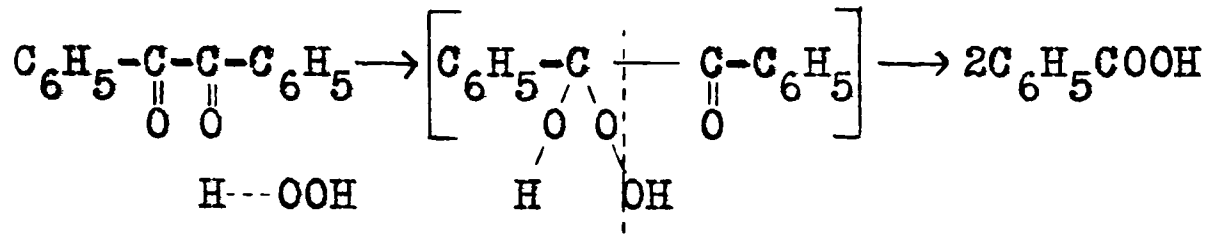
Having learned that the simple aliphatic open chain ketones yield explosive peroxides, and that the simple aromatic ketones appear to give an indifferent reaction towards hydrogen peroxide — nitric acid mixtures, it was decided to discover how diketones and hydroxy ketones would behave.

Pastureau (41) in his work, found that hydrogen peroxide in sulphuric acid solution, cleaved benzil with the production of two molecules of benzoic acid. Weitz and Scheffer (42) observed that alkaline hydrogen peroxide cleaved 1,2,diketones very readily, and they developed this cleavage reaction to a considerable degree. Since then, alkaline peroxide has become a specific cleavage reagent for 1,2,diketones, the most highly hindered compounds cleaving with ease when subjected to its action. These authors stated that the mechanism of the reaction proceeded through a 1,4, addition of hydroxyl groups to the ends of the system of twinned carbonyl groups. Thus the reaction is:



(25)

The matter was taken up by Barnes and Lewis (43), who postulated a 1,2, addition to one of the carbonyl groups, followed by subsequent cleavage. They proposed the following reaction:



(26)

EXPERIMENTAL

3 grams benzoin were added to P.N. acid consisting of 70 cc. of 22% hydrogen peroxide and 30 cc. of 70% nitric acid, the latter having a temperature of about 30°C. The ketone floated about on top of the acid solution, showing no great tendency to dissolve. The system was stirred at frequent intervals, and allowed to stand at room temperature for about six days. At the end of this period, the entire solution had turned a pale yellow. The solid was filtered off and purified; tests showed that no reaction had taken place. A mixed melting point with benzoin showed no depression. (M. Pt. 133-134°C.).

4 grams benzil were added to an acid mixture of the same concentration as above. The ketone floated about

on top of the solution, but dissolved completely after the passage of four or five days, to give a clear, water-white solution. At this point, a small portion was poured into water, but nothing happened. The main solution was partially neutralized with sodium carbonate and left to stand with occasional stirring; after seven days, a crystalline precipitate had separated out. This was filtered, washed and dried. M. Pt. 118-125°C. The material was dissolved in alcohol and recovered by evaporation of the solvent to yield a slightly yellow, crystalline compound. A melting point determination showed no change from the original value. The substance burned with a yellow, smoky flame, was insoluble in cold water but quite soluble in hot, was soluble in dilute alkalis and insoluble in dilute acids. This behaviour suggested that the compound might be an acid. Recrystallization from water resulted in white, flaky plates. M. Pt. 121-123°C. A mixed melting point with a known sample of benzoic acid (M. Pt. 121°C.) resulted in no depression. M. Pt. 121-123°C.

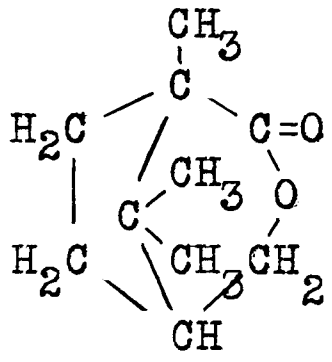
The process was considerably accelerated by first dissolving the benzil in glacial acetic acid, before adding the P.N. acid. Partial neutralization of the acidic solution, after standing for about fifteen hours, yielded the cleavage product after a further short interval.

It is to be observed, therefore, that a mixture of hydrogen peroxide and nitric acid will cleave benzil, a 1,2, diketone, to form benzoic acid. The reaction is not as rapid nor as quantitative as the more familiar alkaline hydrogen peroxide reagent of Weitz and Scheffer.

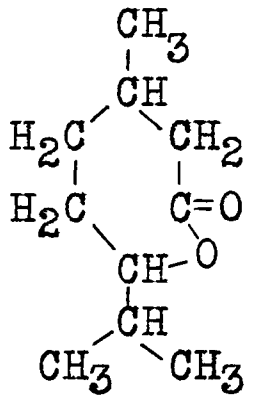
No reaction was observed in the case of benzoin. According to Pastureau (41), a very small amount of benzoic acid is said to have been recovered after the prolonged action of a mixture of dilute hydrogen peroxide and concentrated sulphuric acid.

CYCLOHEXANONE

Baeyer and Villiger (37) in their investigation of the action of Caro's acid on ketones, had occasion to treat substituted cyclic ketones, such as menthone and camphor, with this oxidizing agent. They obtained the ϵ-lactones of these two compounds:

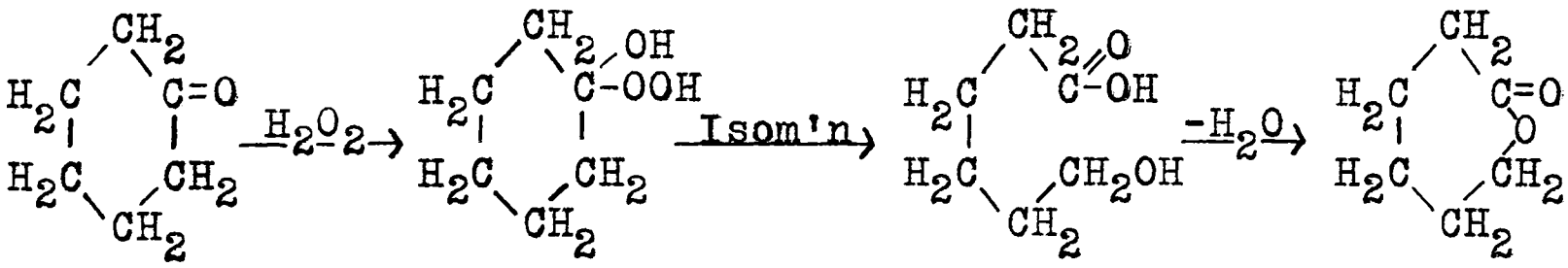


Camphor-lactone

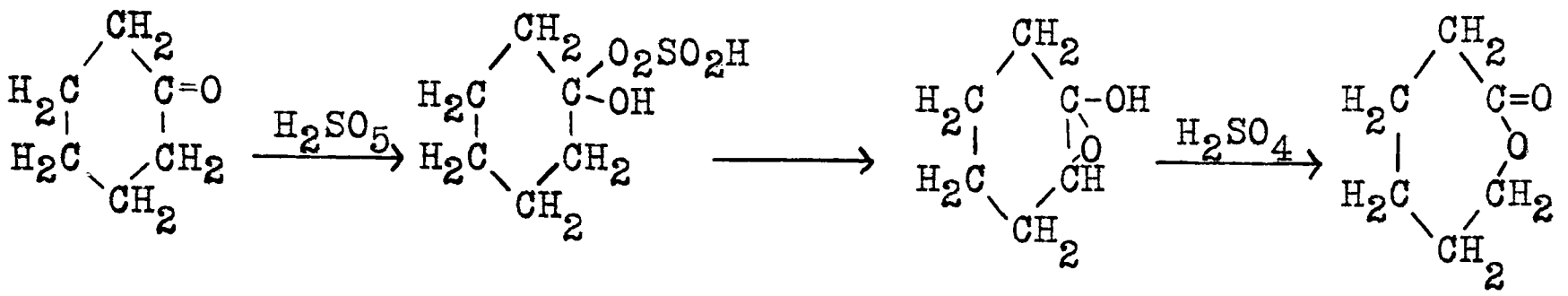


Menthone-lactone

On the basis of these reactions, Baeyer and Villiger stated that cyclic ketones in general give rise to ϵ-lactones. Assuming this reaction to hold, many authors have taken it up as a good example of its type, and have postulated that hydrogen peroxide and Caro's acid react with cyclohexanone in the following manner (44):

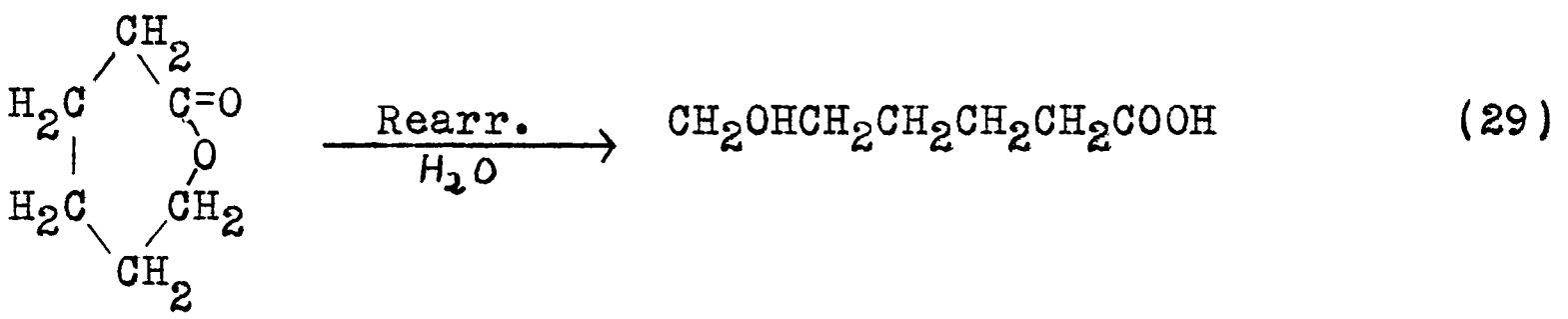


(27)



(28)

Actually this reaction has no foundation on fact, for it is well known that unsubstituted ϵ-lactones are quite unstable, rearranging very readily to the corresponding ϵ-hydroxy acid.



(29)

Furthermore, this reaction when actually carried out, does not proceed in this manner. Indeed, Baeyer and Villiger (37) obtained an explosive peroxide, rather than a lactone, when they treated methyl-cyclohexanone with Caro's acid.

Stoll and Scherrer (45) observed that the oxidation of large ring ketones, i.e., those containing C_{15}, C_{17}, etc., carbon atoms gave rise to lactones when treated with persulphuric or Caro's acid. This was quite in accordance with the findings of Baeyer and Villiger. The former, however, in conjunction with Ruzika (46) observed that relatively little work had been done in this direction with the lower ring ketones such as cyclopentanone and

cyclohexanone.

Cyclohexanone was added to the P.N. acid, resulting in an opaque, milky solution. After a short interval, a viscous, sticky material separated out, to float on top of the solution. Upon removal of this material, it was found possible to work the resulting oil up into the solid state, capable of ready purification from ethyl acetate or petroleum ether (B. range 60-90°C.). Assuming an action similar to that described by Stoll and Scherrer, this material is cyclohexanone peroxide.

In other experiments attempted, it proved to be impossible to alter the state of the oil first formed. Purification from ether, ethyl acetate or petroleum ether, yielded only a clear, water-white oil. Its peroxide-like nature was indicated by the violent explosion which occurred when it was placed in the flame. This oil did not seem to consist of any definite compound; rather it might have been a mixture of the peroxide-hydrate and dicyclohexanone peroxide-hydrate, as well as possibly unchanged cyclohexanone. The oil was soluble in all the usual organic solvents, (ether, petroleum ether, acetone, ethyl acetate and benzene), insoluble in water, and liberated iodine from potassium iodide solution very readily.

EXPERIMENTAL

The cyclohexanone employed was first distilled to present a clear, water-white appearance. (B. range 154.5-157°C.). 18.9 grams of the ketone were added to P.N. acid consisting of 64.8 grams of 24% hydrogen peroxide and 56.8 grams of 70% nitric acid, this acid mixture being cooled to 15°C. before the ketone was added. After addition, the solution immediately turned milky and quite opaque, the temperature rising to 42-43°C. The system was shaken at frequent intervals, a gummy mass soon separating out on top of the acid solution. This was allowed to stand over-night at room temperature. After the elapse of 10 to 12 hours, the main solution had acquired a distinct yellow colour, and in addition to the oil, a quantity of white, amorphous material had precipitated out on the bottom of the flask.

This solid was separated, washed well with water and dried in the air. M. Pt. 119-126°C. The oil was removed, taken up with ether, washed with sodium bicarbonate solution and water until neutral, and dried over anhydrous sodium sulphate. The solvent was then removed by evaporation. The oil thus obtained presented a clear, transparent, water-white appearance with no indications of its assuming the solid state. A small quantity of methyl alcohol was added and the whole

stirred vigorously. This treatment brought about the separation of a white amorphous material, similar to that first recovered. This was treated as described above. M. Pt. 119-126°C.

The two portions were joined together and crystallized from ethyl acetate. A fine, white, crystalline material was recovered (M. Pt. 125-126°C.). When melting, the evolution of a few bubbles of gas was observed, which, however, had no effect upon the melting point.

The solubility in various media was determined: the peroxide is insoluble in water, dilute sodium hydroxide and hydrochloric acid, 85% syrupy phosphoric acid; it is slowly soluble in concentrated sulphuric acid, accompanied by a slight explosion, indicating decomposition. It is quite soluble in ether, acetone, benzene, ethyl acetate and petroleum ether (B. range 60-90°C.). When the peroxide was recrystallized from the latter solvent, it was found to have a melting point of 129-130°C., a behaviour which was observed by Stoll and Scherrer. For that matter, several recrystallizations from ethyl acetate yielded a material melting at this same temperature.

The peroxide, when placed in the Bunsen flame,

flashed up with a yellow flare, and exploded with considerable violence. In the recrystallizations from ethyl acetate and petroleum ether, the compound had a tendency to creep up the sides of the beaker. Any investigator is warned against working the material down with a stirring-rod in an effort to loosen it, since it is sensitive to shock (although not quite to the same extent as is cyclopentanone peroxide)

Another set of experiments was carried out, employing the same amount of ketone as above, with acid mixtures of varying concentrations. In each case, the acid mixture was cooled to 15°C., the ketone being cooled to a like temperature. The P.N. acid was made up to the following concentrations:

Experiment 1: 38.1 grams of 24% hydrogen peroxide and 5.68 grams of 70% nitric acid

" 2: 38.1 grams of 24% hydrogen peroxide and 11.36 grams of 70% nitric acid

" 3: 38.1 grams of 24% hydrogen peroxide and 22.72 grams of 70% nitric acid.

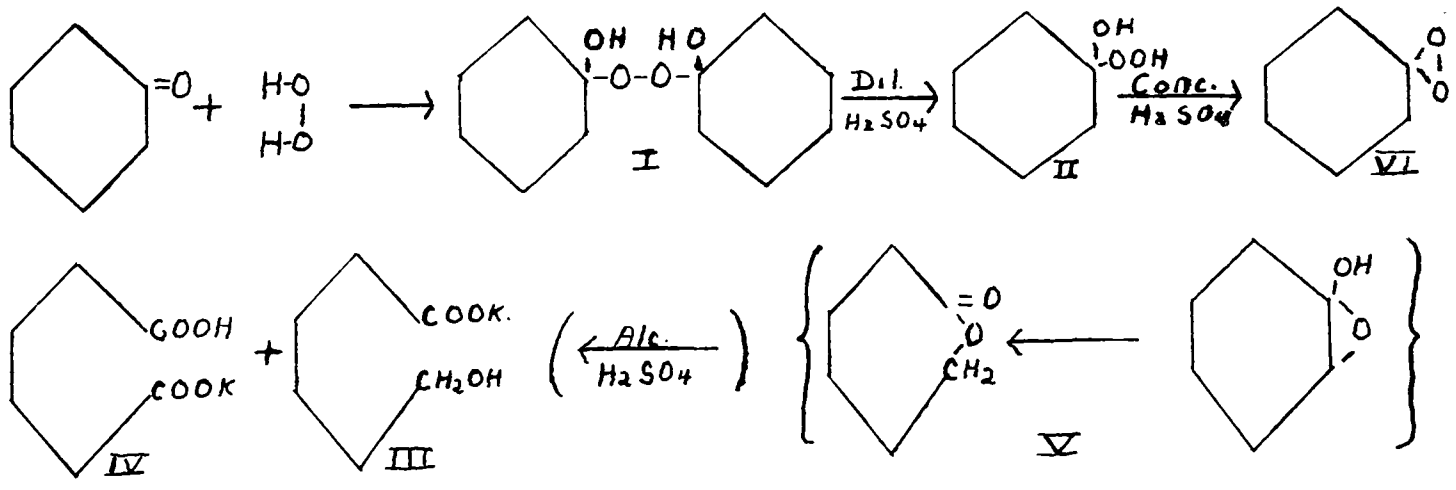
Cloudy, opaque solutions resulted, with the subsequent separation of the viscous, sticky oil. The temperature rose to varying degrees between 30°C. and 35°C.

After standing for about 48 to 50 hours, with occasional agitation, Experiment 3 was the only case wherein

solid peroxide was obtained. This was separated, washed well with water and dried. The oil resulting from this reaction, moreover, could be converted to the solid condition by treatment with methyl alcohol.

Experiments 1 and 2, however, yielded the oil alone. The two lots were joined together, but the usual treatment produced no solid peroxide. All that it was possible to do was to free it from acid and dry it, which treatment produced a clear, water-white viscous oil. This oil, when introduced into the Bunsen flame, exploded with considerable violence, liberated iodine from potassium iodide solution, and possessed much the same solubilities as the solid cyclohexanone peroxide.

Stoll and Scherrer (45) postulated the formation of peroxide according to the following series of equations:



(30)

An attempt to prepare the salt of adipic and ϵ-hydroxy caproic acid (III and IV above) was made by treating

both oil and peroxide with sodium hydroxide, but without success.

According to these authors, analysis showed cyclohexanone peroxide to be $C_6H_{10}O_2$, indicated in formula VI above.

Molecular weight determinations were carried out by the cryoscopic method, using benzene as solvent.

(a) 0.2153 grams material dissolved in 17.5022 grams of benzene produced a freezing point depression of 0.265°.

$(C_6H_{10}O_2)_2$ Found - 232 Calc. - 228

(b) 0.2265 grams material dissolved in 17.5022 grams of benzene produced a freezing point depression of 0.285°.

$(C_6H_{10}O_2)_2$ Found - 231.6 Calc. - 228

These results would appear to indicate a dimolecular modification of cyclohexanone peroxide rather than the monomolecular form postulated by Stoll and Scherrer.

m-METHYL CYCLOHEXANONE

In an attempt to prepare an ϵ-lactone from methyl cyclohexanone, Baeyer and Villiger (37) merely succeeded in isolating a simple peroxide, which did not apparently undergo any rearrangement to form a lactone. They did not investigate the reaction any further. According to V. von Richter (47) methyl cyclohexanone gives rise to a lactone, which, on breaking down, passes into methyl-ϵ-hydroxy caproic acid.

P.N. acid produced a thick, viscous, sticky oil with definite peroxide-like properties. Outside of its preparation, not a great deal could be done with it, owing to the great difficulty in obtaining it pure.

EXPERIMENTAL

To 100 cc. of P.N. acid (60 cc. of 24% hydrogen peroxide and 40 cc. of 70% nitric acid) which had been cooled to room temperature, were added 10 cc. m-methyl cyclohexanone, whereupon the solution turned milky and opaque, the temperature rising to 38°C. A yellow, sticky mass immediately formed and separated out, to float on top of the acid solution. (The colour was due to the light yellow of the original ketone). The system was allowed to stand for some 18 to 20 hours at

room temperature, with occasional agitation.

By this time, the material had congealed somewhat and could be gathered up on a stirring-rod. Accordingly, the mass was removed and taken up with ethyl acetate, in which solution was readily effected. Cooling produced no crystallization. The solvent was permitted to evaporate, and, after being exposed for four days, several relatively large crystals had formed, which proved to be contaminated with ethyl acetate. The viscous oil, plus crystals, were then taken up with petroleum ether (B. range 60-90°C.) in which the former only was soluble. The crystals were separated, dried and the melting point determined. The material began to soften around 300°C. and finally melted at about 310-312°C. The solid, when put into the Bunsen flame, merely melted and finally boiled away; it did not burn, nor did it explode. The oil, on the other hand, was quite explosive when subjected to this treatment.

10 cc. of the ketone were added all at once to a slightly stronger solution of P.N. acid (70 cc. of 24% hydrogen peroxide and 30 cc. of 70% nitric acid), the latter having been cooled to 10°C. The resulting temperature of the system was 21°C. The same phenomenon was observed as mentioned above, but this time under no circumstances was any solid

matter obtained. The oil was recovered in a clear, transparent condition by dissolving in ether, washing well with water and 10% sodium bicarbonate solution until neutral, drying over anhydrous sodium sulphate and evaporating off the solvent. The addition of a few drops of water caused the oil to become white and opaque.

The oil is quite soluble in ether, ethyl acetate, benzene, petroleum ether and acetone. Its sensitivity in the flame would seem to bear out its peroxide-like properties.

The amount of solid material first obtained was so meagre as to render further investigation as to its identity impossible. All succeeding attempts to prepare the solid proved to be unsuccessful.

CYCLOPENTANONE

No one appears to have subjected cyclopentanone to the action of any oxidizing agent such as Caro's acid, hydrogen peroxide, or any of the peracids which have been employed to such excellent advantage in other fields of endeavour.

Since the activity of the carbonyl group in cyclohexanone was such as to give a favourable reaction with P.N. acid, it was assumed that cyclopentanone should react as readily, if not more so, the carbonyl group in this ketone being notoriously active.

Experiment amply justified this assumption, for an extremely sensitive peroxide was obtained as the result of a very vigorous reaction. In this instance, the formation of any viscous oil was conspicuously absent. Its sensitivity, compared with cyclohexanone peroxide indicated the possibility of a somewhat similar relationship between them as there exists between the two peroxides of acetone.

EXPERIMENTAL

A preliminary test was made wherein the ketone was

added to the P.N. acid, the latter having a temperature of about 30°C. A very vigorous reaction ensued about two minutes after mixing, and it is most surprising that the system did not explode. The temperature mounted rapidly to 100°C., the solution boiled vigorously, and turned quite yellow in colour, oxides of nitrogen being evolved most abundantly, and the odour of cyclopentanone pervaded the atmosphere of the laboratory. A small quantity of white, amorphous material was scattered about. It was obvious from what had occurred that rigorous conditions had to be observed in order to control the reaction.

Accordingly, a second experiment was very carefully carried out. 23.75 grams of cyclopentanone were added to 100 cc. of P.N. acid, consisting of 70 cc. of 28.5% hydrogen peroxide and 30 cc. of 70% nitric acid. Both components were cooled down to 10°C. before being brought together. The system immediately assumed a paste-like consistency, owing to the precipitation of a large quantity of white, amorphous material. The flask was surrounded by an ice-salt mixture throughout the course of the reaction. After standing for about five minutes, a series of snapping noises occurred, as if to indicate decomposition of the newly-formed product.

This was at once arrested by swamping the system with water, filtering off the precipitate and washing well with water. A yield of about 10 grams of crude air-dried product was obtained.

The solubility in various solvents was determined. The compound is very soluble in ether, ethyl acetate, benzene, acetone and petroleum ether (B. range 60-90°C.); it is insoluble in ethyl alcohol, methyl alcohol, water, and dilute acids and alkalis. In the Bunsen flame, the material explodes very violently, leaving no residue and producing no smoke.

Upon attempting to take a melting point, it was discovered that the peroxide suffered considerable decomposition. Therefore a decomposition point rather than a melting point would more nearly describe the phenomenon. The crude peroxide decomposed between 160-170°C., accompanied by considerable frothing. A fresh sample was introduced into the melting point apparatus at 120°C., and after a moment or two suddenly exploded, utterly shattering the melting point tube.

The peroxide was crystallized from ethyl acetate, to give a white, crystalline product. Its decomposition

point was 166-168°C. A recrystallization from petroleum ether yielded a peroxide quite similar to the above. Decomposition point 166-167°C. The peroxide is extremely sensitive to shock and even slight friction. When the petroleum ether was allowed to evaporate to dryness, the peroxide was found to have crept up the sides of the beaker. Upon attempting to loosen this material, and rub it down with a stirring-rod, so as to collect it, a series of small explosions occurred, indicating clearly its extraordinary sensitivity. This procedure was hastily abandoned. As in the case of the trimolecular modification of acetone peroxide, one cannot be cautioned too greatly to exercise extreme care when handling this peroxide.

The properties and behaviour of the compound described above would indicate that the product formed between cyclopentanone and P.N. acid is a peroxide, considerably more sensitive than cyclohexanone peroxide. It may be considered to be on a par with acetone peroxide, with respect to sensitivity and ease of formation. Since this resemblance appears to be so close, it was thought that here too, perhaps, is a trimolecular modification. Subsequent molecular weight determinations appeared to bear

out this assumption.

Molecular weight determinations were made by the cryoscopic method, employing the usual Beckmann apparatus, with benzene as solvent.

(a) 0.2585 grams peroxide dissolved in 17.5022 grams of benzene produced a freezing point depression of 0.218°.

$(C_5H_8O_2)_3$ Found - 275 Calc. - 284

(b) 0.2595 grams peroxide dissolved in 17.5022 grams of benzene produced a freezing point depression of 0.261°.

$(C_5H_8O_2)_3$ Found - 291 Calc. - 284

Average - 283

ACETOACETIC ESTER

Acetoacetic acid itself is relatively unstable, and consequently cannot be employed to any great extent, owing to its ready decomposition to acetone and carbon dioxide when slightly warmed. On the other hand, β-ketonic esters are considerably more stable, and as a result of this greater stability, have been extensively employed in syntheses; any products obtained are hydrolyzed to the acid if so desired.

At first sight, acetoacetic ester did not appear to give any reaction with P.N. acid, although shortly after the two had been brought together, a considerable evolution of gas was observed. It was assumed that this gas might be oxygen, produced from the decomposition of the hydrogen peroxide; this was soon disproved, however, since a glowing splint thrust into the flask was extinguished, rather than burning more vigorously. After a considerable period of time, there was observed the deposition of a white, amorphous material, which was augmented in quantity as time went on. This precipitate was filtered, washed free from acid and dried. The acid filtrate was preserved

and after a short interval, more precipitate appeared, which was also removed and joined with the lot first obtained. In all, about four grams of crude material were obtained. It is conceivable that, if the reaction had been permitted to proceed for a sufficient length of time, a good yield of product might have been realized.

The identity of the material was investigated, and found to be quite soluble in the usual organic solvents. Purification from petroleum ether and ethyl acetate produced a splendid, white, crystalline product. (M. Pt. 128-130°C.). The melting point of the crude material was 123-126°C., with no signs of the evolution of gas bubbles. Its solubility, behaviour in the flame, in which it exploded violently, general appearance and odour very closely resembled the dimolecular modification of acetone peroxide. A mixed melting point with a sample of the latter gave no depression. It was assumed, therefore, that the compound obtained from acetoacetic ester was also the dimolecular modification of acetone peroxide.

EXPERIMENTAL

10 grams acetoacetic ester were added to P.N. acid

made up from 70 cc. of 20% hydrogen peroxide and 30 cc. of 70% nitric acid, and which had previously been cooled to room temperature, 20°C. The ester dissolved completely in the acid solution, there being no appreciable generation of heat. Agitation of the flask containing the reagents caused the evolution of a considerable quantity of a gas. Evolution of the gas continued even when the flask was kept at rest, and persisted for five days, the system being allowed to stand quietly at room temperature. Outside of this phenomenon, no discolouration of the solution, or precipitation of any kind was observed. Some seven days later, i.e., twelve days after the beginning of the experiment, a small quantity of white, amorphous solid separated out. The precipitate was removed, washed free from acid with water, in which it is insoluble, and dried in the air. Gas bubbles continued to be evolved from the acid filtrate, and accordingly it was permitted to stand for another ten days, during which period, more precipitate was thrown down. This was joined with the first lot. Purification from ethyl acetate and petroleum ether resulted in a white, crystalline product having a melting point of 128-130°C. A mixed melting point with the dimolecular modification of acetone peroxide earlier described,

produced no depression.

As a result of the above behaviour, it was decided that acetone peroxide is the product arising from the action between acetoacetic ester and P.N. acid. The reaction may well proceed as follows:

$$CH_3COCH_2COOC_2H_5 \xrightarrow{\text{Acid Hydrolysis}} CH_3COCH_2COOH \qquad (31)$$

$$CH_3COCH_2COOH \xrightarrow{-CO_2} CH_3COCH_3 \qquad (32)$$

$$CH_3COCH_3 \xrightarrow{\text{P.N. acid}} \left[(CH_3)_2CO_2\right]_2 \qquad (33)$$

UREA AND THIOUREA

UREA

Urea contains a carbonyl group, modified, it is true, by the presence of two amino groups, and it was decided to investigate its behaviour towards P.N. acid. It is known that certain acids form addition salts with urea, which can be readily obtained from a concentrated solution. Notable among these salts is that of nitric acid ($CO(NH_2)_2.HNO_3$) and that of oxalic acid $\left[(COOH)_2.2CO(NH_2)_2\right]$. It is also known that urea hydrolyzes very readily, to form ammonium carbonate, an hydrolysis which is accelerated by the presence of hydrogen or hydroxyl ions.

EXPERIMENTAL

A small amount of urea was dissolved in water, and to this solution was added P.N. acid, cooled to 10°C., and consisting of 70 cc. of 25% hydrogen peroxide and 30 cc. of 70% nitric acid. No visible reaction appeared to take place, no discolouration of the solution occurred and no heat of reaction was apparent. The system was permitted to stand at room temperature for several days, but no precipitate

of any description was observed. It was possible that a soluble addition compound between the urea and nitric acid was formed, but it was inadvisable to heat the solution in order to concentrate it, and consequently the test was abandoned.

Another experiment was carried out, this time adding the acid mixture to the dry urea. The P.N. acid was of the same composition as above, and was previously cooled to 15°C. A white amorphous material remained suspended in the solution, being either unaltered urea or some insoluble reaction product. The temperature rose to 21°C. The solution was allowed to stand for about 48 hours, when most of the insoluble matter had disappeared; at the end of this time, a considerable evolution of gas was observed when the flask was agitated.

It has been mentioned that urea hydrolyzes to form ammonium carbonate. This reaction is accelerated by hydrogen ions, and the following reaction may well take place:

$$CO(NH_2)_2 + 2H_2O \xrightarrow{H^+} CO(ONH_4)_2 \longrightarrow H_2CO_3 \longrightarrow CO_2 + H_2O \qquad (34)$$

It would appear, therefore, that hydrolysis takes place, rather than oxidation or addition compound formation, as a result of the action between urea and P.N. acid.

THIOUREA

Potassium permanganate, in cold aqueous solution, oxidizes thiourea to urea. In nitric acid solution, or by means of hydrogen peroxide in oxalic acid solution, salts of a disulphide ($NH_2C=(NH)S-S(NH)=CNH_2$) are said to be produced, although such are not known in the free state (48). A compound was obtained as a result of the action of P.N. acid upon thiourea, which proved to be quite unstable, and which decomposed spontaneously shortly after its preparation.

EXPERIMENTAL

The thiourea on hand was crystallized from alcohol before subjecting it to the action of P.N. acid. M. Pt. - 173-175°C. A small quantity was dissolved in glacial acetic acid, the resulting solution acquiring a somewhat pinkish colouration. P.N. acid was prepared from 70 cc. of 25% hydrogen peroxide and 30 cc. of 70% nitric acid, and was cooled down to 1°C. before it was added to the thiourea. After addition, a white, amorphous material immediately separated out, the temperature rising rapidly to 21°C. The precipitate was filtered and washed (the removal taking

place within five minutes after the beginning of the experiment) and spread out to dry. After being exposed for four hours, the material decomposed, leaving a brown mass in the shape of small cones. The odour of sulphur dioxide was quite noticeable during, and for a short period after, the decomposition. During this process, the material bubbled up as though it were being gently heated over the flame, the while evolving a pale blue vapor. A portion which had been kept damp lasted longer, but once dry, behaved in the same manner.

A second experiment was conducted, but in this case dry thiourea was added to the P.N. acid of the same concentration as above, and cooled to 5-6^{o}C. There was a slight effervescence as the two came together, but otherwise no reaction appeared to take place. A white material remained suspended in the solution which appeared to possess somewhat the same crystalline form as the original thiourea. After the elapse of about an hour, the precipitate was filtered off, washed with a small quantity of water and spread out to dry. The compound was found to be soluble in water, and when introduced into the flame, melted to a yellow liquid, evolved white fumes and finally left a yellow residue which could be blasted away without difficulty. The odour of sulphur dioxide was distinct. A melting point determination

indicated decomposition at 125-126°C. A fresh sample introduced into the melting point apparatus at 120°C., resulted in sudden decomposition accompanied with a slight hiss. The same phenomenon took place with the melting point apparatus at 80°C. A portion was left to dry in the air, and after about two hours, decomposed in the manner described above. A larger portion had been put into a test-tube, where it remained intact for a much longer period, probably due to the slower rate of drying out. After fifteen hours, it decomposed, leaving a yellow residue. The odour of sulphur dioxide was very distinct, and considerable heat was generated during the decomposition, the resulting temperature being between 30°C. and 40°C.

As a result of this behaviour, it would appear that oxidation of some kind had occurred, to produce some type of unstable sulphone. The compound may be a mono- or dimolecular modification, sufficiently loaded up with oxygen to be capable of spontaneous decomposition, at the same time, producing sulphur dioxide.

DISCUSSION OF RESULTS

It will be noted that all the compounds which have been treated with P.N. acid have one feature in common, namely, they all contain a carbonyl group. In practically every case investigated, the resulting product proved to be a peroxide, indicating rather clearly that somewhat mild oxidation took place. Certainly the reagent does not appear to be sufficiently vigorous to break down or degrade the molecule upon which it acts, but merely serves to introduce oxygen atoms, which appear to be capable of very ready removal. The work of Baeyer and Villiger served to show that Caro's acid reacted in a like manner with ketones, to produce explosive peroxides. The action of P.N. acid undoubtedly appears to be parallel, and would serve to indicate the possibility of the existence of a peracid, here, pernitric acid.

The types of compounds capable of reaction with P.N. acid are by no means exhausted. The aldehydes, always capable of ready oxidation, might be expected to give rise to explosive peroxides; it should be possible to oxidize certain types of unsaturated compounds; α- and β-naphthol should lead to interesting results.

From the behaviour of hydrogen peroxide — nitric acid mixtures towards the compounds mentioned in the foregoing pages, it may be concluded that oxidation occurs in such a way as to produce explosive oxidation products, which might not be capable of preparation by means of more vigorous oxidizing agents. Milder reagents, on the other hand, might not be sufficiently active to bring about this result, especially if any heating should prove to be necessary.

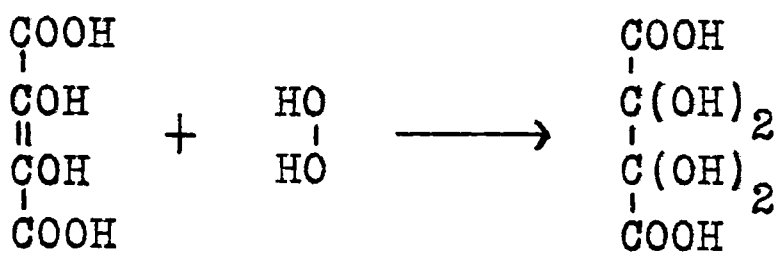
The reagent is easily prepared and may be handled without difficulty, the only conditions being that too concentrated solutions and temperatures much above 40°C. must be avoided.

As will be seen later, the structure of hydrogen peroxide has not been settled by any means. It has been shown that hydrogen peroxide is very slightly ionized, and the equilibrium:

$$\begin{matrix} H \\ \diagdown \\ \quad O \rightarrow O \\ \diagup \\ H \end{matrix} \rightleftharpoons H\text{-}O\text{-}O\text{-}H \rightleftharpoons H^{+} + OOH^{-} \qquad (35)$$

is always possible. Thus any highly ionized substance that may be present in a peroxide solution would depress this ionization. It has been shown by Hatcher and Sturrock (49) that in the oxidation of dihydroxy maleic acid,

hydrogen peroxide adds to the double bond to form dihydroxy tartaric acid:



(36)

the peroxide apparently adding in the manner indicated.

It would appear from the reactions that have been studied, that there is an addition of one or more oxygen atoms, usually one atom per molecule of ketone. This occurrence would indicate the first formula in equation (35), a structure which might be expected to yield its oxygen quite readily. The formula H-O-O-H would not be expected to do this.

In the oxidation of the aliphatic straight chain ketones, the acid reagent introduces one atom of oxygen and causes what may be termed a mild polymerization. Acetone is enolized to a small extent, the equilibrium ordinarily lying well on the keto side. This enolization is quite ignored as far as oxidation is concerned. Diisopropyl ketone would not be expected to enolize to any great degree, and no reaction was observed with this compound, a possible reason being the interference of the

alkyl groups. Cyclohexanone and cyclopentanone are enolized considerably more than is acetone, and here also, any possibility of addition across the double bond is overlooked.

With acetoacetic ester, acetone peroxide is formed as the result of oxidation by P.N. acid. The enol form is present in this compound at ordinary temperatures, but it would appear that the equilibrium is shifted, ketone hydrolysis taking place and acetone being produced.

When acetone peroxide was first prepared by Wolffenstein (36), hydrogen peroxide alone was employed, and several months were required for the production of even a small quantity of the product. Subsequent investigations (37, 38) showed that the reaction was considerably accelerated by the addition of a small amount of sulphuric acid. The latter was regarded as a catalyst. D'Ans and Frey (7) employed sulphuric acid as a catalyst in the preparation of peracids, which they obtained in good yield. In view of the fact that reaction between hydrogen peroxide and sulphuric acid takes place to form Caro's acid, it is possible that the latter is responsible for carrying out a rapid and effective oxidation.

The work of Hatcher and others (1, 34) served to show that complexes immediately formed between peroxide and organic, sulphuric and nitric acids, which more slowly break down to form peracid; this is especially true of the organic acids. It will be shown in Part 2, that the amount of peracid formed from hydrogen peroxide and nitric acid is very small indeed, with the dilute solutions employed, and therefore, the large decrease in conductivity (34) observed in such solutions can only be explained by the formation of the un-ionized complex. This has been further substantiated in experiments conducted by Hatcher and Hughes (50), which indicate the complex to be $HNO_3.H_2O_2$.

With slightly ionized hydrogen peroxide and highly ionized nitric acid, therefore, a 1:1 complex is formed. It is this complex which may be influential in effecting the transfer of oxygen atoms, or the small amount of peracid produced may perform this office.

The equilibrium:

$$H_2O_2 + HNO_3 \rightleftharpoons [HNO_3.H_2O_2] \rightleftharpoons HNO_4 + H_2O \qquad (37)$$

may exist. Certainly any ionization due to the structure HO-OH is definitely repressed, and it is even likely that a further shift to the left in equation (35) occurs to provide a form capable of readily liberating oxygen.

PART 2

THE REFRACTIVE INDEX

HISTORICAL

Reference has largely been made to Smiles - Physical Properties and Chemical Constitution of Chemical Compounds, for the following historical development of the measurement of refractive index and its relation to the determination of chemical constitution and structure (51).

For over a century, the refractivity of both organic and inorganic compounds has been studied, and the relations between this property and chemical constitution are perhaps better known than with most other physical properties. Among the first to conduct experiments in this direction were Arago (52) and Biot (53), who claimed to have shown that the refractivities of various gaseous compounds were equal to the sum of the refractivities of the constituents. The additive features of this property being the more obvious, it was but natural for them to concentrate their efforts upon this particular aspect of the problem.

Several years later, Dulong (54) repeated the work of Biot and Arago, this time making very accurate measurements. He discovered that mixtures of gases obeyed the additive law, but when combination took place, the resulting refractivity was sometimes greater, sometimes less than the sum of the effects of the components.

Isomeric compounds were first studied by Deville (55) and by Becquerel and Cahours (56), who discovered that in the case of liquid isomers with the same density, the refractive indices were identical. Gladstone and Dale (57) and Landolt (58) carried on this work regarding isomeric compounds, and the former authors observed that the refractivities were alike, provided that the chemical nature was the same. Thus was made the first observation concerning the constitutive nature of the refractive index.

Delffs (59) and Berthelot (60) extended their investigations to include a few homologous series. Berthelot found an increase with increasing molecular weight, and calculated a value for the methylene group, equal to about 18 units.

Gladstone and Hibbert (61) conducted a series of experiments with various strong acids and their salts. It was found that the refractivity in aqueous and alcoholic solution was much the same as for the pure material, either liquid or solid, the agreement holding within quite wide limits of dilution.

Brühl, Landolt, Conrady and Eykman accomplished a great deal of work in developing this property with respect to constitution and molecular structure.

The refractive index varies considerably with the physical state of a substance, and efforts were made to link up the property with the density. Among the first to propose such a relationship was Laplace (62), who corrected for the density and for the refractive index value for air, to obtain:

$$\frac{n^2-1}{d} = R = \text{Constant} \qquad (38)$$

This formula was employed for a considerable length of time, but proved to be inaccurate when the undulatory theory of light superseded the emission theory. The relationship was finally discarded in favour of an equation developed empirically by Gladstone and Dale (63)

$$\frac{n-1}{d} = R' = \text{Constant} \qquad (39)$$

A few years later, a third formula was proposed almost simultaneously by Lorentz (64) of Leyden and Lorenz (65) of Copenhagen. This took the form:

$$\frac{n^2-1}{n^2+2} \cdot \frac{1}{d} = R'' = \text{Constant} \qquad (40)$$

In actual practice, one form is found to have little or no advantage over the other. The constant "R" is known as the Specific Refractive Power.

Multiplying the above expressions by the molecular weight of the substance gives what is known as the Molecular Refractive Power. As a result of the extensive researches carried out with the refractive index, it has been possible to assign a value to each atom of the molecule — the atomic refractivity. The molecular refractivity may thus be regarded as the sum of the refractive effects of the component atoms.

The specific refractive power of a liquid compound is obtained by the measurement of the refractive index and the density at the same temperature. When the substance is a solid, the usual method is to

dissolve it in a suitable solvent and measure the resulting solution. Calculation is made from the admixture formula:

$$W\frac{N-1}{D} = w_1\frac{n_1-1}{d_1} + w_2\frac{n_2-1}{d_2} \qquad (41)$$

which, generally speaking, gives fairly accurate results, provided that the difference in refractive index between solute and solvent be not too great; otherwise reliance cannot be placed in the result.

The immediate problem in this work has been to amass data and to devise a means to determine the structure of hydrogen peroxide and of the peracids, both organic and inorganic.

With regard to hydrogen peroxide, various formulae have been proposed, based upon different types of evidence and different methods of approach. The most popular structure for the molecule has been:

H-O-O-H

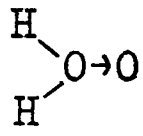
Evidence for this has been produced from various reactions encountered — the slight acidity of the compound, the structure of sodium and barium peroxide,

and the types of derivatives obtained from different reactions. A formula with quadrivalent oxygen present, as in:

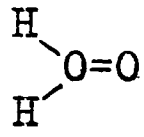
H-O≡O-H

has also been proposed, but this structure does not agree very well with the reactions of peroxide, or the various physical properties possessed by the molecule, the refractive index in particular.

Within recent years, Maass and co-workers have submitted a long series of papers dealing with all types of physical properties of hydrogen peroxide, and their evidence appears to lead to the structure:



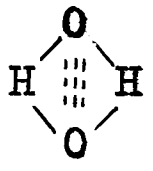
with a semi-polar oxygen linkage. A structure similar to this was originally proposed by Kingzett in 1884, quadrivalent oxygen being involved:



Regarding this latter structure, Gieb and

Harteck (66) carried out experiments with hydrogen and oxygen at very low temperatures. The two gases were brought together at temperatures ranging around -150°C., and from the absorption spectra data obtained, hydrogen peroxide was apparently formed, in what the authors termed "a new form". The formula proposed was that indicated above. It would appear that these authors consider their work to be somewhat pioneering in nature; evidently they did not consider any of the work done by others upon the same subject.

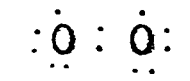
Rius (67) had a contribution to make regarding the structure of hydrogen peroxide. He examined the existing formulae and carried out experiments to test their validity, under varied conditions. He was not satisfied with any of them and proposed his own:



but it really is not quite clear as to just what this structure is intended to explain.

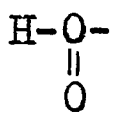
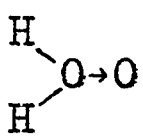
With reference to the work done by Maass and

co-workers, the former together with Hatcher (68) measured the magnetic susceptibility of hydrogen peroxide. Oxygen is definitely paramagnetic, which has been explained by the following structure for the molecule:

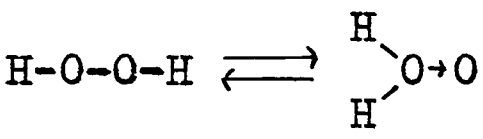


where the odd electrons on each atom contribute to this effect. Water, on the other hand, is diamagnetic, and it was discovered that hydrogen peroxide is even more diamagnetic than water. This would suggest that oxygen in peroxide is not linked as in the oxygen molecule.

Maass and Cuthbertson (69) concluded that neither the refractive power nor the dispersive power appeared to offer decisive proof as to the structure or correct formula of hydrogen peroxide. Applying Sugden's (70) parachor, the following information was obtained:

	1.	2.	3.
Formula	H-O-O-H		
P. (Calc.)	74.1	97.7	72.5
P. (Found)	69.6		

Sugden favoured formula 1, the above authors formula 3; formula 2 is certainly too high. In the words of the authors: "It appears reasonable to suppose that the calculated values of the molecular refractive power and dispersive power of hydrogen peroxide would agree were the atomic refractive power of a co-ordinate linked oxygen atom known. On the basis of the deviations shown for the three cases, three is to be taken as correct, and the atomic refractive power of a co-ordinate oxygen linked to oxygen is 2.1." The possibility of an equilibrium existing between the two forms:



(42)

is not excluded.

Brühl (71), in his classical work upon the refractive index and its relation to constitution, measured hundreds of organic nitrogen compounds. Of special interest was the relationship found between nitric acid and the alkyl nitrates and nitrites. The outcome of his experiments was a proposal for the following formula for nitric acid:

H-O-O-N=O

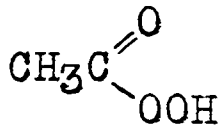
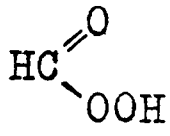
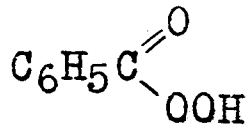
(refer page 16). He did not declare that this structure was always possessed by the acid, for it is highly ionized, but it might be an intermediate form assumed by the molecule under propitious conditions. It is well known that nitric acid is highly unstable when pure, and begins to decompose very shortly after its preparation. According to Friend (72), pure nitric acid always contains free nitrogen pentoxide. Consequently, any physical measurements made upon such material must be taken with reservation. Again, in many reactions, nitric acid is decomposed, as is the case with the peracids, when they are employed as oxidizing agents. In the latter instance, it is true that the peracid does not break down entirely, but it does lose its peculiar properties.

In support of Brühl's proposal, Klason and Carlson (73) observed that alkyl peroxide is formed as an intermediate product in the alkaline saponification of alkyl nitrates. They suggested, therefore, that alkyl nitrates should be represented as:

R-O-O-N=O

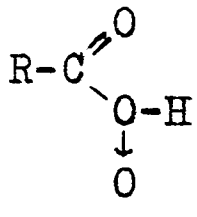
One should not lose sight of the fact that the esters of nitric acid, methyl nitric ester and ethyl nitric ester, are sensitive to shock, and are said to explode with considerable violence when heated rapidly. Other esters, such as acetyl nitrate, behave in a similar manner. On the other hand, alkyl halides, acetyl halides, ethyl sulphuric acid and diethyl sulphate are reactive, but not explosive. Such behaviour on the part of the nitric acid esters might well point to some kind of instability.

In the case of the organic peracids, the formulae which have usually been accepted are:

but none has really been proved.

Hatcher and Powell (9) proposed the possible formula for a simple peracid:



i.e., a molecule containing a semi-polar bond between

oxygen. If, therefore, a value for the molecular refractivity can be found for the peracid, proof of the above structure should be given by employing the value for co-ordinate oxygen as found by Maass and Cuthbertson (69), and observing the agreement between the observed and calculated values.

It has been the purpose of the measurements of refractive index to obtain data which ultimately might be employed in association with other physical properties, such as conductivity, parachor, magnetic rotatory power, magnetic susceptibility and dielectric constant, to arrive at a method to determine the structure of the compounds which have been discussed in the foregoing pages.

DESCRIPTION OF THE APPARATUS AND METHOD EMPLOYED

The method employed in the determination of the refractive index of the various solutions prepared was the "Method of Minimum Deviation". Owing to the corrosive character of nitric acid, a refractometer of the Abbé type could not be used. Moreover, the ground flint glass of such an instrument offers a rough surface which would cause the rapid decomposition of the hydrogen peroxide present in the solution.

Accordingly, an instrument has been devised, after the style of a spectrometer. It has been made possible to mount a small triangular glass cell of about 5 cc. capacity, having angles approximately equal to 60°.

The refractometer consists of a collimator tube having an adjustable slit at one end and at the other a lens by means of which the rays of light may be rendered parallel. The collimator is clamped in a fixed position, being fastened to the base of the instrument. Behind this is placed a graduated circle, which, being fastened to the telescope, permits of rotation in any desired direction. Provision is made for the support of a cylinder,

having adjustable slits to permit the passage of the light rays, and an inlet and outlet for the continual passage of water for temperature control. The triangular glass cell is placed within this cylinder, and is centered by means of a suitable support. Thus the lower portion of the cell is surrounded by water, and the solution being measured may be brought to any desired temperature, which was read by an Anschutz thermometer (Range 0-60°C.). Provision is made so that the cylinder containing the cell may be rotated independently of the scale and telescope. The entire solution was brought to uniform temperature by gentle agitation with a medicine dropper.

In order to adjust the refractometer, the telescope was removed and the position of the eye-piece altered until the cross-hairs were in focus, the telescope being directed towards a plain bright background. It was then adjusted for parallel rays by pointing to some distant object, at least one or two hundred yards away, and the whole tube containing eye-piece and cross-hairs moved until the object was sharply focussed.

The telescope was replaced onto the refractometer, and brought into line with the collimator tube. The slit

was illuminated, and its distance from the collimating lens altered until it (the slit) appeared sharply defined through the telescope. Since the telescope was adjusted for parallel light, it follows that the light from the collimator is parallel. This was all carried out with the cylinder and prism removed from its position upon the graduated circle. The reading of the scale in this position was taken as the zero point.

The Method of Minimum Deviation depends upon the principle that when a beam of light, abcd, Fig. 1, traverses a prism in such a way that the angles "i" and " i' " are equal, the beam suffers the minimum amount of deviation in its path of any possible course through the prism. At the outset, the angle α of the cell was measured on the goniometer.

The cell, containing the solution to be measured, was placed within the cylinder, which was already in position upon the circle, and was rotated to the left, followed by the telescope, and adjustment made to bring the slit into view. The position of minimum deviation is attained when, by turning the cell alone, the slit reaches a fixed point, remains stationary for a moment and then moves away to the left, no matter in what direction the cell may be rotated.

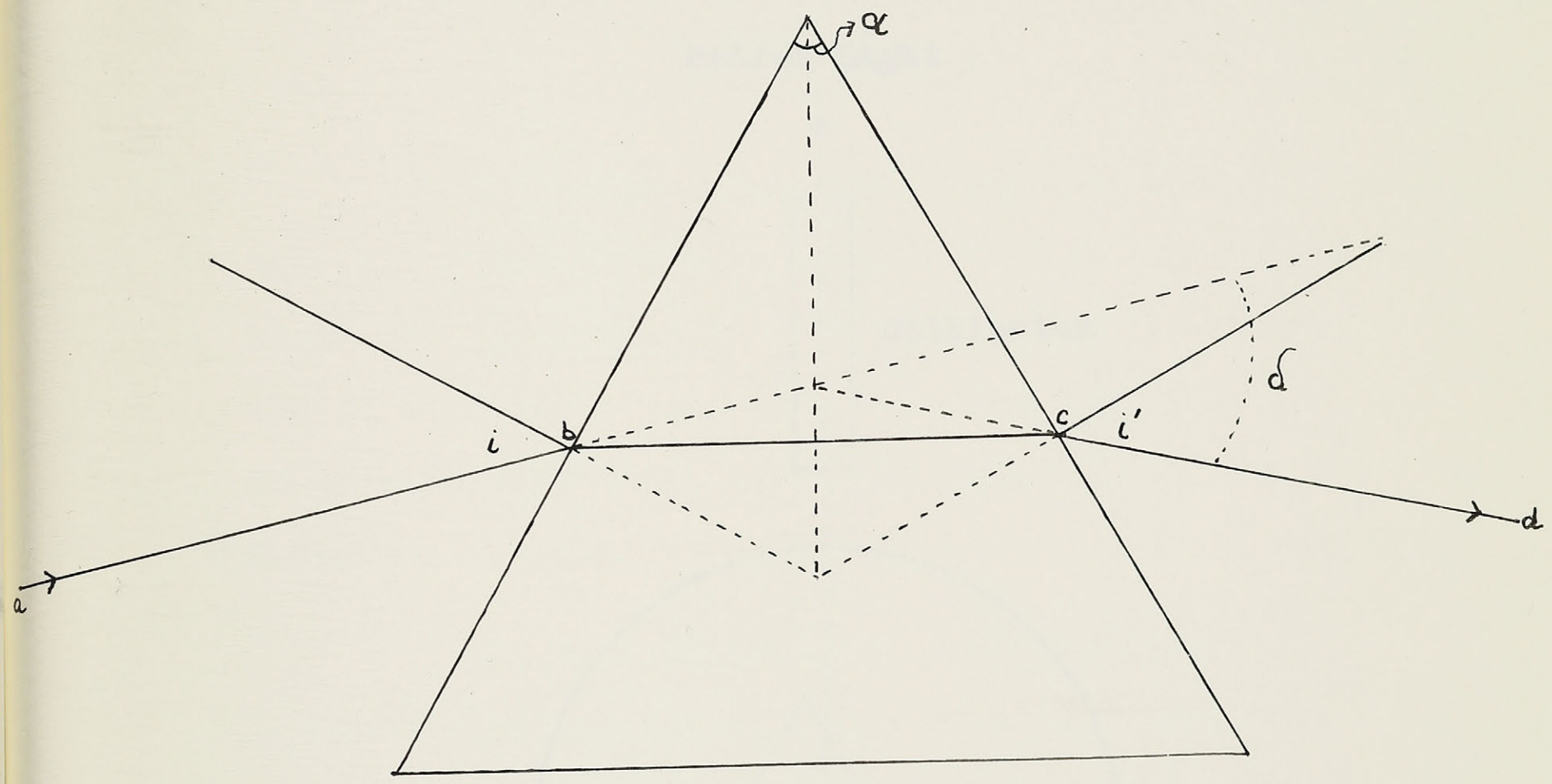


Figure 1.

Final adjustment was made before the reading was taken, to give the angle δ . The arrangement of the instrument when making a measurement was essentially as shown in Fig. 2.

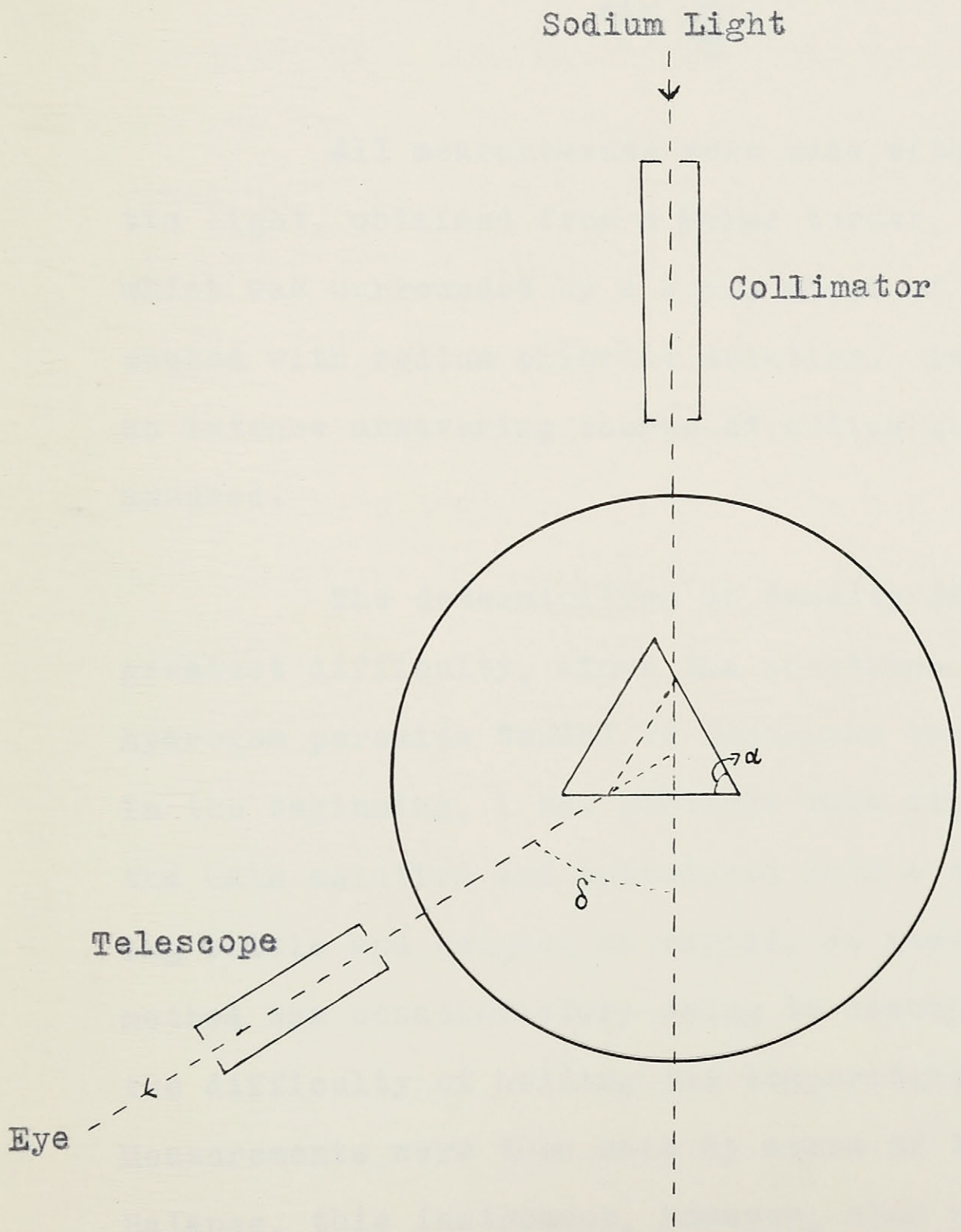


Figure 2.

Calculation of the refractive index was made by means of the relationship:

$$n = \frac{\sin \frac{(\alpha+\delta)}{2}}{\sin \frac{\alpha}{2}} \qquad (42)$$

All measurements were made with monochromatic light, obtained from a Meker burner, the head of which was surrounded by a small sheet of asbestos soaked with sodium chloride solution. In this way, an intense unwavering source of sodium light was assured.

The determination of density offered the greatest difficulty, since the solutions containing hydrogen peroxide tended to decompose very readily. In the beginning, 1 cc. portions were pipetted from the main solution and introduced into a tared weighing bottle and weighed as rapidly as possible. The method was unsatisfactory owing to decomposition and the difficulty of holding the temperature at 20°C. Measurements were then made by means of the Westphal Balance, this instrument, however, also presenting difficulties. The glass bob and the platinum wire tended to gather bubbles of oxygen upon them and gave

a low value. The densities, therefore, were not as accurate as it would have been desired, and when applied to the calculation of the specific refractive power, tend to introduce a source of error, which together with other approximations, accumulate in the final result. The values obtained, however, indicate the way for further work in this direction, and are undoubtedly of value for the determination of the structure of the compounds in which the present interest lies.

A new method for the determination of density has been devised, which appears to remove all trouble as far as decomposition, amount of sample required, etc., are concerned. It is expected that in further work, which is being carried out in this direction, the new instrument will produce much more accurate results.

The solutions included in the tables which follow were in general prepared by the direct weighing of the reagents. In some cases, solutions were made up by diluting a weighed amount of a stock solution with known quantities of distilled water. In

some instances, the refractive index was determined over a temperature range, from which it was possible to obtain a temperature coefficient. The specific refractive powers were calculated by means of the Lorentz-Lorenz relationship in all cases.

EXPERIMENTAL

Various compounds were selected at random, and their refractive index measured with a view to determining the accuracy of the refractometer. The values found, when compared with those given in the literature, agree quite favourably except in one or two instances. The tendency appears for the observed values of refractive index to be a little low.

Compound	Ref. Ind. Na_D^{20}	Literature
Methyl alcohol	1.3197	$1.33118^{14.5}$
Water	1.3330	1.33299
Alcohol	1.3488	1.36242^{18}
Acetone	1.3576	$1.35886^{19.7}$
Ethyl acetate	1.3710	$1.37216^{18.9}$
Cyclopentanone	1.4364	1.4366
Chloroform	1.4455	1.46305^{15}
m-Methyl-cyclo-hexanone	1.4424	1.44313^{25-15}
Benzene	1.4961	1.50165

SERIES 1

HYDROGEN PEROXIDE — NITRIC ACID MIXTURES

By direct titration with 0.1031N. $KMnO_4$, the hydrogen peroxide was found to contain 12.65% H_2O_2.

By direct titration with 0.5992N NaOH, the commercial C.P. nitric acid was found to contain 69.94% HNO_3.

Solution	$\%H_2O_2$	$\%HNO_3$	d^{20} g/cc.	n_D^{20}	R"
1.	1.76	3.37	1.0304	1.3390	0.20288
2.	4.03	7.72	1.0634	1.3470	0.20078
3.	6.52	12.51	1.1024	1.3550	0.19769
4.	9.41	18.03	1.1496	1.3657	0.19644

SERIES 2

By direct titration with 0.1031N. $KMnO_4$, the hydrogen peroxide was found to contain 28.12% H_2O_2.

Solution	$\%H_2O_2$	$\%HNO_3$	d^{20} g/cc.	n_D^{20}	R"
1.	8.66	48.31	1.3168	1.3974	0.18304
2.	11.29	41.85	1.2969	1.3937	0.18432
3.	13.29	36.88	1.2733	1.3896	0.18600
4.	16.04	30.05	1.2528	1.3842	0.18671
5.	18.75	23.30	1.2251	1.3792	0.18872
6.	20.51	18.61	1.1936	1.3741	0.19138
7.	22.52	13.94	1.1684	1.3668	0.19208

SERIES 3

By direct titration with 0.1031N. $KMnO_4$, the hydrogen peroxide was found to contain 65.96% H_2O_2.

Solution	$\%H_2O_2$	$\%HNO_3$	d_D^{20} g/cc.	n_D^{20}	R"
1.	12.14	22.30	1.1619	1.3708	0.19505
2.	12.29	22.60	1.1655	1.3717	0.19487
3.	14.22	26.10	1.1935	1.3780	0.19317
4.	17.05	31.30	1.2342	1.3871	0.19523
5.	24.09	44.39	1.3500	1.4015	0.18017

HYDROGEN PEROXIDE — ACETIC ACID MIXTURES

SERIES 1

By direct titration with 0.1031N. $KMnO_4$, the hydrogen peroxide was found to contain 28.12% H_2O_2.

By direct titration with 0.05992N. NaOH, the glacial acetic acid was found to contain 98.51% CH_3COOH.

Solution	$\%H_2O_2$	%HAc	d^{20} g/cc.	n_D^{20}	R"
1.	9.76	17.18	1.0546	1.3509	0.20450
2.	12.70	22.34	1.0726	1.3582	0.20483
3.	18.67	32.86	1.1009	1.3675	0.20420

Values of refractive index over a temperature range.

Temp.	Solution 1	Solution 2	Solution 3
10°C.	1.3539	1.3599	1.3762
20	1.3509	1.3582	1.3675
30	1.3488	1.3552	1.3645
40	1.3463	1.3531	1.3624
Temp. Coeff.	-0.00025	-0.00023	-0.00046

Comparison of Observed and Calculated Values.

Refractive Index			Specific Refractive Power		
$n_{obs.}$	$n_{cal.}$	D(o-c)	$R''_{obs.}$	$R''_{cal.}$	D(o-c)
1.3509	1.3471	0.0038	0.20450	0.20436	0.00014
1.3582	1.3513	0.0069	0.20483	0.20386	0.00097
1.3675	1.3599	0.0076	0.20420	0.20284	0.00136

SERIES 2

By direct titration with 0.1031N. $KMnO_4$, the hydrogen peroxide was found to contain 27.00% H_2O_2.

By direct titration with 0.05992N. NaOH, the glacial acetic acid was found to contain 98.51% CH_3COOH.

Solution	$\%H_2O_2$	%HAc	d^{20} g/cc.	n_D^{20}	R''
1.	5.43	13.05	1.0326	1.3454	0.20588
2.	6.23	14.99	1.0389	1.3476	0.20582
3.	7.68	18.45	1.0453	1.3501	0.20590
4.	9.03	21.68	1.0516	1.3535	0.20646
5.	10.79	25.94	1.0624	1.3594	0.18918
6.	12.05	28.95	1.0640	1.3603	0.20748
7.	16.28	39.12	1.1205	1.3700	0.20185

Comparison of Observed and Calculated Values.

Refractive Index			Specific Refractive Power		
$n_{obs.}$	$n_{cal.}$	D(o-c)	$R''_{obs.}$	$R''_{cal.}$	D(o-c)
1.3454	1.3421	0.0033	0.20588	0.20548	0.00040
1.3476	1.3435	0.0041	0.20582	0.20539	0.00043
1.3501	1.3460	0.0041	0.20590	0.20523	0.00067
1.3535	1.3483	0.0052	0.20646	0.20508	0.00138
1.3594	1.3513	0.0081	0.18918	0.20491	-0.01573
1.3603	1.3534	0.0069	0.20748	0.20994	-0.00246
1.3700	1.3606	0.0094	0.20185	0.20434	-0.00249

Values of refractive index over a temperature range.

Temp.	Solution 1	Solution 2	Solution 3	Solution 4
10°C.	1.3480	1.3493	1.3527	1.3561
20	1.3454	1.3476	1.3501	1.3535
30	1.3450	1.3454	1.3484	1.3510
40	1.3437	1.3433	1.3463	1.3488
Temp. Coeff.	-0.00014	-0.00020	-0.00021	-0.00024

Temp.	Solution 5	Solution 6	Solution 7
10°C.	1.3620	1.3628	1.3725
20	1.3594	1.3603	1.3700
30	1.3561	1.3582	1.3662
40	1.3535	1.3561	1.3632
Temp. Coeff.	-0.00028	-0.00022	-0.00031

SERIES 3

By direct titration with 0.1031N. $KMnO_4$, the hydrogen peroxide was found to contain 25.18% H_2O_2.

The glacial acetic acid employed contained 98.51% CH_3COOH, and was kept constant throughout this series at 29.72%.

Solution	$\%H_2O_2$	d^{20} g/cc.	n_D^{20}	R"
1.	10.07	1.0679	1.3603	0.20682
2.	11.83	1.0724	1.3615	0.20658
3.	13.60	1.0766	1.3632	0.20615
4.	15.11	1.0850	1.3637	0.20529
5.	16.37	1.0886	1.3641	0.20479
6.	17.59	1.0923	1.3649	0.20453

Comparison of Observed and Calculated Values.

Refractive Index			Specific Refractive Power		
$n_{obs.}$	$n_{cal.}$	D(o-c)	$R"_{obs.}$	$R"_{cal.}$	D(o-c)
1.3603	1.3523	0.0080	0.20682	0.20554	0.00128
1.3615	1.3536	0.0079	0.20658	0.20671	-0.00023
1.3632	1.3549	0.0083	0.20615	0.20430	0.00185
1.3637	1.3560	0.0077	0.20529	0.20376	0.00153
1.3641	1.3569	0.0072	0.20479	0.20332	0.00133
1.3649	1.3578	0.0071	0.20453	0.20289	0.00164

Values of refractive index over a temperature range.

Temp.	Solution 1	Solution 2	Solution 3	Solution 4
10°C.	1.3627	1.3658	1.3662	1.3670
20	1.3603	1.3632	1.3637	1.3641
30	1.3573	1.3598	1.3611	1.3615
40	1.3552	1.3578	1.3586	1.3590
Temp. Coeff.	-0.00025	-0.00027	-0.00025	-0.00027

Temp.	Solution 5
10°C.	1.3670
20	1.3649
30	1.3611
40	1.3590
Temp. Coeff.	-0.00027

SERIES 4

By direct titration with 0.1031N. $KMnO_4$, the hydrogen peroxide was found to contain 24.58% H_2O_2.

The acetic acid was kept constant at 29.70%.

Solution	$\%H_2O_2$	d^{20} g/cc.	n_D^{20}	R"	% Peracid
1.	11.06	1.0688	1.3599	0.20638	3.62
2.	12.54	1.0742	1.3615	0.20623	3.37
3.	13.76	1.0787	1.3624	0.20581	3.25
4.	14.75	1.0814	1.3632	0.20571	2.95
5.	15.73	1.0850	1.3637	0.20529	2.97
6.	17.17	1.0895	1.3641	0.20464	3.11

Comparison of Observed and Calculated Values.

Refractive Index			Specific Refractive Power		
$n_{obs.}$	$n_{cal.}$	D(o-c)	$R''_{obs.}$	$R''_{cal.}$	D(o-c)
1.3599	1.3529	0.0070	0.20638	0.20519	0.00119
1.3615	1.3540	0.0075	0.20623	0.20468	0.00155
1.3624	1.3549	0.0075	0.20581	0.20424	0.00157
1.3632	1.3556	0.0076	0.20571	0.20389	0.00182
1.3637	1.3564	0.0073	0.20529	0.20354	0.00175
1.3641	1.3574	0.0067	0.20464	0.20303	0.00161

Values for Peracetic acid

	Refractive Index	Specific Refractive Power
1.	1.5856	0.23122
2.	1.6172	0.24451
3.	1.6246	0.24677
4.	1.6474	0.25966
5.	1.6431	0.25724
6.	1.6109	0.25643

AQUEOUS HYDROGEN PEROXIDE SOLUTIONS

Solution	$\%H_2O_2$	d^{20} g/cc.	n_D^{20}	R"
1.	2.15	1.0051	1.3338	0.20510
2.	4.99	1.0136	1.3357	0.20445
3.	8.02	1.0261	1.3370	0.20309
4.	10.97	1.0341	1.3387	0.20200
5.	11.05	1.0368	1.3389	0.20160
6.	13.85	1.0463	1.3411	0.20094
7.	17.57	1.0577	1.3437	0.20005
8.	20.06	1.0727	1.3443	0.19766
9.	21.04	1.0703	1.3468	0.19940
10.	22.81	1.0781	1.3472	0.19818
11.	23.33	1.0817	1.3468	0.19729
12.	25.17	1.0850	1.3494	0.19800
13.	26.44	1.0886	1.3501	0.19770
14.	43.09	1.1615	1.3626	0.19124
15.	51.51	1.1947	1.3677	0.18826
16.	65.86	1.2656	1.3800	0.18303
17.	100.00	1.4419	1.4063	0.17074 ★

★ Maass and Hatcher, J.A.C.S. 42, 2548, (1920)

Comparison of Observed and Calculated Values.

Refractive Index			Specific Refractive Power		
$n_{obs.}$	$n_{cal.}$	D(o-c)	$R''_{obs.}$	$R''_{cal.}$	D(o-c)
1.3338	1.3345	-0.0007	0.20510	0.20529	-0.00019
1.3357	1.3366	-0.0009	0.20445	0.20429	0.00016
1.3370	1.3388	-0.0018	0.20309	0.20322	-0.00013
1.3387	1.3410	-0.0023	0.20200	0.20219	-0.00019
1.3389	1.3410	-0.0021	0.20160	0.20215	-0.00055
1.3411	1.3431	-0.0020	0.20094	0.20116	-0.00022
1.3437	1.3458	-0.0021	0.20005	0.19984	0.00021
1.3443	1.3477	-0.0034	0.19766	0.19717	0.00049
1.3468	1.3484	-0.0016	0.19940	0.19862	0.00082
1.3472	1.3496	-0.0024	0.19818	0.19799	0.00019
1.3468	1.3500	-0.0032	0.19729	0.19781	-0.00052
1.3494	1.3514	-0.0020	0.19800	0.19716	0.00084
1.3501	1.3523	-0.0022	0.19770	0.19671	0.00099

AQUEOUS NITRIC ACID SOLUTIONS

Solution	%HNO_3	d^{20} g/cc.	n_D^{20}	R"
1.	13.47	1.0660	1.3514	0.20256
2.	14.84	1.0760	1.3535	0.20176
3.	18.24	1.0895	1.3573	0.20119
4.	23.39	1.1248	1.3646	0.19845
5.	32.24	1.1818	1.3780	0.19506
6.	40.83	1.2261	1.3860	0.19156
7.	54.12	1.3011	1.3990	0.18591

AQUEOUS NITRIC ACID SOLUTIONS ✱

Solution	%HNO_3	n_D^{20}
1.	2.28	1.33593
2.	3.38	1.33733
3.	4.76	1.33905
4.	11.33	1.34770
5.	18.93	1.35811
6.	25.98	1.36781
7.	41.15	1.38698
8.	64.82	1.40325
9.	69.73	1.40369
10.	77.83	1.40231

✱ Landolt, Börnstein Physikalisch-Chemisch Tabellen, 5th. Ed. Vol 2, Pt. 2, P. 831.

AQUEOUS ACETIC ACID SOLUTIONS

Solution	$\%CH_3COOH$	d^{20} g/cc.	n_D^{20}	R"
1.	10.23	1.0109	1.3403	0.20754
2.	24.66	1.0299	1.3505	0.20917
3.	32.91	1.0367	1.3556	0.21053
4.	46.14	1.0438	1.3628	0.21290
5.	54.63	1.0482	1.3683	0.21489
6.	65.52	1.0537	1.3729	0.21615
7.	65.66	1.0528	1.3729	0.22653
8.	74.13	1.0561	1.3754	0.21695
9.	75.67	1.0565	1.3758	0.21708
10.	87.55	1.0588	1.3779	0.21769
11.	91.61	1.0579	1.3775	0.21764
12.	98.51	1.0446	1.3733	0.21828

Comparison of Observed and Calculated Values.

Refractive Index			Specific Refractive Power		
$n_{obs.}$	$n_{cal.}$	D(o-c)	$R''_{obs.}$	$R''_{cal.}$	D(o-c)
1.3403	1.3370	0.0033	0.20754	0.20711	0.00043
1.3505	1.3430	0.0075	0.20917	0.20859	0.00058
1.3556	1.3463	0.0093	0.21053	0.20944	0.00109
1.3628	1.3515	0.0113	0.21290	0.20978	0.00312
1.3683	1.3550	0.0133	0.21489	0.21168	0.00321
1.3729	1.3594	0.0135	0.21615	0.21280	0.00335
1.3729	1.3594	0.0135	0.22653	0.21281	0.01372
1.3754	1.3628	0.0126	0.21695	0.21369	0.00326
1.3758	1.3635	0.0123	0.21708	0.21384	0.00324
1.3779	1.3682	0.0097	0.21769	0.21506	0.00263
1.3775	1.3699	0.0076	0.21764	0.21548	0.00216
1.3733	1.3727	0.0006	0.21828	0.21619	0.00209

Values of refractive index over a temperature range.

Temp.	Solution 1	Solution 2	Solution 3	Solution 4
10°C.	1.3418	1.3522	1.3578	1.3662
20	1.3403	1.3505	1.3556	1.3628
30	1.3386	1.3480	1.3535	1.3603
40	1.3369	1.3459	1.3505	1.3573
Temp. Coeff.	-0.00016	-0.00021	-0.00024	-0.00030

Temp.	Solution 5	Solution 6	Solution 7	Solution 8
10°C.	1.3712	1.3758	1.3758	1.3804
20	1.3683	1.3729	1.3729	1.3754
30	1.3649	1.3691	1.3691	1.3720
40	1.3620	1.3666	1.3662	1.3687
Temp. Coeff.	-0.00030	-0.00030	-0.00032	-0.00040

Temp.	Solution 9	Solution 10	Solution 11	Solution 12
10°C.	1.3787	1.3813	1.3813	solidified
20	1.3758	1.3779	1.3775	1.3736
30	1.3721	1.3741	1.3725	1.3691
40	1.3687	1.3700	1.3696	1.3653
Temp. Coeff.	-0.00030	-0.00040	-0.00050	-0.00040

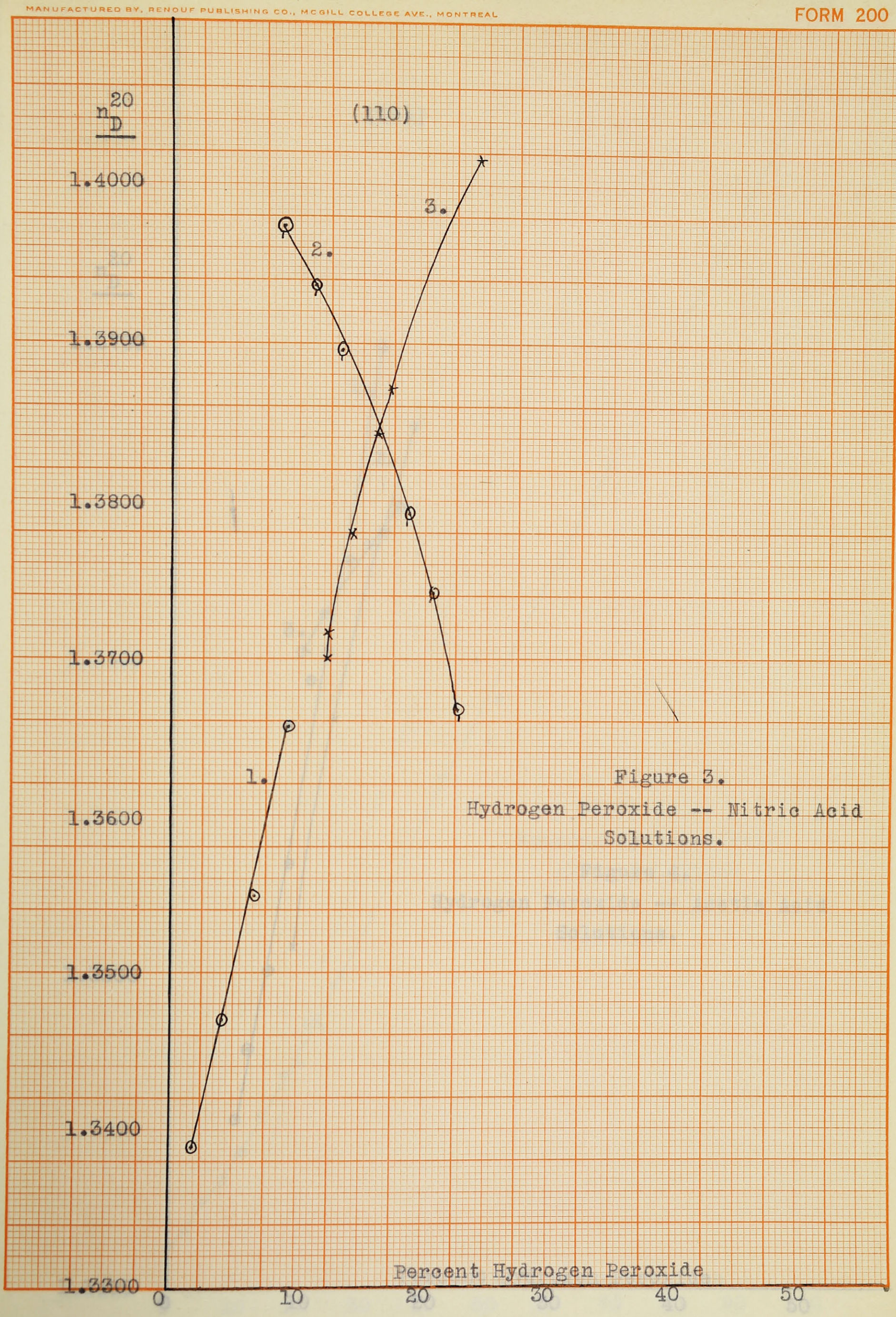


Figure 3.
Hydrogen Peroxide -- Nitric Acid Solutions.

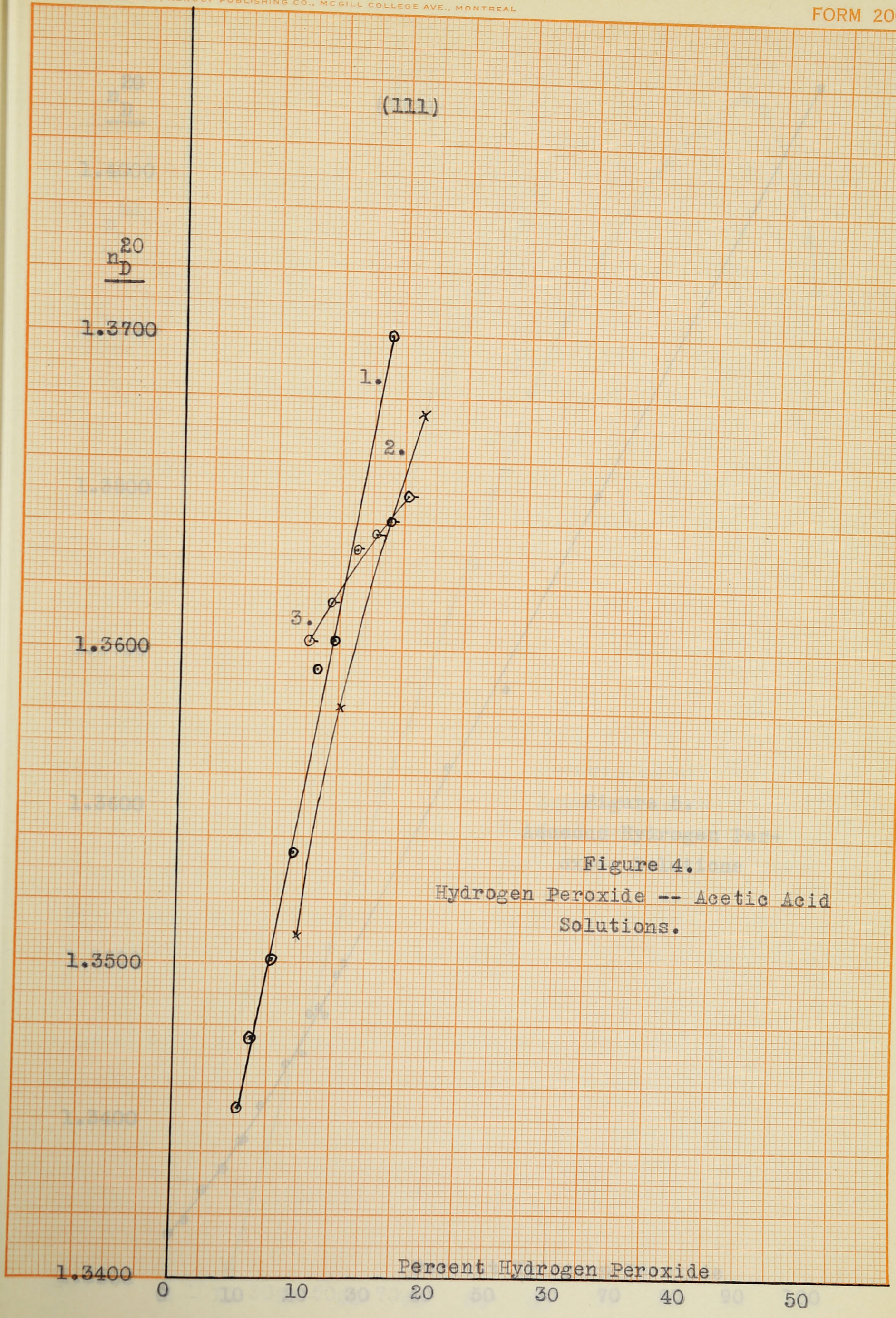


Figure 4.
Hydrogen Peroxide -- Acetic Acid
Solutions.

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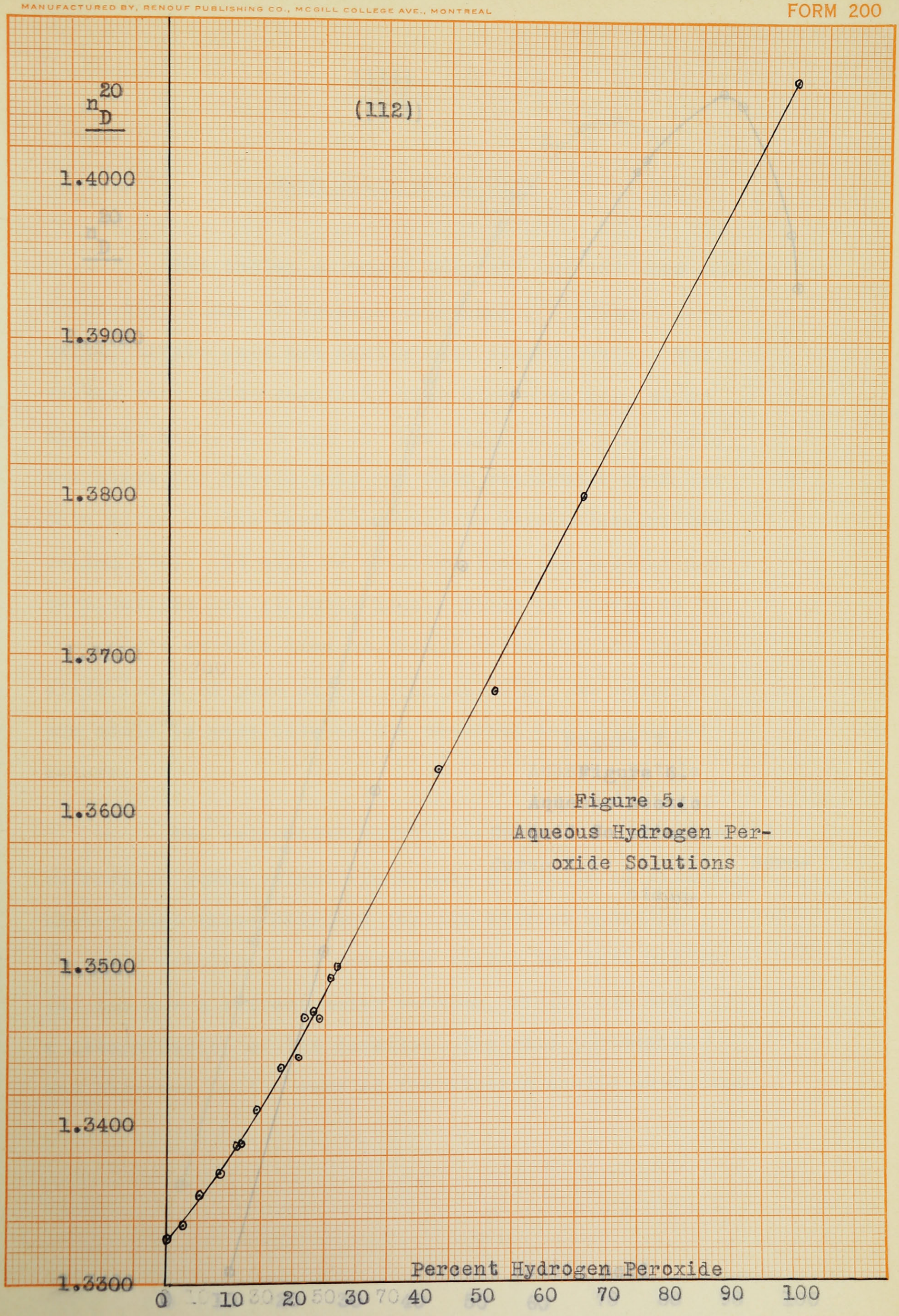

Figure 5.
Aqueous Hydrogen Peroxide Solutions

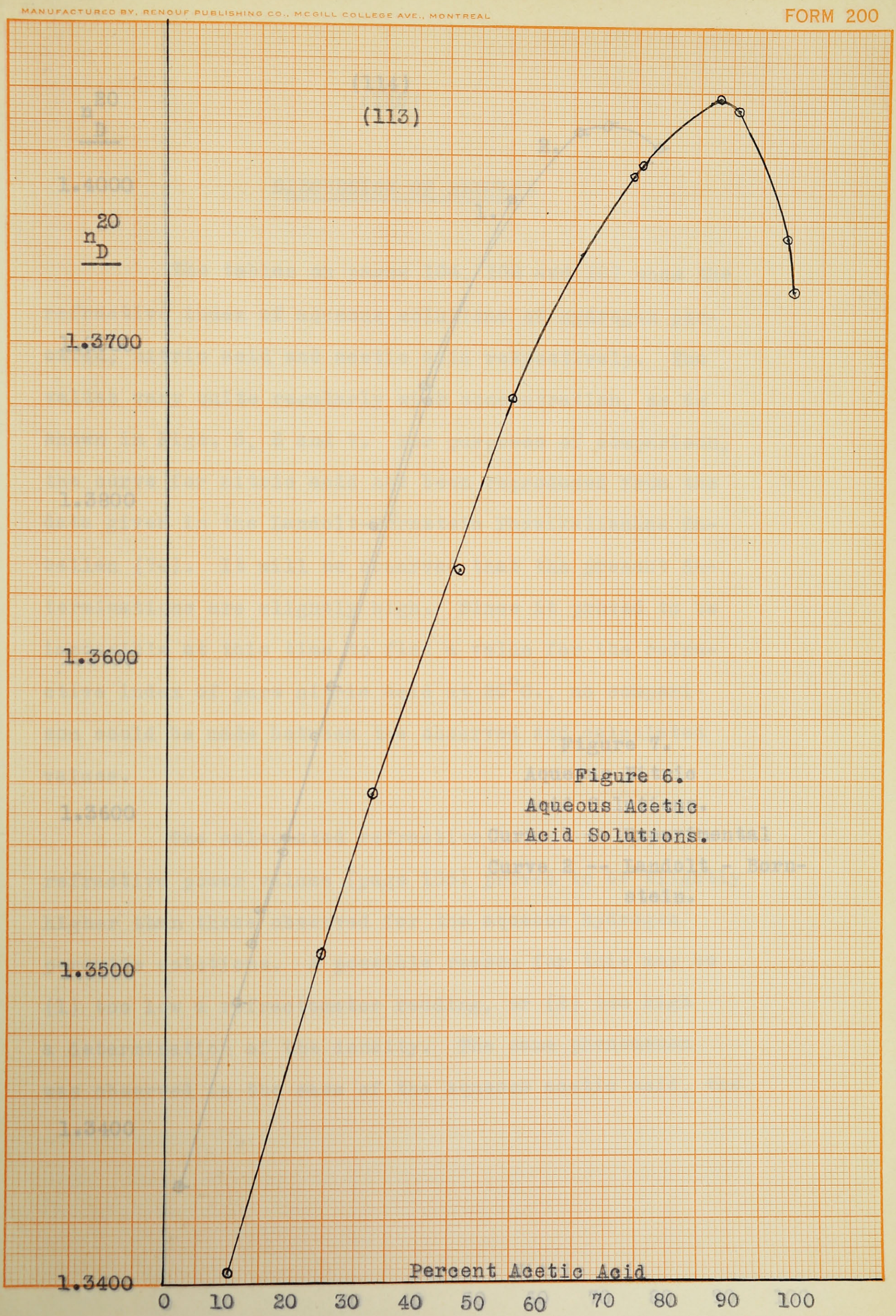

Figure 6.
Aqueous Acetic
Acid Solutions.

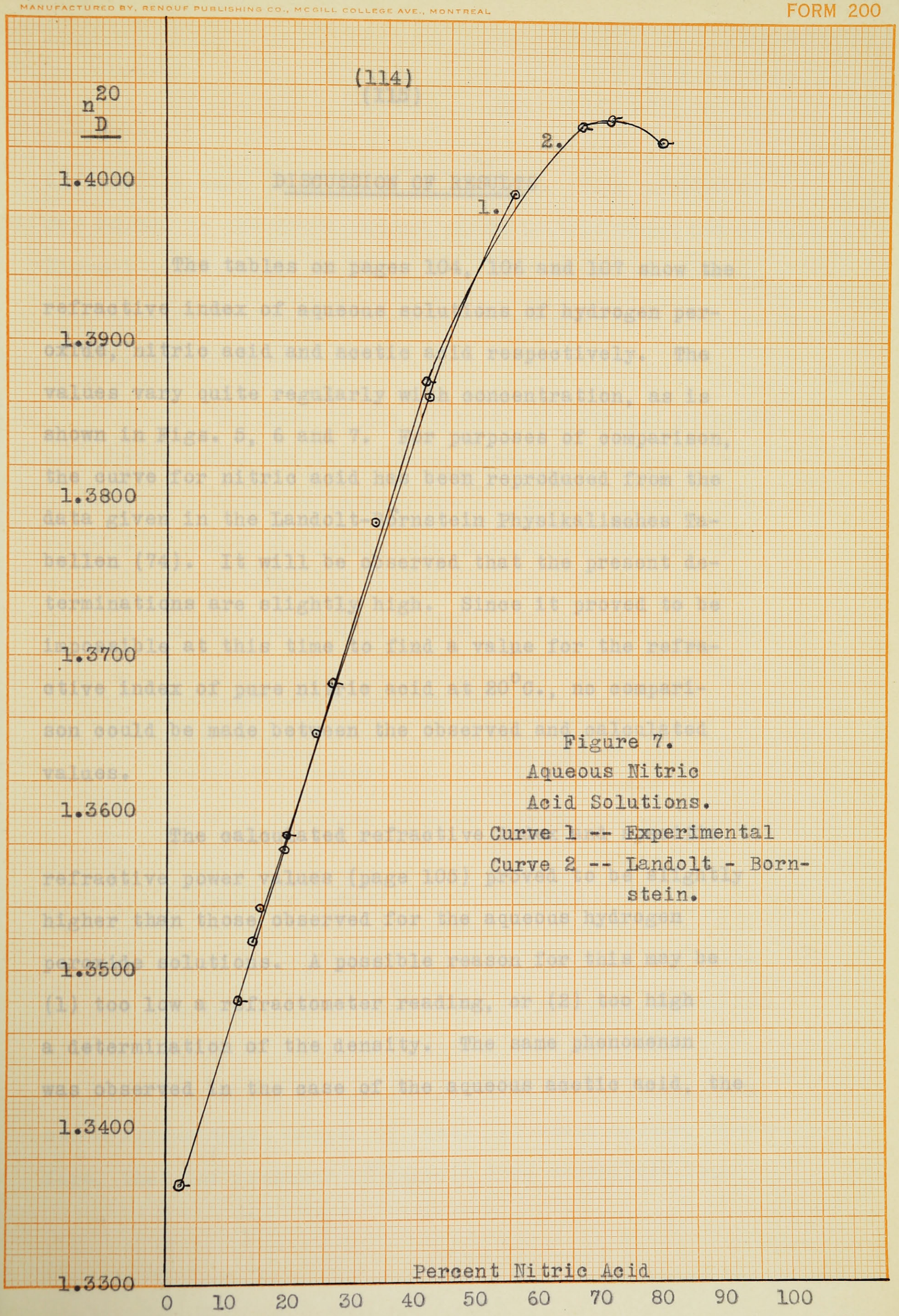

Figure 7.
Aqueous Nitric
Acid Solutions.
Curve 1 -- Experimental
Curve 2 -- Landolt - Born-
stein.

DISCUSSION OF RESULTS

The tables on pages 104, 106 and 107 show the refractive index of aqueous solutions of hydrogen peroxide, nitric acid and acetic acid respectively. The values vary quite regularly with concentration, as is shown in Figs. 5, 6 and 7. For purposes of comparison, the curve for nitric acid has been reproduced from the data given in the Landolt-Börnstein Physikalisches Tabellen (74). It will be observed that the present determinations are slightly high. Since it proved to be impossible at this time to find a value for the refractive index of pure nitric acid at 20°C., no comparison could be made between the observed and calculated values.

The calculated refractive index and specific refractive power values (page 105) proved to be slightly higher than those observed for the aqueous hydrogen peroxide solutions. A possible reason for this may be (1) too low a refractometer reading, or (2) too high a determination of the density. The same phenomenon was observed in the case of the aqueous acetic acid, the

differences here being a little greater. This occurrence may be due to the above causes, although Gladstone and Hibbert (61) showed that there is a variation in aqueous solution, which cannot be predicted and may be due to several different factors.

In the case of the mixtures of hydrogen peroxide and acetic acid, the differences between the observed and calculated refractive indices are noticeably higher. The refractive index of a particular solution, moreover, is higher than the value of either component at that concentration. An example will serve to clarify this statement.

Solution 6, Series 2, Page 99:

Hydrogen peroxide	12.05%
Acetic acid	28.95%
Refractive index	1.3603
Aqueous hydrogen peroxide	12.05%
Refractive index	1.3394
Aqueous acetic acid	28.95%
Refractive index	1.3532

Such hydrogen peroxide — acetic acid solutions produce relatively large quantities of peracid, the amount of which was determined in Series 4, page 102. The percentages are approximately the same, all solutions having stood for an equal length of time. It would appear, therefore, that the presence of peracid does contribute some

effect towards the value of refractive index.

Now, the refractive index of a solid may be determined by means of the admixture formula (equation 41, page 80). The relationship may well be extended to include the specific refractive power, when it will take the form:

$$WR'' = w_1 r_1'' + w_2 r_2'' \qquad (43)$$

One might expect this formula to apply in much the same manner as the previous equation, the same conditions holding good. Employing equations 41 and 43, the refractive index and specific refractive power values of peracetic acid were calculated, and appear on page 103. It is admitted that the method is not an accurate one, and gives rise to many sources of error which would tend to accumulate in the final result, as is shown by the wide variation. Nevertheless, such a calculation serves to show in what direction these values lie, and that the peracid does raise the refractive index values. It should be possible to prepare concentrated solutions which would yield upwards of 50% peracid, and thus influence the refractive index considerably more. Work in this direction is already being carried out.

Series 1, 2 and 3, pages 97 and 98, consist of solutions of hydrogen peroxide and nitric acid. Here, too, the refractive indices increase in a regular manner, when plotted against the concentration of hydrogen peroxide. (Fig. 3). The solutions of Series 2, however, were prepared more or less at random, when it chanced that the concentration of nitric acid decreased as that of the hydrogen peroxide increased. When plotted, the refractive index followed the trend of the acid. Since it was well in excess, it appears to be the controlling factor. In these instances, also, the refractive index of a solution proved to be higher than the value of either component at the same concentration.

This phenomenon parallels that of hydrogen peroxide — acetic acid solutions. It may be the result of one or both of the two factors:

(1) Pernitric acid, or a complex which breaks down to form it may be present, and possesses such a refractive index which would tend to raise the value, or,

(2) The increase may be due to the removal of a small amount of water from aqueous nitric acid, say, and substituting an equivalent amount of hydrogen peroxide, having a higher refractive index, or vice versa.

In support of the complex or peracid formation are the findings of Hatcher and MacLaughlan (34) regarding the immediate decrease in conductivity of hydrogen peroxide — nitric acid solutions. These authors also demonstrated its presence by means of various specific qualitative tests.

An attempt was made to determine the amount of peracid formed in these dilute solutions. The procedure followed was the "high dilution method" as developed by Hatcher and co-workers (1). A 2.5 gram sample liberated iodine from potassium iodide readily enough, but the amount thus set free was too small for accurate measurement: only 3.10 cc. of 0.01512N. sodium thiosulphate solution were required to discharge the colour of the free iodine.

Peracid, or a substance possessing the properties of a peracid, undoubtedly appears to be present as a result of the foregoing considerations. It has been mentioned elsewhere that concentrated nitric acid — hydrogen peroxide solutions are explosive; consequently only dilute solutions were employed in Hatcher and MacLaughlan's work, as well as in the present investigation. Since, under these circumstances, such a small amount of pernitric acid is formed, the concentration of un-ionized

complex must be greater to account for the considerable drop in conductivity. Refinements in the method of measurement of the refractive index, and especially of density, may permit of the use of stronger solutions, at least those which, although explosive, do have an appreciable time lag before decomposition. This would tend to increase the concentration of peracid, which will have a still greater effect upon the refractive index, which can then be accurately measured.

The situation being as described at the present time, only sixteen solutions in all were measured, and it is doubtful as to whether a great deal can be deduced from the data thus far obtained.

Caro's acid is produced as the result of the interaction of sulphuric acid and hydrogen peroxide, the reaction requiring concentrated reagents. Hatcher and MacLaughlan (34) measured a couple of such solutions, when the same behaviour was observed as was displayed by the hydrogen peroxide — nitric acid systems. The occurrence would indicate quite clearly the presence of Caro's acid or an un-ionized complex, which would eventually produce it. Such solutions were not considered in this work, but most certainly will be investigated in the near future. One or

two solutions were prepared, however, and the amount of peracid determined. Again it proved to be impossible to make an accurate measurement.

Those cases in which the refractive index was measured over a temperature range of 30°C., showed that in general the differences were quite constant, the temperature coefficients all having much the same value.

It is to be concluded, then, that peracid is produced in the acid hydrogen peroxide solutions which have been investigated, and this peracid has a definite influence upon the refractive index. This effect may be intensified by the use of more concentrated solutions than have hitherto been employed. A more accurate measurement of the refractive index should be possible with concentrated aqueous solutions of the various peracids. The admixture formula may be more exactly employed with the use of pure succinic monoperacid, and in this latter instance, there would be no complications due to excess hydrogen peroxide and excess organic or mineral acid, all of which tend to introduce errors.

Hatcher and Holden (1), in the course of their experiments on oxidation with hydrogen peroxide, determined the equilibrium constant for the reaction:

$$CH_3COOH + H_2O_2 \rightleftharpoons CH_3COOOH + H_2O \qquad (44)$$

and found it to be K = 3.248.

Applying this constant in Series 3, page 101, a calculation was made to discover how much peracetic acid would be present at equilibrium, and the resulting value applied in the admixture formula, to give the following results:

% Peracid at equil.	n_D^{20}	R"
4.16	1.5889	0.23774
4.09	1.5941	0.23389
4.27	1.5667	0.23442
Average	1.5832	0.23535

These calculations are very approximate and were made only to see whether anything of interest would result. The average value above compares rather favourably with one of the values shown on page 103.

Employing the value R" = 0.23122 for peracetic acid, the following information may be gained:

R" - 0.23122

MR" - 17.572

	CH_3COOH		CH_3COOOH
MR"	12.410		17.572
R"(CH_3)	5.654		5.654
-COOH	6.756	-COOOH	11.918

The extra oxygen in the peracid appears to contribute 5.162 units. This value is greater by 0.962 units than two co-ordinate linked oxygen atoms. The discrepancy between the residues of the two acids is of the same order as was found by Hatcher and Maddock (75) for formic and performic acids.

Miss Homfray (76) has determined the refractive power of quadrivalent oxygen in a number of salts of pyrone, where the oxygen is supposed to be quadrivalent. The value obtained was 2.55 units. The former value of 5.162 units is greater by only 0.062 units than two quadrivalent oxygen atoms.

The situation at present is such that it is too early to postulate the structure for the carboxyl group of the peracid, but the circumstances appear to be such as to indicate the possibility of two quadrivalent oxygen atoms, or two co-ordinate linked atoms, or even an atom of each type of oxygen being present.

Further work regarding this problem should undoubtedly lead to information which will serve to arrive at the proper configuration as it exists in the peracids, and ultimately settle the structure of the hydrogen peroxide molecule.

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Claim for original work in the preceding pages is made as follows:

The action of P.N. acid upon various types of organic compounds has been investigated.

By varying the concentrations of acetone, nitric acid and hydrogen peroxide, both modifications of acetone peroxide were produced in a very short time. Conditions were found whereby they could be prepared at will. Cyclohexanone, acetone and cyclopentanone produced peroxides which proved to be very explosive. On decomposition, they displayed considerable shattering power, and extreme caution is required when handling them.

Molecular weight determinations showed that the peroxides of cyclopentanone and cyclohexanone are trimolecular and dimolecular respectively. The latter ketone does not form an ϵ-lactone with P.N. acid.

Acetoacetic ester apparently undergoes ketone hydrolysis, to produce acetone which then forms the dimolecular modification of acetone peroxide.

Urea hydrolyzes to carbon dioxide and thiourea yields an unstable oxidation product, which decomposes

spontaneously very shortly after its preparation.

Refractive index measurements were made of hydrogen peroxide — acetic acid and hydrogen peroxide — nitric acid solutions, at various concentrations and over a 30°C. temperature range.

Calculations have been made to show the approximate value of the refractive index and specific refractive power of peracetic acid, with a view to determining its structure, and ultimately to apply these data to inorganic peracids, and hydrogen peroxide itself.

Estimation of the amount of pernitric and persulphuric acids proved that in dilute solutions, the quantities are too small for accurate measurement.