THE REACTIONS OF ACTIVE NITROGEN WITH PHOSPHINE AND HYDROGEN CHLORIDE

by

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FOREWORD

A great deal of experimental and theoretical work has been done since 1900 in an effort to elucidate the exact nature and properties of active nitrogen. Since 1946 the kinetics of nearly thirty active nitrogen reactions have been studied in this laboratory. As a result there has been a tendency in recent years for theses on the subject to become relatively lengthy, this tendency arising from the authors' attempts to present a comprehensive historical background and a critical review, not only for active nitrogen, but in some cases for hydrogen atom and free radical chemistry as well.

This thesis represents a drastic departure from the practice in the past in that it contains a minimum of historical and experimental detail and has been written for use by scientists who are familiar with chemical kinetics and have a reasonably complete chemical library at their disposal. The author has intended that books, such as Steacie's monograph on atom and free radical reactions (1), the various reviews on active nitrogen (2,3,62), and other publications to which reference is made in the text of the thesis should be used, where necessary, to supplement the subject matter that follows.

This thesis is primarily concerned with the reactions of phosphine and hydrogen chloride with active nitrogen. The corresponding reactions with atomic hydrogen were investigated, to determine what effect they might have on the active nitrogen processes. Limited studies were also made of the reactions of hydrogen atoms with hydrogen iodide, hydrogen bromide and ethyl chloride, as possible means for estimating the hydrogen atom flow rate in the Wood-Bonhoeffer system used.

INTRODUCTION

PRODUCTION OF ATOMS

The passage of electrical discharges through diatomic gases at low pressure has been found to dissociate the molecules into atoms. Although the processes that may occur in a discharge are of interest in the present work, the information available on the subject is largely empirical and qualitative and the theoretical treatment is far from complete. Nevertheless the descriptions given in the literature (2,4,5) of the dissociation processes resulting from electrical excitation are adequate for consideration of the problem at hand.

Hydrogen atoms have been produced from molecular hydrogen in flow systems with continuous, condensed or high frequency electrodeless discharges. In static systems atomic hydrogen is formed when molecular hydrogen impinges on hot filaments (6,7,8) and it has been produced in both photolytic (9) and mercury photosensitized decompositions (10).

Active nitrogen (which contains at least appreciable quantities of nitrogen atoms) has been produced from molecular nitrogen by various forms of electrical excitation and more recently by condensed discharges through ammonia and nitric oxide (11).

ATOMIC HYDROGEN

Wood (12,13) noticed the presence of a brilliant Balmer spectrum in a continuous discharge through moist molecular hydrogen, though the atomic lines were absent when dry hydrogen was used. He was able to explain his observations (13) on the assumptions that hydrogen atoms were produced in the discharge and that the presence of water vapor reduced the catalytic effect of the wall for their recombination. Bonhoeffer (14) confirmed Wood's results and examined the properties of atomic hydrogen more thoroughly. He found, for example, that the percentage of ions in the active gas was small (15) and that saturated and unsaturated hydrocarbons suffered hydrogen abstraction and addition, respectively, in reactions with H atoms (16). Other workers (17) noted qualitatively the effects of atomic hydrogen on many inorganic and organic substances, gases, liquids, solutions and solids, without identifying the products or suggesting mechanisms by which the reactions might occur.

The identity of the active species in hydrogen subjected to a discharge was the subject of some controversy. Many investigators (see, for example, (18,19,20)) considered the possibility that the reactive species was triatomic hydrogen, H_3, and the existence of this species apparently is theoretically possible (21). However, a great deal of evidence for the presence of atoms has been accumulated. For example, Wrede (22) and Harteck (23) used a diffusion gauge to identify the presence of atoms, and Bay and Steiner (24) found that estimates of atom concentrations based on Wrede gauge measurements agreed with those based on spectroscopic data. It is generally agreed now that all of the chemical activity in active hydrogen is due to hydrogen atoms.

REACTIONS OF ATOMIC HYDROGEN

Hydrogen atom reactions have been investigated more thoroughly than those of any other atomic species. A few reactions will be mentioned at this point to illustrate the behaviour typical of hydrogen atoms in the presence of various types of reactant molecules.

1. Organic Compounds

Atomic hydrogen has been shown to abstract hydrogen from saturated hydrocarbons, i.e.,

$$H + RH \rightarrow H_2 + R.$$

It is agreed that this is the first step in the relatively slow reaction with methane (see (1), vol. 1, pp. 448-456) although the activation energy and steric factor have not been definitely established (25,26,27). The situation is similar with ethane (see (1), vol. 1, pp. 456-467); there is disagreement about the kinetic constants but the primary step is undoubtedly hydrogen abstraction (28,29,30). Analogous abstractions occur with higher paraffins.

Atomic hydrogen reactions with methyl chloride (31,32,33) and ethyl chloride (32) have been studied by several methods and the initial steps are considered to be abstraction of chlorine by hydrogen. Hydrogen atoms also abstract chlorine from carbon tetrachloride (34) and abstract hydrogen from the NH_2 group of methylamine (35). Hydrogen abstraction would appear, therefore, to be a general characteristic of the reactions of atomic hydrogen with saturated molecules.

Although H atom reactions with unsaturated hydrocarbons are not involved in any aspect of the present study, it might be mentioned that, in general, addition of H atoms followed by subsequent degradation of the radical formed is frequently observed in such systems (see (1), vol. 1, pp. 434-448).

2. Inorganic Compounds

The results of two investigations (36,37) have indicated that hydrogen atoms do not react with ammonia. Dixon (38) obtained up to 5 per cent reaction but the hydrogen used was saturated with water vapor which renders the results of doubtful value. Freeman and Winkler (39), using the discharge tube method, found no reaction at room temperature, a small amount above 400°C and a fast, more extensive reaction at -67°C. They suggested a change in mechanism with temperature, with the reaction

$$H + NH_3 \rightarrow H_2 + NH_2$$

occurring only at the higher temperatures (40).

Phosphine has been subjected to the action of hydrogen atoms produced in an electrodeless discharge in a search for higher hydrides of phosphorus (41). Decomposition occurred but the brilliant yellow solid obtained was not completely analysed and no mechanism for the reaction was suggested.

Only a small amount of experimental work has been reported on the effect of atomic hydrogen on the hydrogen halides. Boehm and Bonhoeffer (36) attributed the rapid destruction of hydrogen atoms by hydrogen chloride and hydrogen bromide to reactions of the type

$$H + HCl \rightarrow H_2 + Cl. \qquad (1)$$

Cremer et al. (31) concluded that the reaction

$$H + HBr \rightarrow H_2 + Br \qquad (2)$$

goes to completion, with an activation energy less than 3 kcal. According to Rodebush and Spealman (42), reaction (1) occurs in the gas phase and is followed by the rapid recombination of H and Cl atoms on the wall. Molecular chlorine was recovered in some of their experiments, but the validity of their results is questionable because of water vapor and nitrogen which were present in the system.

Bodenstein and co-workers (43) studied the rate of reaction (1) relative to that of

$$H + Cl_2 \rightarrow HCl + Cl. \qquad (3)$$

The ratio of rate constants, k_3/k_1, was found to be 201 at 30°C, 60 at 90°C and 40 at 160°C, in a flow system.

ACTIVE NITROGEN

The discovery of active nitrogen by Lewis in 1900 and his subsequent observations (44) led to a great deal of interest in the effect of electrical discharges on molecular nitrogen. Strutt (45) (later Lord Rayleigh) confirmed most of Lewis' work and investigated in more detail the spectroscopic (46), physical and chemical properties (47) of the "chamois-yellow mist". During the next few years a great deal of work was done by Strutt and others in an effort to explain the complex properties of active nitrogen. Strutt (48) and Koenig and Elöd (49) ascribed the afterglow to nitrogen only; Comte (50), Lewis (51) and Tiede and Domcke (52) insisted that oxygen was necessary for the production of the afterglow. It has since been agreed that impurities which assist in the production of the afterglow do so by reducing the catalytic activity of the walls for the recombination of nitrogen atoms.

THE ACTIVE SPECIES

The chemical activity of active nitrogen and the characteristic afterglow associated with it have been variously attributed to nitrogen atoms, ions and molecules, in various energy states. Triatomic nitrogen, N_3, has also been proposed (53,54) as the active component in active nitrogen, but evidence for its existence at ordinary temperatures has never been obtained.

Rayleigh believed that his observations (55) could be explained in terms of nitrogen atoms and his views received support from Sponer (56). Mitra (57) and Kaplan and Cario (58) postulated metastable atoms as the active species to explain certain aspects of the afterglow spectrum, and Jackson and Broadway (59) detected the presence of metastable atoms with a Stern-Gerlach experiment. However, it has since been shown (60) that most of the atoms in active nitrogen are in the ground state, and since the establishment of the dissociation energy of molecular nitrogen (61), the spectrum can be explained satisfactorily in terms of ground state atoms.

Molecular ions, N_2^+ , have been suggested by Mitra (62) and by Kaplan (63) as the reactive component but Worley (64) and Benson (65) were unable to detect such a species. In addition it has been shown many times (45,47,65,66,67) that the chemical and physical properties of active nitrogen are not altered by attempts to remove charged particles from the gas.

The presence of excited nitrogen molecules has been suggested as responsible for the afterglow and has been used to account for the chemical reactivity of active nitrogen. Saha and Sur (68) postulated the presence of electronically excited nitrogen molecules;

Birge (69), Constantinides (70) and Foote and Ruark (71) concluded that active nitrogen consisted of excited metastable molecules. Willey and Rideal (72) also believed the chemical activity to be due to metastable molecules, with energies of about 2 ev., but to reconcile their results with those of other investigators, Willey (73) suggested that nitrogen atoms were responsible for the afterglow. Kaplan and Cario (58) attempted to explain the supposed independence of chemical activity and glow (accepted by some (47,73) but denied by others (74,75)) in terms of three species. There was general agreement (76,77,78) that the afterglow was due to the recombination of atoms and that the decay of the afterglow was a third order process; the presence of metastable species was postulated to account for the chemical reactivity. However all known electronically excited molecules (and atoms) of nitrogen would probably show an absorption spectrum over the range 2000 to 8700 Å (79) and active nitrogen does not absorb light in this region.

A great deal of evidence for the presence in active nitrogen of nitrogen atoms in the ground state has been accumulated since Strutt first explained his observations on that basis. Atomic nitrogen arc lines were observed by Herzberg (80) and by Bay and Steiner (81) while Wrede (22) used the familiar diffusion gauge to demonstrate that active nitrogen contains several per cent atoms. Recently, in mass spectrometric studies of active nitrogen, Jackson and Schiff (82) and Berkowitz et al. (83) obtained evidence for the presence of nitrogen atoms in the ground state but no indication of triatomic nitrogen or electronically excited molecules.

The production and properties of the afterglow are readily explained in terms of nitrogen atoms. The emission of the afterglow is a termolecular process in the gas phase, first order in molecular nitrogen, second order in active species. The yellow glow contains the visible bands of the first positive system of the nitrogen molecule (see ref. 84 for a diagram of the electronic energy levels) with selected enhancement of some bands in the red, yellow and green, and therefore it results from transitions from the $B^3\Pi_g$ state to the $A^3\Sigma_u$ state.

In summary, there seems to be little doubt that nitrogen atoms in the ground state are responsible for some and perhaps all of the chemical activity associated with active nitrogen (55,57,84,85,86,87,88).

REACTIONS OF ACTIVE NITROGEN WITH ORGANIC MOLECULES

The reactions between organic compounds and active nitrogen had not been investigated in quantitative experiments until the first study of this type was reported from this laboratory in 1949. Since then, more than twenty such reactions have been studied and the results interpreted on the assumption that nitrogen atoms were responsible for the chemical effects observed. The reactions with saturated hydrocarbons all showed similar characteristics in that hydrogen cyanide and hydrogen were invariably produced, and yet the differences observed are interesting and significant. The results with methane (89,90) indicated concomitant hydrogen atom reaction. With ethane (89,90) and neopentane (91), abrupt changes in the calculated activation energies with temperature were found and were attributed to hydrogen atom reactions, or to the presence of two active species, or, in the case of neopentane, to alternative modes of active nitrogen attack. Complete consumption of nitrogen atoms by propane (92) was possible under certain conditions but could not be attained in the slower but similar cyclopropane reaction (93,94). It was found that reactions of active nitrogen with n- and iso-butanes (95) and with cyclobutane (94) have similar activation energies and proceed at similar rates.

Unsaturated hydrocarbons have been found to react faster than the paraffins and again hydrogen cyanide was always a major product. In the acetylene reaction (96) large amounts of polymer were formed and yields of cyanogen and total hydrogen passed through a maximum at an acetylene flow rate corresponding to the active nitrogen flow rate. A detailed study of the ethylene reaction (97), in agreement with an earlier investigation (98), showed that this reaction proceeds with complete consumption of the reactant present in lesser amount. The yields of the minor products cyanogen, methane and acetylene passed through maxima as in the acetylene reaction. The reaction with propylene (99), while similar to that with ethylene in many respects, appeared to differ in that ethylene was a major primary product. An excess of any of the butenes (100) appeared to consume active nitrogen completely and it was concluded that the initial step led to the formation of hydrogen cyanide, hydrogen and propylene. Attack of active nitrogen on an olefin therefore appears to result in step-wise degradation of the hydrocarbon.

The reactions between active nitrogen and methyl, ethyl, vinyl, propyl and iso-propyl chlorides (101) were all found to be fast and all yielded hydrogen cyanide, hydrogen chloride, and small quantities of cyanogen and a polymer. Product flow rates suggested complete consumption of one reactant if the other were present in excess, although with methyl chloride, the limiting extent of reaction increased with temperature. Similar mechanisms, postulated to account for the various results of the five reactions, included a primary step in which a nitrogen atom attacked at a shielded carbon atom to form a relatively long-lived complex.

In the active nitrogen-methylamine reaction (102) the rates of methylamine destruction and hydrogen cyanide formation increased with temperature and, at 447°, the rate of ammonia production seemed to make up the difference between these two quantities. A tentative mechanism was suggested in terms of two active species, one of which reacted with the NH_2 group and a second which reacted with the CH_3 group.

In the methyl cyanide-active nitrogen reaction (103) the maximum rate of hydrogen cyanide formation, which apparently corresponded to complete consumption of available nitrogen atoms, increased with increasing temperature. It was suggested that the reaction of methyl cyanide with atomic hydrogen, produced in the primary nitrogen atom reaction, became significant at higher temperatures.

A dependence of limiting hydrogen cyanide yield on reaction temperature has been observed in the reactions of methyl chloride, methyl cyanide and methylamine with active nitrogen. An explanation of this behaviour has been proposed (104) which supposes the reactant to act as a third body for the recombination of nitrogen atoms. The extent of this catalytic action depends on the lifetime of the nitrogen atom-reactant complex, which decreases with increasing temperature.

Armstrong and Winkler have investigated the reactions of active nitrogen with azomethane (105) and with mercury diethyl (106) in an attempt to obtain some information about the rates of alkyl radical-active nitrogen reactions. Both methyl and ethyl radicals reacted rapidly with atomic nitrogen to give hydrogen cyanide and hydrogen but both parent reactants appeared to catalyse the recombination of nitrogen atoms.

UNIFIED MECHANISM

A consistent, unified mechanism has been developed by Evans, Freeman and Winkler (107) to explain the results of the reactions of organic molecules with active nitrogen. It is assumed in this unified treatment that a chemically identical complex may be formed in the initial stage of the interaction of a nitrogen atom with molecules containing the same number of carbon atoms. Major reaction products are usually formed either in the initial step or by spontaneous decomposition of the nitrogen atom-reactant complex; minor products are formed in secondary reactions. The possible contribution by vibrationally excited molecules is considered and, in choosing between alternative processes, cognisance is taken of the principle of conservation of spin momentum.

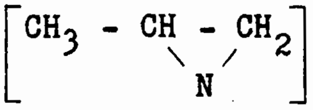
In the publication by Evans et al. (107) comparison of the reactions with propylene, normal and iso-propyl chloride, and propane is considered, the suggested primary steps being

$$N + C_3H_6 \rightarrow N.C_3H_6$$

$$N + C_3H_7Cl \rightarrow N.C_3H_6 + HCl$$

$$N + C_3H_8 \rightarrow N.C_3H_6 + H_2.$$

The $N.C_3H_6$ complex formed in each case is assumed to have the structure



and the rate of its formation, its stability, and the rate of its decomposition depend on the energy content which increases in the order propane, propyl chlorides, propylene. The change in relative rates of the reactions

$$N + N.C_3H_6 \rightarrow C_3H_6 \text{ (triplet state) } + N_2$$

$$N.C_3H_6 \rightarrow HCN + C_2H_5$$

with temperature for each of the three reactants is used to explain the observed products.

Analogous arguments are presented to support similar mechanisms suggested for other organic compounds. A discussion of elementary molecular orbital theory is included to show the possibility of the formation of complexes sufficiently long-lived to permit the occurrence of the hydrogen shifts and spin changes which the unified mechanism requires.

REACTIONS OF ACTIVE NITROGEN WITH INORGANIC COMPOUNDS

Lewis (108), Steiner (109) and Dixon and Steiner (110) found that ammonia was formed when active nitrogen and atomic hydrogen were mixed. Apparently the mechanism of the reaction is one which depends on three body interactions and in which the stationary concentration of NH radicals remains low (110).

Spealman and Rodebush (111) studied the reactions of nitric oxide and nitrogen dioxide with active nitrogen and they concluded that the elementary processes which occurred were the interactions of atomic nitrogen and atomic oxygen with both oxides.

Dixon and Steiner (110) found that ammonia was decomposed slightly by active nitrogen and detected a small amount of hydrazine as product. However, the only products detected by Freeman and Winkler (39) in a study of this reaction were hydrogen and nitrogen. They showed that the change in extent of ammonia consumption with temperature appeared to be due to a concomitant hydrogen atom-ammonia reaction, and that the maximum rate of ammonia destruction by active nitrogen was about one sixth of the maximum rate of production of hydrogen cyanide from ethylene. Mixtures of ethylene and ammonia were reacted with active nitrogen and the ammonia reaction at higher ammonia flow rates appeared to be unaffected by the presence of ethylene. The authors were unable to explain these results in terms of nitrogen atoms as the only reactive species in active nitrogen, and it was suggested, therefore, that there might be two active species present. On the other hand, the results obtained in a study of the active nitrogen-hydrazine reaction (112) gave no evidence that excited nitrogen molecules make a large contribution to the chemical reactivity of active nitrogen.

Willey and Rideal (73) reported that HI and HBr, but not HCl, were decomposed by active nitrogen.

They observed that HCl was formed when hydrogen-chlorine mixtures were subjected to active nitrogen. Ewart and Rodebush (113) observed that the reactions of active nitrogen with HI and with HBr gave brilliant blue and brilliant orange flames, respectively, but that HCl merely destroyed the afterglow. They suggested the reaction

$$N + HX \rightarrow NH + X$$

as the primary step in hydrogen halide reactions and, on this basis, suggested that HI and HBr should react readily whereas HCl should react sparingly or not at all.

THE PRESENT PROBLEM

The reaction of active nitrogen with ammonia is the only one so far reported for which a mechanism could not be suggested with nitrogen atoms as the sole reactive species. The results obtained with ammonia and with ammonia-ethylene mixtures (11,39) have defied explanation in terms of any single active species.

Vibrationally excited molecules (N_2^*) have been suggested by Evans and Winkler (84) as a possible second active species. These authors have shown that this species could exist and have explained how most reactant molecules would be decomposed by collisions of the second kind with N_2^*.

Of the compounds whose reactions with active nitrogen have been studied, ammonia is the only one for which it has seemed necessary to postulate a slow reaction with nitrogen atoms and a relatively rapid reaction with a second species. The work reported in this thesis was undertaken in an effort to detect similar behaviour in other reactions. It was felt that perhaps phosphine, as an analogue of ammonia, or hydrogen chloride, with a relatively high bond dissociation energy and a large negative heat of formation, might react slowly with nitrogen atoms and hence indicate the presence of a second active species.

The reactions of atomic hydrogen with phosphine and with hydrogen chloride were also investigated to determine what part they might play in the corresponding active nitrogen reactions. The H atom reactions with hydrogen iodide, hydrogen bromide and ethyl chloride were studied to a limited extent with a view to obtaining a measure of the atomic hydrogen flow rate in the system.

EXPERIMENTAL

MATERIALS

Hydrogen, 99.7% pure, was obtained from Linde Air Products Co., and was dried before use by passing it through a trap immersed in liquid nitrogen.

Nitrogen, 99.7% pure, was obtained from Linde Air Products Co. Analysis with a mass spectrometer indicated less than 0.1% oxygen and a trace of argon. The nitrogen was purified before use by passing it through a tube containing copper turnings heated to 400°C and through a trap immersed in liquid nitrogen.

Hydrogen iodide (114) and hydrogen bromide (115) were prepared by standard methods. The gases were carried in a stream of dry hydrogen through two traps at -100°C before they were condensed with liquid nitrogen. They were purified further by bulb-to-bulb distillations and care was taken in subsequent experiments to prevent their contact with mercury.

Ethyl chloride (British Pharmacopoeia grade) was obtained from Ingram and Bell Ltd., Montreal. It was purified before use by two vacuum distillations in which only the middle fractions were retained.

Phosphine was prepared in the laboratory using three different methods: (i) by decomposing phosphonium iodide with dilute base; (ii) by treating calcium phosphide with dilute acid; (iii) by treating white phosphorus with boiling aqueous potassium hydroxide solution. In each case hydrogen was passed through the reaction flask and the mixture of hydrogen and phosphorus hydrides was passed through 6N HCl and 25% KOH solutions, through two traps immersed in freezing ethanol and finally through a trap, surrounded by liquid nitrogen, to condense the phosphine. Prior to its use, phosphine was distilled twice from a trap cooled to -130°C.

Ethylene, 99% pure, was obtained from the Ohio Chemical Co., and was purified by two bulb-to-bulb distillations.

Anhydrous hydrogen chloride, 99% pure, and chlorine, 99.5% pure, were obtained from the Matheson Co. Inc., and were purified by two vacuum distillations and distillation from a trap at -120°C.

APPARATUS

The apparatus used for both the hydrogen atom and the active nitrogen reactions is shown schematically in Figure 1. It is a typical Wood-Bonhoeffer fast flow system constructed of Pyrex glass.

<u>FIGURE 1</u>

DIAGRAM OF APPARATUS

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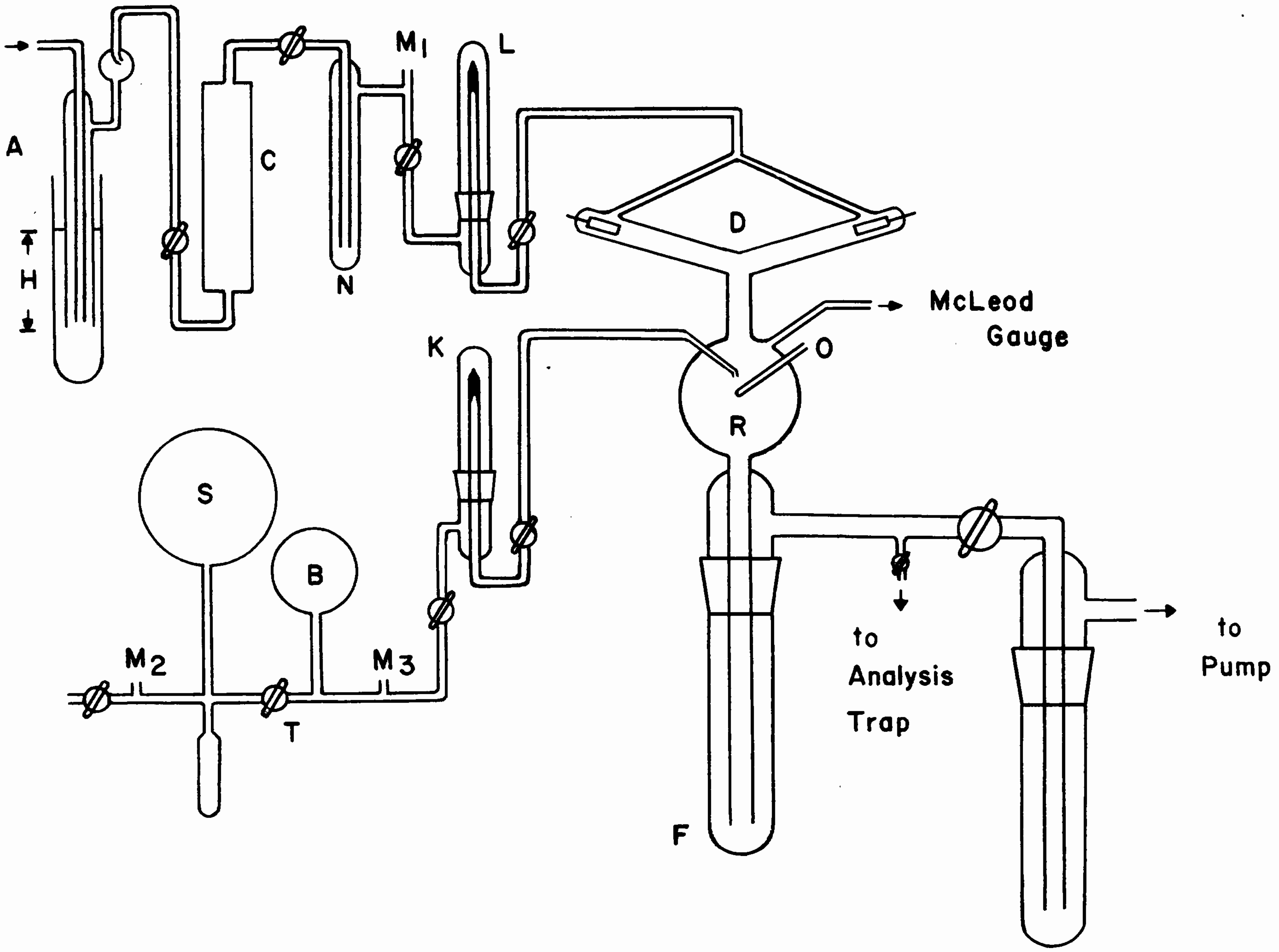

A
H
C
N
M1
L
D
McLeod Gauge
O
K
R
S
B
M2
T
M3
F
to Analysis Trap
to Pump

Hydrogen (or nitrogen) from the cylinder entered the system through the pressure regulator A and was dried by passage through the liquid nitrogen trap N. (When nitrogen was used, copper turnings in the furnace C were kept at 400°C to remove traces of oxygen from the gas). The gas was maintained at a constant pressure head of 77 cm., indicated on the manometer at M_1, behind the flow meter L so that it would flow into the discharge tube D at a constant rate. The height H of the dibutyl phthalate in the manostat A was adjusted to compensate for fluctuations in the atmospheric pressure.

The molecular hydrogen flow rate was always 124 micro-moles per sec. which gave a total pressure of 0.87 mm. in the reaction system, with the discharge operating. The molecular nitrogen flow rate was maintained at 115 micro-moles per sec. which resulted in a total pressure of 1.35 mm. in the reaction vessel, with the discharge operating. These flow rates were determined by measuring the rate of evacuation of a calibrated volume through the flow meter L.

A cylindrical aluminum electrode fastened to a tungsten lead was sealed into each end of the discharge tube. The inner surfaces of the discharge tube and reaction system were poisoned with a 2% metaphosphoric acid solution.

The gaseous reactants (ethyl chloride, hydrogen iodide, hydrogen bromide, phosphine, ethylene, hydrogen chloride) were stored, when needed, in the reservoir S. During an experiment, the pressure in the ballast volume B, as indicated by the manometer at M_3, was kept constant by slowly transferring gas into B from S through a scratched stopcock T. The rate of reactant flow through the flow meter K, from B into the reaction vessel R, was controlled by maintaining the pressure in volume B. Any reactant flow rate could be obtained by choosing this pressure appropriately.

The reaction temperatures reported were measured with the glass-enclosed, copper-constantan thermocouple at O, located just below the reactant inlet in the centre of the spherical 500 ml. reaction vessel R. Experiments at higher temperatures were made with an electrical heater surrounding the reaction vessel and the lower 5 cm. of the tube that connected it to the discharge tube. The temperature recorded for a given experiment represented the temperature half-way through that experiment.

All gases flowing from the reaction vessel which could be condensed with liquid nitrogen were quantitatively frozen out of the gas stream in the product trap F. (The trapping efficiency was found to be excellent even in the phosphine experiments). All experiments in which the reactant flow rate exceeded 3 micro-moles per sec. lasted 100 seconds; the others were continued for 300 seconds. After each experiment the products and the unused reactant were distilled into a small removable trap containing an appropriate absorbing solution, which had been de-gassed and frozen.

A condensed discharge was made to flash through the discharge tube with a frequency of about 10 per sec. in the active nitrogen work and about 20 per sec. for atomic hydrogen production. The electrical circuit consisted of a 3000 volt transformer (Hammond) connected to two half-wave rectifier tubes (Raytheon 866-A) in parallel, which produced D.C. to charge a 4 microfarad condenser through 3000 ohm resistors. The condenser was connected in parallel with the electrodes in the discharge tube and discharged between them whenever the critical potential was reached. The flash rate was controlled by a variac in the 115 V A.C. line leading to the primary of the transformer.

FLOW RATE MEASUREMENTS

Estimates of hydrogen atom flow rates were obtained from limited investigations of the reactions of atomic hydrogen with hydrogen iodide, hydrogen bromide and ethyl chloride. The ethyl chloride-H atom reaction was of some interest because it had been used previously (116) as a chemical method for determining H atom flow rates. It was felt that HI and HBr might react 100% at 65°C and would therefore be better than C_2H_5Cl which reacts to less than 40% at that temperature (32).

Active nitrogen flow rates were assumed to correspond to the maximum limiting hydrogen cyanide yield produced in the active nitrogen-ethylene reaction (97,98).

In the experiments with ethyl chloride and atomic hydrogen, the removable trap contained 15 ml. of 0.1 N NaOH solution. The amount of HCl produced was then determined by titrating the unreacted base in the trap with 0.1 N H_2SO_4 solution to a methyl red end-point.

Hydrogen cyanide produced in the ethylene-active nitrogen reaction was distilled under special conditions. A coating of carbon tetrachloride was frozen onto the product trap, immediately after the Dewar flask containing liquid nitrogen had been removed, so that the distillation proceeded slowly and without melting and subsequent polymerisation of the HCN. Hydrogen cyanide was collected in the removable trap containing 15 ml. distilled water and was determined by the

Liebig-Dénigès method (117).

Flow rates of ethyl chloride and of ethylene were calculated from changes in pressure in the known volume of the reactant reservoir during the course of an experiment ("PV" change).

Phosphine not consumed during an experiment was distilled from the product trap into the removable trap containing dilute silver nitrate solution. The precipitated silver was removed by filtration and excess silver nitrate was determined by the Volhard method (117). Phosphine flow rates were determined in the same way in a series of "blank" experiments during which the hydrogen (or nitrogen) was not activated.

Hydrogen bromide and hydrogen iodide flow rates were measured in "blank" experiments by distilling the condensate from the product trap (kept at -100°C for HBr, -60°C for HI) into the removable trap containing standard NaOH solution, and back titrating the excess alkali with standard acid. The extent of reaction was determined by collecting and measuring unreacted HBr and HI in the same manner.

In the experiments with hydrogen chloride, the extent of reaction with active nitrogen was found by determining chlorine and unreacted HCl simultaneously, using a method similar to that described by Rodebush and Klingelhoeffer (118). Hydrogen chloride flow rates, measured in a series of "blank" experiments, were found to agree with values based on the "PV" change during the experiments. A limited investigation was made of the effects of added molecular hydrogen and molecular chlorine on the rate of decomposition of hydrogen chloride by active nitrogen in an attempt to determine the extent to which various back-reactions might regenerate HCl. In the HCl-H_2 experiments, molecular hydrogen flow rates were based on measurements of "PV" change. For the work with HCl-Cl_2 mixtures, chlorine flow rates were measured by determining iodometrically the amounts collected in "blank" experiments.

RESULTS

ATOMIC HYDROGEN

With a molecular hydrogen flow rate of 124 micro-moles per sec. and a flash rate of about 20 per sec. the pressure in the reaction vessel was 0.87 mm. and the temperature indicated by the thermocouple was 40°C.

Reactions of Atomic Hydrogen with C_2H_5Cl, HI and HBr

The temperature during the ethyl chloride, hydrogen iodide and hydrogen bromide reactions was 65°C in each case. The dependence of reactant decomposition on reactant flow rate is shown by the results given in Table I, which are plotted in Figure 2. It is obvious from the graph that, when present in excess, the hydrogen halides reacted to the same extent and that the maximum rate at which they were decomposed is roughly three times the maximum rate of production of HCl from ethyl chloride.

Reaction of Atomic Hydrogen with Phosphine

The only products of the reaction between phosphine and hydrogen atoms were molecular hydrogen and red phosphorus. The latter was deposited in a uniform layer on the inside wall of the reaction vessel and it changed from a light golden to a deep amber color as the

TABLE I

Reactions of Atomic Hydrogen with Ethyl Chloride, Hydrogen Iodide and Hydrogen Bromide at 65°C.

REACTANT	REACTANT FLOW RATE*	REACTANT RECOVERED*	REACTANT CONSUMED*
C_2H_5Cl	12.8	-	3.20
	14.5	-	3.35
	16.6	-	3.20
	18.2	-	3.00
	18.9	-	3.30
	20.9	-	3.05
HI	12.2	3.2	9.0
	16.2	6.3	9.9
	20.1	10.1	10.0
	22.0	12.0	10.0
	3.1	0.6	2.5
	7.9	1.5	6.4
HBr	8.9	0.4	8.5
	5.6	0.9	4.7
	24.9	15.0	9.9
	15.3	5.4	9.9
	12.2	3.2	9.0

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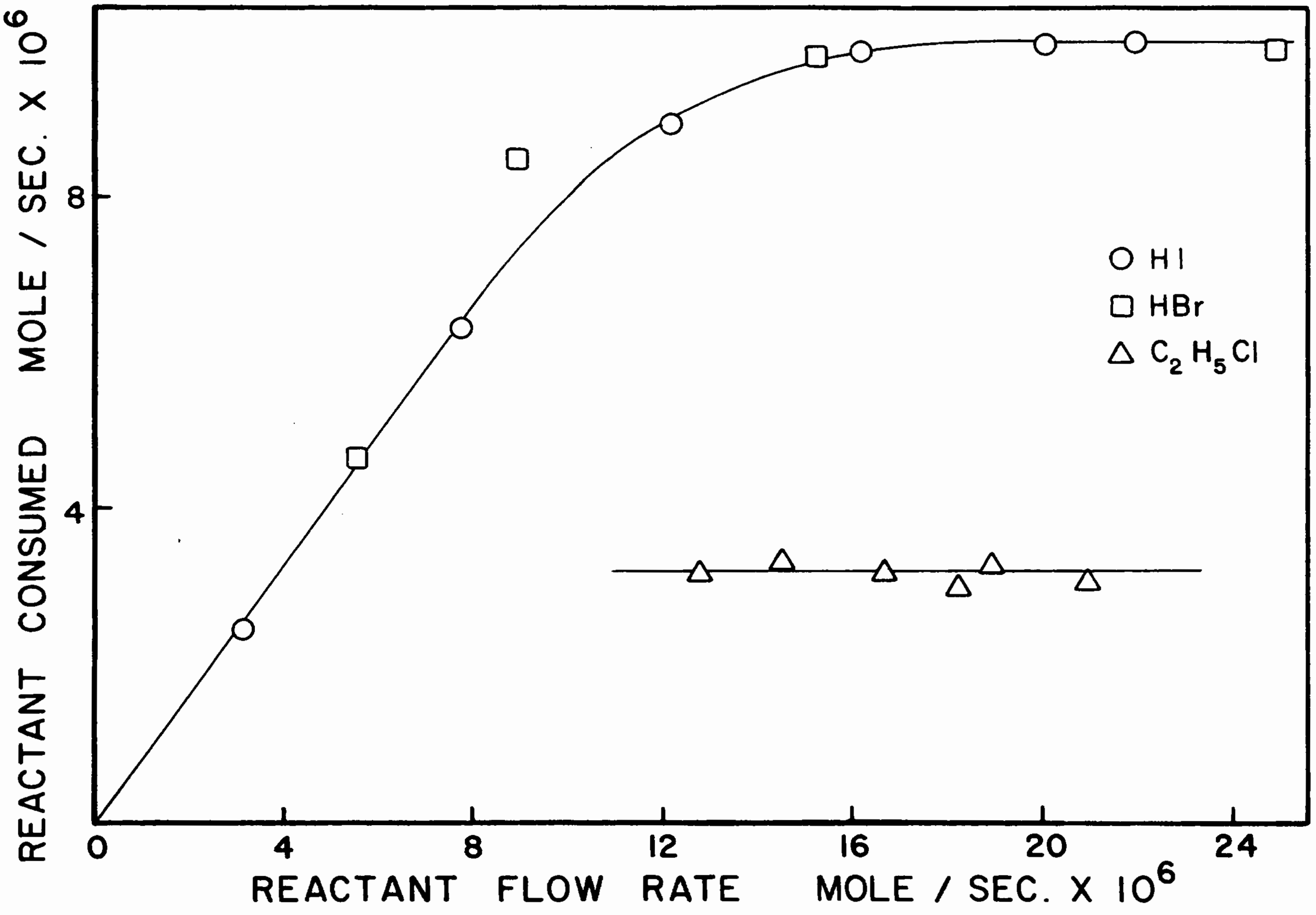
*The units are mole/sec. x 10^{-6}.

FIGURE 2

THE REACTIONS OF ATOMIC HYDROGEN
WITH ETHYL CHLORIDE, HYDROGEN
IODIDE AND HYDROGEN BROMIDE
AT 65°C.

REACTANT CONSUMED MOLE / SEC. X 10^6
8
4
0
4
8
12
16
20
24
REACTANT FLOW RATE MOLE / SEC. X 10^6
○ HI
□ HBr
△ C_2H_5Cl

thickness increased. When hydrogen atoms reacted with this coating it was consumed completely in such a manner that the clearly-defined horizontal boundary between clean and phosphorus-covered glass moved gradually down the reaction vessel wall. Few hydrogen atoms appeared to exist beyond the phosphorus level. This process resulted in the conversion of the red phosphorus to phosphine and a small amount of diphosphine, and it occurred at an appreciable rate for temperatures at which the vapor pressure of red phosphorus is quite low. However, the rate of this conversion was noticeably faster at higher temperatures. The traces of diphosphine, which were invariably formed, ignited spontaneously in contact with air and this prevented the quantitative determination of the amount of red phosphorus by conversion of the layer to phosphine.

The results of the reaction between hydrogen atoms and phosphine at three temperatures are given in Table II and are shown graphically in Figure 3.

Reaction of Atomic Hydrogen with Hydrogen Chloride

It was desirable to determine, if possible, the effect that this reaction might have had on the results obtained in the analogous reaction with active nitrogen. An investigation was made, with the same atomic hydrogen flow rates used in the other work, at

TABLE II

Reaction of Atomic Hydrogen with Phosphine
at Various Temperatures

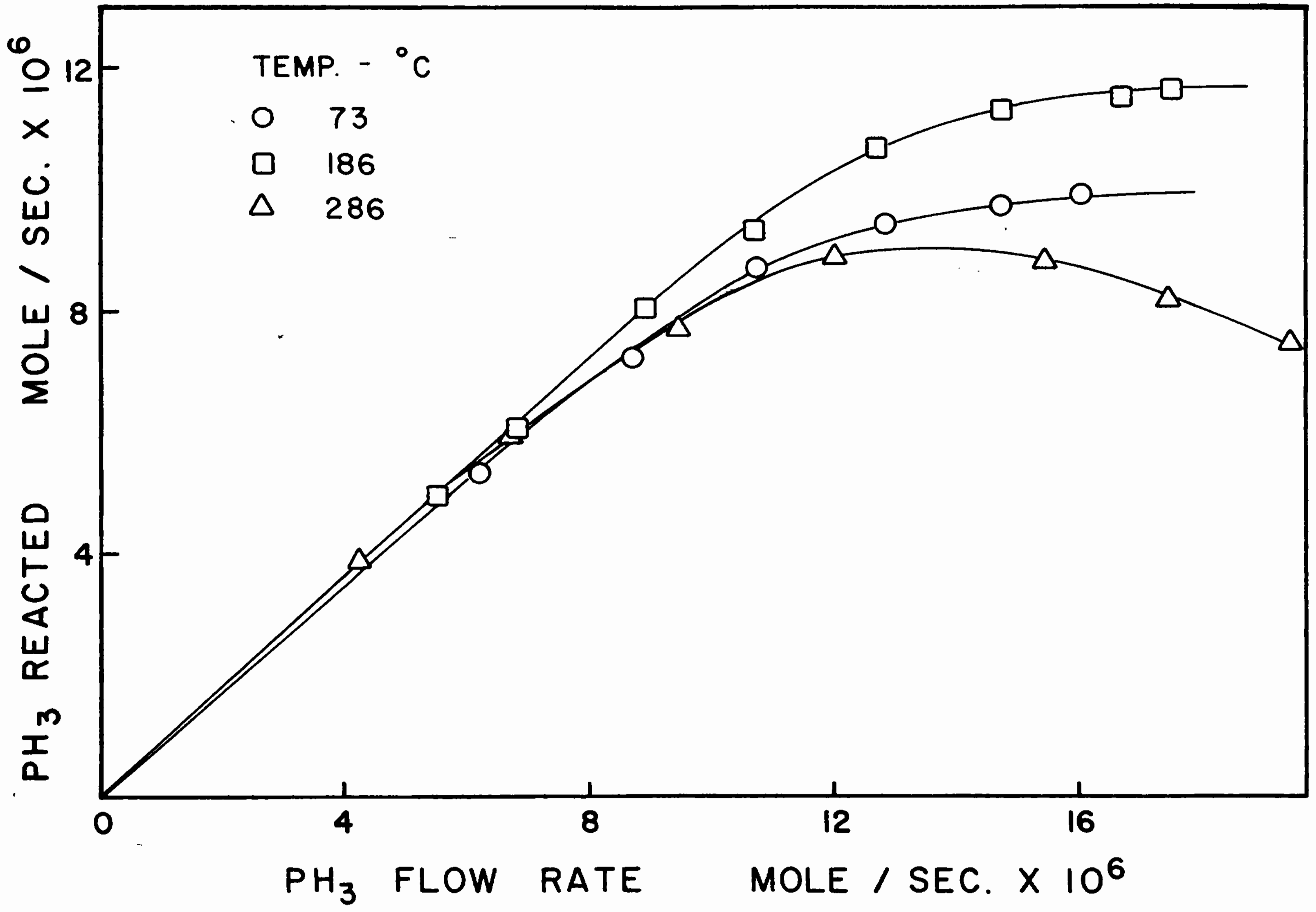
TEMP. °C	PH_3 FLOW RATE*	PH_3 RECOVERED*	PH_3 REACTED*
73 ± 5	8.7	1.4	7.3
	16.0	6.0	10.0
	14.7	4.9	9.8
	12.8	3.3	9.5
	10.7	1.9	8.8
	6.2	0.8	5.4
186 ± 5	5.5	0.5	5.0
	6.8	0.7	6.1
	8.9	0.8	8.1
	10.7	1.3	9.4
	12.7	1.9	10.8
	14.7	3.3	11.4
	17.4	5.4	12.0
	16.7	4.9	11.8
286 ± 5	6.7	0.6	6.1
	12.0	3.0	9.0
	15.4	6.5	8.9
	17.4	9.1	8.3
	19.4	11.7	7.7
	9.4	1.6	7.8
	4.2	0.2	4.0

*The units are mole/sec. x 10^{-6}.

FIGURE 3

THE REACTION OF ATOMIC HYDROGEN
WITH PHOSPHINE AT VARIOUS TEMPERATURES

BIND HERE


TEMP. - °C
○ 73
□ 186
△ 286
PH_3 REACTED MOLE / SEC. X 10^6
0
4
8
12
16
PH_3 FLOW RATE MOLE / SEC. X 10^6

three temperatures, 50°, 300° and 440°C, and at a wide variety of HCl flow rates. No net decomposition of hydrogen chloride was detected in any of these experiments, although it appeared that hydrogen atoms were consumed.

ACTIVE NITROGEN

With a molecular nitrogen flow rate of 115 micro-moles per sec. and with a flash rate of about 10 per sec., the pressure in the reaction vessel was 1.35 mm. and the temperature indicated by the thermocouple was 70°C.

Reaction of Active Nitrogen with Ethylene

The maximum rate of hydrogen cyanide production in the active nitrogen-ethylene reaction was investigated at several temperatures in the range 80° to 450°C. The limiting HCN yield at 80°C was 10 micro-moles per sec. and anywhere in the range 250° to 450°C it was 20 micro-moles per sec. These values were determined before and after every series of experiments and, of necessity, in several freshly poisoned reaction systems; the precision between values for each temperature was always better than ± 5%.

Reaction of Active Nitrogen with Phosphine

The results for the active nitrogen-phosphine reaction at 83° and 290°C are shown in Table III and Figure 4.

TABLE III

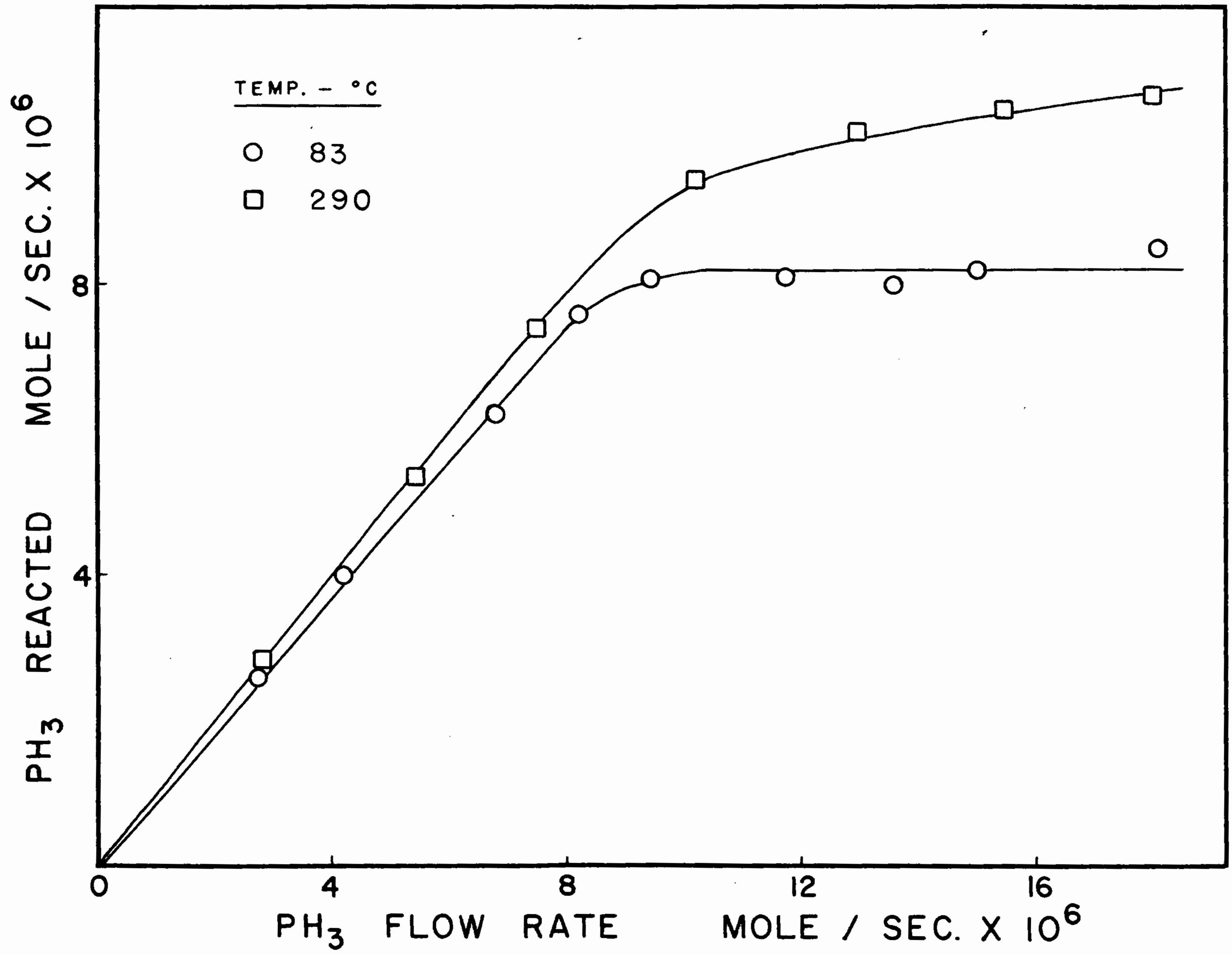
Reaction of Active Nitrogen with Phosphine

TEMP. °C	PH_3 FLOW RATE*	PH_3 RECOVERED*	PH_3 REACTED*
83 ± 5	6.8	0.6	6.2
	4.2	0.2	4.0
	8.2	0.6	7.6
	2.7	0.1	2.6
	9.4	1.3	8.1
	18.1	9.8	8.3
	11.5	3.4	8.1
	15.0	6.8	8.2
	13.6	5.6	8.0
290 ± 10	2.8	0.0	2.8
	5.4	0.0	5.4
	7.5	0.1	7.4
	10.2	0.8	9.4
	12.9	2.8	10.1
	15.4	5.0	10.4
	18.0	7.4	10.6

*The units are mole/sec. x 10^{-6}.

FIGURE 4

THE REACTION OF ACTIVE NITROGEN
WITH PHOSPHINE


TEMP. – °C
○ 83
□ 290
PH_3 REACTED MOLE / SEC. X 10^6
0
4
8
12
16
PH_3 FLOW RATE MOLE / SEC. X 10^6

As it entered the active nitrogen stream, phosphine extinguished the afterglow and a small, pale-green reaction flame was observed. The main products of the reaction were hydrogen and an opaque, reddish-brown polymer which formed on the walls of the reaction vessel. Its non-volatility, color, behaviour in hot and cold concentrated H_2SO_4, and insolubility in the usual solvents suggested that the polymer was the alpha form of $(PN)_n$, phosphorus paranitride. The layer was removed in small flakes from the inner walls of the reaction vessel by leaching with NH_4OH solution, which presumably dissolved the underlying metaphosphoric acid used to poison the walls of the reaction system. The material was thoroughly washed and dried and two samples (each 0.3 gm.) were hydrolysed for 48 hours in a sealed tube at 200°C, following the procedure described by Moureu and Wetroff (119). Aliquots from each of these solutions were analysed for nitrogen by the Kjeldahl method. Phosphorus present in the polymer solution was expected to be partly in the form of phosphite and mostly in the form of phosphate. Hence, aliquots from both solutions were analysed for phosphite with a volumetric method (using $KMnO_4$ solution - see (119) for experimental details) and for phosphate gravimetrically (precipitated as magnesium ammonium phosphate - see (117) for details). Results of duplicate determinations agreed within ± 1% and, using average values, they indicated that the polymer contained 46.8% nitrogen and 46.5% phosphorus on an atom per cent basis.

The condensate in the product trap was analysed, after several experiments, in a low temperature still (120) and no trace of ammonia was detected. It should also be mentioned that the presence of $(PN)_n$ on the reaction vessel walls did not affect the limiting HCN yield in the active nitrogen-ethylene reaction at any temperature.

In connection with the active nitrogen-phosphine reaction, a very limited investigation of two other reactions was made. A relatively thick layer of red phosphorus was deposited on the clean wall of the reaction vessel by reacting phosphine with hydrogen atoms. It was found that when this layer was subjected to attack by active nitrogen at 300°C, considerable $(PN)_n$ was formed.

A brief study was also made of the reaction of hydrogen atoms with $(PN)_n$ deposited on the walls in the active nitrogen-phosphine reaction. The attack of atomic hydrogen on the polymer layer was found to produce phosphine, slowly at 60°C, more rapidly at 300°C. This indicated that hydrogen atoms decomposed the nitride to phosphorus and nitrogen, and hence attempts were made to detect the presence of nitrogen atoms. Propane was led into the reaction vessel through the reactant inlet during some of the H atom-$(PN)_n$ experiments, and HCN was produced in quantities roughly equivalent to the phosphine formed. The active nitrogen produced from the nitride polymer was also found to decompose ammonia, although to only a slight extent.

Reaction of Active Nitrogen with Hydrogen Chloride

This reaction was studied at 80°, 200°, 310° and 440°C. The results are shown in Table IV and Figure 5. The only product recovered was molecular chlorine and it was found that the calculated amount of HCl consumed was generally in good agreement with the quantity of chlorine recovered. The minor discrepancies between these two quantities, observed in a few experiments, were not reproducible and were believed to have no kinetic significance. They were attributed to difficulties inherent in handling chlorine in the type of apparatus used, and although included in Table IV, they have not been indicated in Figure 5.

At flow rates above 5 or 6 micro-moles per sec. HCl destroyed the afterglow, and the reaction flame was somewhat more reddish than the characteristic yellow afterglow, although the difference was not striking. The reaction flame was diffuse and completely filled the reaction vessel and the tube leading to the product trap, but its intensity was visibly greater on the walls

TABLE IV

Reaction of Active Nitrogen with Hydrogen Chloride at 80° and 200°C.

TEMP. °C	HCl FLOW RATE*	HCl RECOVERED*	HCl REACTED*	Cl PRODUCED*
80 ± 4	1.3	1.0	0.3	0.3
	2.7	2.1	0.6	0.6
	6.5	5.6	0.9	0.9
	9.0	8.0	1.0	1.0
	11.6	10.7	0.9	1.0
	13.4	12.3	1.1	1.0
	4.6	3.8	0.8	0.8
	15.7	14.4	1.3	1.1
	18.2	16.9	1.3	1.3
	17.2	16.0	1.2	1.1
	7.0	6.1	0.9	0.9
	2.6	2.1	0.5	0.5
	10.5	9.5	1.0	0.9
	4.8	4.0	0.8	0.7
200 ± 7	17.0	14.0	3.0	2.8
	14.0	10.9	3.1	2.9
	9.4	6.7	2.7	2.7
	5.8	4.0	1.8	1.8
	2.5	1.5	1.0	1.0
	11.8	9.2	2.6	2.5

---

*The units are mole/sec. x 10^{-6}.

TABLE IV (continued)

Reaction of Active Nitrogen with Hydrogen Chloride at 310° and 440°C.

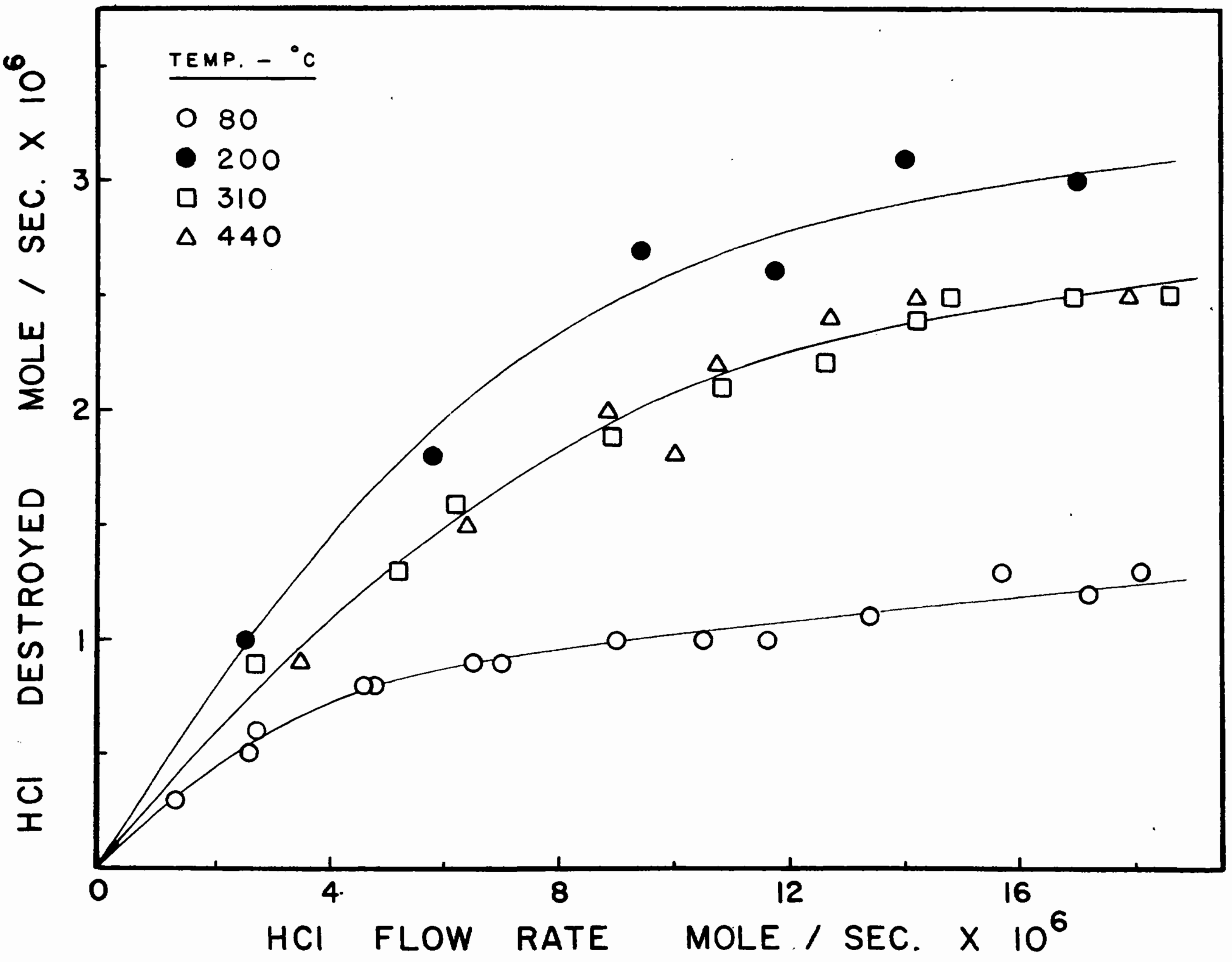
TEMP. °C	HCl FLOW RATE*	HCl RECOVERED*	HCl REACTED*	Cl PRODUCED*
310 ± 5	2.7	1.8	0.9	0.9
	5.2	3.9	1.3	1.3
	14.8	12.3	2.5	2.5
	8.9	7.0	1.9	1.9
	18.6	16.1	2.5	2.4
	16.9	14.4	2.5	2.5
	14.2	11.8	2.4	2.4
	10.8	8.7	2.1	2.0
	12.6	10.4	2.2	2.2
	6.2	4.6	1.6	1.7
440 ± 10	3.5	2.6	0.9	0.9
	6.4	4.9	1.5	1.5
	10.0	8.2	1.8	1.8
	14.2	11.7	2.5	2.5
	17.9	15.4	2.5	2.4
	12.7	10.3	2.4	2.4
	8.8	6.8	2.0	2.1
	10.7	8.5	2.2	2.3

---

*The units are mole/sec. x 10^{-6}.

FIGURE 5

THE REACTION OF ACTIVE NITROGEN
WITH HYDROGEN CHLORIDE


TEMP. – °C
○ 80
● 200
□ 310
△ 440
HCl DESTROYED MOLE / SEC. X 10^6
1
2
3
0
4
8
12
16
HCl FLOW RATE MOLE / SEC. X 10^6

and the thermocouple tube than in the body of the gas.

It is important to note that apparently no ammonia was formed in this reaction. It would have appeared, of course, as ammonium chloride which has a sufficiently low vapor pressure at room temperature that it would have collected in the product trap during a series of experiments. However, nothing appeared to have accumulated anywhere in the system at any temperature.

The effects of different amounts of added molecular hydrogen and molecular chlorine on the extent of HCl decomposition are given in Table V and Figure 6 for each of four temperatures. The change in these effects with HCl flow rate was investigated to a limited extent. It was found that, for a series of experiments in which the hydrogen and hydrogen chloride flow rates were the same, the curve showing the change in rate of HCl destruction with changing HCl flow rate was somewhat below, but parallel to, the same curve with no hydrogen present. This behaviour is illustrated by the results obtained at 310° and 440°C which are shown in Figure 7. The same type of information could not be obtained for chlorine-hydrogen chloride mixtures because, as can be seen in Figure 6B, all but the smallest flow rates of chlorine caused the complete regeneration of hydrogen chloride.

TABLE V

A: The Effect of Added Molecular Hydrogen on the Rate of Hydrogen Chloride Decomposition at Various Temperatures, with a Constant HCl Flow Rate of 4.6 mole/sec. x 10^{-6}

H_2 FLOW RATE*	HCl DESTROYED*			
	at 80°C	at 200°C	at 310°C	at 440°C
0	0.8	1.6	1.2	1.2
5.2	0.4	0.7	0.5	0.5
11.0	0.3	0.4	0.3	0.3

B: The Effect of Added Molecular Chlorine on the Rate of Hydrogen Chloride Decomposition at Various Temperatures, with a Constant HCl Flow Rate of 13.0 mole/sec. x 10^{-6}

Cl_2 FLOW RATE*	HCl DESTROYED*			
	at 80°C	at 200°C	at 310°C	at 440°C
0	1.1	2.9	2.4	2.4
0.9	0.7	1.9	1.4	1.4
3.0	0	0	0	0

---

*The units are mole/sec. x 10^{-6}.

FIGURE 6

A: THE EFFECT OF ADDED MOLECULAR HYDROGEN ON THE RATE OF HYDROGEN CHLORIDE DECOMPOSITION

B: THE EFFECT OF ADDED MOLECULAR CHLORINE ON THE RATE OF HYDROGEN CHLORIDE DECOMPOSITION

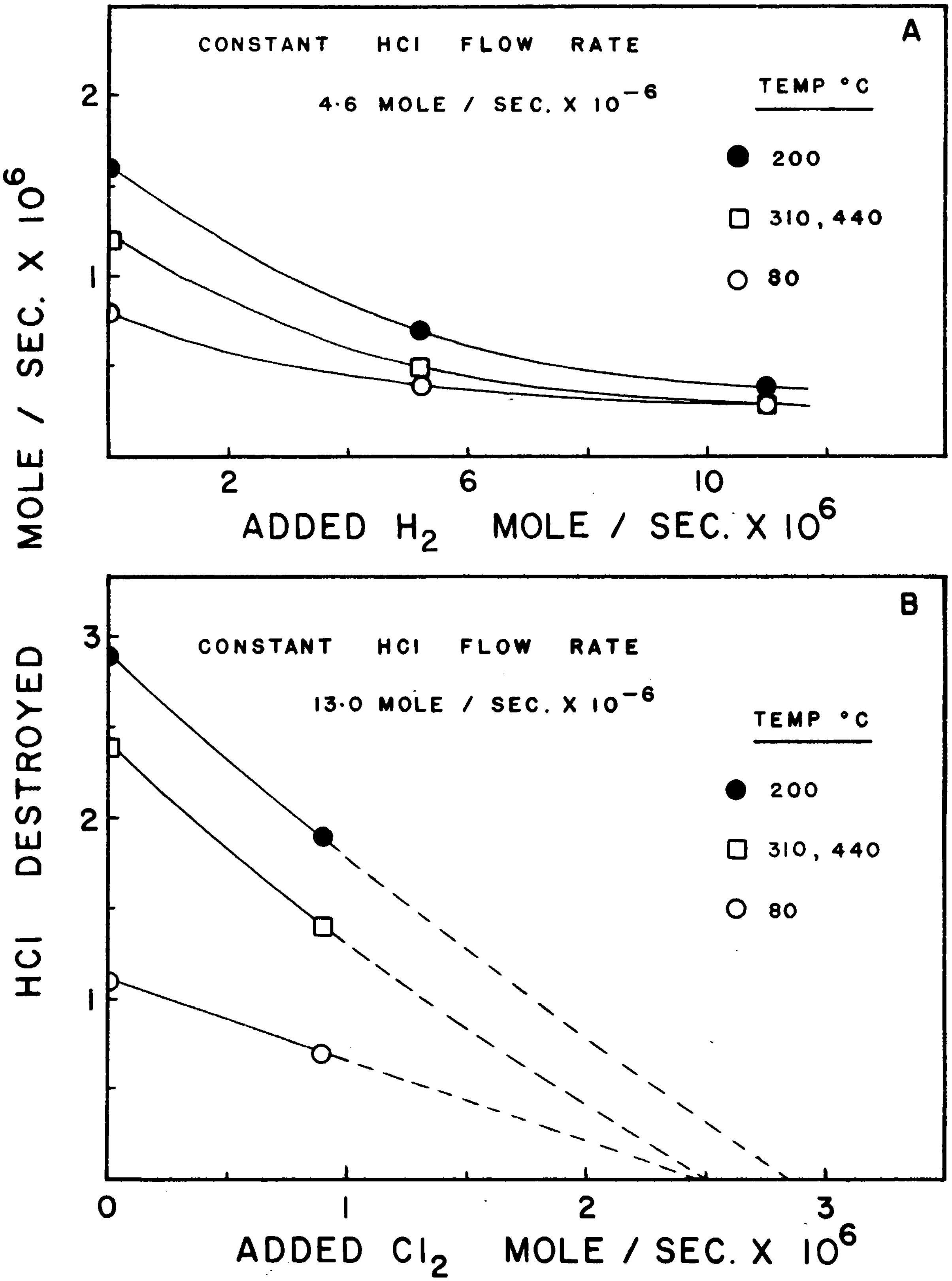

A
CONSTANT HCl FLOW RATE
4·6 MOLE / SEC. X 10^-6
TEMP °C
● 200
□ 310, 440
○ 80
2
1
2
6
10
ADDED H2 MOLE / SEC. X 10^6
B
CONSTANT HCl FLOW RATE
13·0 MOLE / SEC. X 10^-6
TEMP °C
● 200
□ 310, 440
○ 80
3
2
1
0
1
2
3
ADDED Cl2 MOLE / SEC. X 10^6
HCl DESTROYED MOLE / SEC. X 10^6

TABLE VI

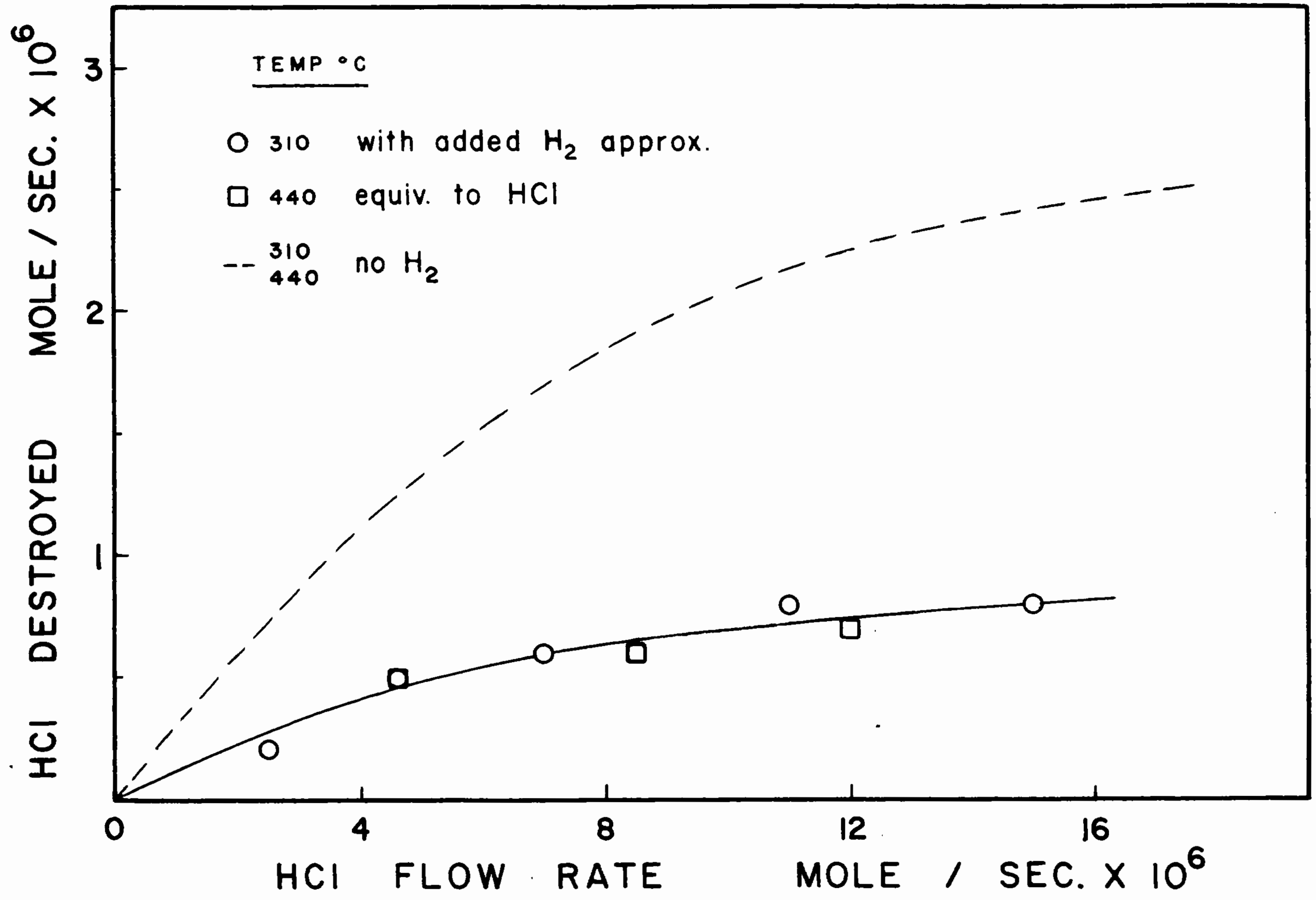
The Effect of Added Molecular Hydrogen on the Rate of Hydrogen Chloride Decomposition at 310° and 440°C

TEMP. °C	HYDROGEN FLOW RATE*	HCl FLOW RATE*	HCl REACTED*
310 ± 10	4.2	2.5	0.2
	8.2	7.0	0.6
	11.0	11.0	0.8
	13.0	15.0	0.8
	5.2	4.6	0.5
440 ± 10	12.0	12.0	0.7
	9.0	8.5	0.7
	5.2	4.6	0.5

*The units are mole/sec. x 10^{-6}.

FIGURE 7

THE EFFECT OF ADDING MOLECULAR
HYDROGEN EQUIVALENT TO THE HYDROGEN
CHLORIDE FLOW RATE


TEMP °C
○ 310 with added H₂ approx.
□ 440 equiv. to HCl
-- 310 440 no H₂
HCl DESTROYED MOLE / SEC. X 10⁶
0
1
2
3
4
8
12
16
HCl FLOW RATE MOLE / SEC. X 10⁶

DISCUSSION

ATOMIC HYDROGEN

Reactions of Atomic Hydrogen with C_2H_5Cl, HI and HBr

The results given in Figure 2 show that hydrogen iodide and hydrogen bromide reacted to the same extent and this is a good indication that both consumed all the available hydrogen atoms. The following elementary steps must have occurred:

$$H + HX \rightarrow H_2 + X \qquad (1)$$

$$X + X + M \rightarrow X_2 + M \qquad (2)$$

$$H + X_2 \rightarrow HX + X \qquad (3)$$

where X is either I or Br and M is a third body. The activation energy for (1) is approximately 1 kcal. per mole (121). Reaction (3) has a small but significant activation energy, practically the same as for (1). According to Williams and Ogg (122), the ratio k_3/k_1 is 3.5 for HI and is essentially independent of temperature. For HBr the ratio k_3/k_1 is 8.4 (121). However, since hydrogen atom consumption is apparently complete with excess of either hydrogen halide, the consumption of atomic hydrogen by I_2 or by Br_2 under these conditions seems to represent a negligibly small percentage of the total H atom concentration available. It is assumed, therefore, that the plateau value for the amount of reactant destroyed may be taken as a measure of the flow rate of hydrogen atoms. On this basis the flow rate in the reaction system was 10 micro-moles per sec. and the ethyl chloride reaction was 32% complete at 65°C (cf. reference 32).

It is of interest that a previous study of the HBr-H atom reaction (31) indicated 100% consumption of hydrogen atoms.

Reaction of Atomic Hydrogen with Phosphine

It is apparent from comparison of Figures 2 and 3 that, at 73°C, phosphine reacts with all available hydrogen atoms since the plateau at that temperature corresponds closely to the maximum amounts of hydrogen iodide and hydrogen bromide destroyed under similar conditions. Assuming this to be the case, and on the basis of the products of the reaction, it seems likely that phosphine reacts according to the following mechanism.

$$PH_3 + H \rightarrow PH_2 + H_2 + 24 \text{ kcal.} \qquad (4)^{*}$$

$$PH_2 + PH_2 \rightarrow P_2 + 2H_2 + 26 \text{ kcal.} \qquad (5)$$

$$P_2 \rightarrow 2P_{red} + 42.6 \text{ kcal.} \qquad (6)$$

---

*Values for the heats of formation, together with their sources, used to calculate the heat of reaction for this and subsequent reactions may be found in the Appendix.

The abstraction of hydrogen is typical of the reactions of atomic hydrogen with saturated compounds and, because of its exothermicity, reaction (4) is the most reasonable primary step. The suggestion that reactions (5) and (6) are plausible steps is substantiated by evidence obtained in investigations of the photochemical and mercury photosensitized decomposition of phosphine. For example, Melville et al. (123) studied the photochemical decomposition of PD_3 and PH_3 and found evidence that PH_2 radicals decompose to give molecular hydrogen. Melville and Gray (124), in a study of the polymerisation of phosphorus, obtained experimental evidence that P_2 molecules condense to red phosphorus. Thus the sequence, reaction (4) followed by (5) and (6), is quite reasonable and would account for the products found in the present study.

The following reactions are also possible, although they appear to occur to only a slight extent at room temperature.

$$PH_2 + H \rightarrow PH + H_2 + 27 \text{ kcal.} \qquad (7)$$

$$PH + PH_2 \rightarrow P_2 + H + H_2 - 0.9 \text{ kcal.} \qquad (8)$$

$$PH + H \rightarrow P + H_2 + 32 \text{ kcal.} \qquad (9)$$

$$PH + PH + M \rightarrow P_2 + H_2 + M + 76 \text{ kcal.} \qquad (10)$$

Reactions (7) and (8) should lower the plateau at 73°C relative to that representing the available hydrogen atoms, but this was not observed. It is therefore reasonable to assume that, at phosphine flow rates corresponding to complete consumption of hydrogen atoms, the unstable PH_2 species reacts according to equation (5) rather than equation (7). If this is the situation, then steps (8), (9) and (10) will not occur since they depend on the formation of PH radicals.

The rates of phosphine decomposition at 73° and 186°C are typical of a reaction, with a small activation energy, in which the reactant present in smaller amount is completely consumed. The experiments at 286°C indicate that a back reaction with a large temperature coefficient appreciably affects the net amount of phosphine decomposed. It is suggested that this back reaction is the attack of hydrogen atoms on red phosphorus, which has been shown to occur in the same system, to produce phosphine. The reactions

$$H + P_{red} \rightarrow PH - 7 \text{ kcal.} \qquad (11)$$

$$PH + H_2 \rightarrow PH_3 + 53 \text{ kcal.} \qquad (12)$$

seem the most likely to account for this result. At lower PH_3 flow rates, corresponding to the rising portion of the curve for 286°C, some of the PH radicals produced in (11) would proceed by (12) to regenerate phosphine; others in the presence of excess hydrogen atoms would be decomposed again to give red phosphorus by (9). At higher phosphine flow rates where hydrogen atom consumption is virtually complete, most of the PH radicals would probably regenerate phosphine by reaction (12). Thus, the observed rate of phosphine decomposition may be reduced not only by consumption of atomic hydrogen by red phosphorus, but also by regeneration of phosphine. Consequently, in accordance with the observed behaviour, the curve for 286°C might be expected to rise to a maximum and fall off slowly as the phosphine flow rate is increased.

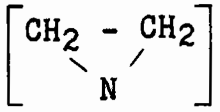
For several reasons, no calculations have been made of rate constants, or of the activation energy and steric factor, for the atomic hydrogen-phosphine reaction. The reaction at 286°C is obviously complicated by a vigorous back reaction which renders the results at this temperature useless for purposes of kinetic calculations. While the reactions at 73° and 186°C do not appear to be influenced by competing back reactions, the rates show little difference, which would suggest the existence of some complicating factor. Moreover, only a rough estimate of the hydrogen atom flow rate is possible at 186°C. In addition, there is considerable uncertainty in the temperature measurements owing to the coating of phosphorus on the thermocouple well which undoubtedly increases the discrepancy between the measured and the actual reaction temperatures. Hence, the results at 73° and 186°C were not considered to be useful for kinetic calculations.

Reaction of Atomic Hydrogen with Hydrogen Chloride

Atomic hydrogen was consumed in this reaction but there was no net decomposition of HCl. Therefore, either HCl catalyses the recombination of hydrogen atoms without itself being changed, or any decomposition which does occur is nullified by the immediate regeneration of hydrogen chloride in back reactions. The results of thermal (125) and photochemical (43,126,127) studies indicate that the latter alternative is correct. This is perhaps reasonable, in view of the appreciable concentration of hydrogen atoms and the large excess of molecular hydrogen in the system.

ACTIVE NITROGEN

Reaction of Active Nitrogen with Ethylene

The maximum yield of hydrogen cyanide from the ethylene-active nitrogen reaction was found to increase by a factor of two (10 micro-moles per sec. to 20 micro-moles per sec.) as the temperature was raised from 80° to 250°C. It is suggested that this observation may be explained in the manner suggested (104) for the similar behaviour observed when methyl chloride and methyl cyanide are caused to react with active nitrogen. There is theoretical (107) and experimental (116) evidence that the primary step in the active nitrogen-ethylene reaction is the formation of a complex . At room temperature this complex will either decompose spontaneously to give HCN or may catalyse the recombination of two nitrogen atoms by collision with a second atom. The extent to which this second process takes place depends on the lifetime of the complex, which may be assumed to decrease with increasing temperature. Hence, the rate of production of hydrogen cyanide should increase with temperature relative to the rate of recombination of nitrogen atoms catalysed by ethylene. Apparently there is little catalytic recombination at or above 250°C since the HCN yield is essentially constant above this temperature. Hence, it may be assumed that the maximum HCN yield at the higher temperatures corresponds to the actual flow rate of active nitrogen, i.e., 20 micro-moles per sec., at all temperatures.

Reaction of Active Nitrogen with Phosphine

The results shown in Figure 3, if considered in comparison with results discussed in the previous section, indicate that phosphine decomposition occurred at 83° and 290°C to the extent of 41% and 53%, respectively, of the nitrogen atom flow rate. The difference in these two values might be due to a difference in the effectiveness of phosphine itself as a catalyst for the recombination of nitrogen atoms at the two temperatures.

On the basis of these considerations it would appear that the reaction of active nitrogen with phosphine can be explained in terms of nitrogen atoms as the only reactive species. The results strongly suggest that the decomposition of one phosphine molecule requires the consumption of two nitrogen atoms. If this be true, then the reaction of phosphine with active nitrogen probably occurs by

$$N + PH_3 \rightarrow NH + PH_2 + 8 \text{ kcal.} \qquad (13)$$

followed by

$$N + PH_2 + M \rightarrow PN + H_2 + M + 163 \text{ kcal.} \qquad (14)$$

$$NH + NH + M \rightarrow N_2 + H_2 + M + 154 \text{ kcal.} \qquad (15)$$

It seems likely that, as the flow rate of phosphine is increased beyond the point corresponding to complete consumption of nitrogen atoms, PH_2 radicals should react according to

$$PH_2 + PH_2 \rightarrow P_2 + 2H_2 + 26 \text{ kcal.} \qquad (16)$$

followed by

$$P_2 \rightarrow 2P_{red} + 42.6 \text{ kcal.} \qquad (17)$$

Failure to detect red phosphorus in the polymer layer might indicate that reaction (14) is fast compared with (13) or that the reaction

$$N + P_{red} \rightarrow PN + 128.3\ \text{kcal.}, \qquad (18)$$

which has been shown to occur in the system, is fast enough to maintain the concentration of phosphorus at a level too low for detection. On the other hand, experiments at sufficiently high flow rates of phosphine might reveal the presence of reactions (16) and (17).

There is no way of measuring directly the relative rates of reactions (13) and (14) or of determining the consumption of nitrogen atoms in reaction (18). Moreover, the temperature measurements, which at best are of questionable accuracy in a fast-flow system, are certain to be particularly inaccurate in this work owing to the thick coating of polymer on the thermocouple well. As a result, no kinetic analysis of the data has been attempted.

There is no indication (Table III) of an appreciable concentration of any active species other than nitrogen atoms. If the ratio of 2:1 (nitrogen atom flow rate compared to maximum rate of phosphine consumption) is real, and it appears to be, then the conversion of each phosphine molecule to the nitride does require two nitrogen atoms. It is likely, then, that reaction (13) is the primary step. It is of interest to note that, of all the active nitrogen reactions investigated to date, the reaction with phosphine is the first one in which hydrogen abstraction by atomic nitrogen appears to be of major significance. Perhaps the occurrence of hydrogen abstraction in the phosphine reaction, and not in the ammonia reaction, partially accounts for the difference in the rate of nitrogen atom attack on these two compounds.

Reaction of Active Nitrogen with Hydrogen Chloride

There are three unusual aspects of the results for the reaction of active nitrogen with hydrogen chloride, shown in Figure 5. In the first place, the maximum rate of HCl decomposition is less than one sixth of the active nitrogen flow rate (3.1 micro-moles per sec. as compared to 20 micro-moles per sec.). Secondly, increasing the temperature above 200°C lowers the rate of HCl consumption, and the rates at 310° and 440°C are the same, within experimental error. Finally, since none of the three curves seems to have levelled off at a plateau value, within the range of flow rates used, the reaction does not appear to be one in which the reactant present in lesser amount is completely consumed.

The first point suggests that no simple reaction between nitrogen atoms and HCl occurs, and this supposition is, of course, substantiated by the fact that the reaction

$$N + HCl \rightarrow NH + Cl \ -16 \text{ kcal.} \qquad (19)$$

is energetically improbable at ordinary temperatures. An alternative to reaction (19) is the decomposition of HCl by reaction with an active species other than nitrogen atoms. However, the results given in Figure 5 can be explained in terms of atomic nitrogen without recourse to reaction (19) or to an additional active species.

It is reasonable to suppose that hydrogen chloride may be destroyed by the energy produced in the recombination of nitrogen atoms catalysed by HCl. It is suggested that a nitrogen atom and a hydrogen chloride molecule can, on collision, form a relatively stable complex, and that, when this complex collides with a second nitrogen atom (or with a second complex) such that N_2 is formed, a sufficient proportion of the recombination energy (9.76 ev. per mole) is left in the H-Cl bond to cause decomposition of the molecule. Hence, the decomposition of hydrogen chloride by active nitrogen is believed to occur by

$$HCl + N \rightarrow \left[H\text{-}Cl\text{-}N\right] \qquad (20)$$

followed by either

$$N + [H\text{-}Cl\text{-}N] \rightarrow N_2 + H + Cl \qquad (21)$$

or

$$2[H\text{-}Cl\text{-}N] \rightarrow N_2 + HCl + H + Cl. \qquad (22)$$

There is no direct experimental evidence for the existence of a nitrogen atom-hydrogen chloride complex with an appreciable lifetime, but there are theoretical considerations which make the suggestion seem reasonable. Many investigators have noted that a small amount of HCl is very effective in catalysing the recombination of hydrogen atoms. A triangular H-Cl-H complex has been postulated (128) to account for this and it has been shown that such a complex should have considerable stability (125,129). It may be predicted (107) that a nitrogen atom, because of its greater electronegativity and its greater mass, should be able to form a similar collision complex more readily than a hydrogen atom, and that the nitrogen complex should have a reasonable lifetime.

The second and third unusual characteristics of Figure 5 mentioned previously indicate that one or more back reactions affect the observed rates by regenerating HCl. The three possible back reactions are

$$H + Cl_2 \rightarrow HCl + Cl + 45.14 \text{ kcal.} \qquad (23)$$

$$Cl + H_2 \rightarrow HCl + H - 1.01 \text{ kcal.} \qquad (24)$$

$$H + Cl + M \rightarrow HCl + M + 103.16 \text{ kcal.} \qquad (25)$$

The activation energies for reactions (23) and (24) have been reported as 3 and 6 kcal. per mole, respectively (121). Hydrogen atoms, besides taking part in reactions (23) and (25), can recombine to form molecular hydrogen or can decompose HCl in the reaction

$$H + HCl \rightarrow H_2 + Cl + 1.01 \text{ kcal.} \qquad (26)$$

which probably has an activation energy of about 5 kcal. per mole (121). Chlorine atoms can either combine to form molecules or can react in (24) or (25).

It is important to determine, if possible, which of the above processes are more important at any given temperature. Morris and Pease (121) estimate that k_{23}/k_{26} is greater than 100 at room temperature (cf. reference (43)) and it has been suggested (126) that k_{23}/k_{24} is at least 100, up to 25°C. Figure 6B shows that very small amounts of added chlorine drastically reduce the observed rate of HCl decomposition by active nitrogen, which indicates that at temperatures up to 440°C, even with excess HCl, hydrogen atoms react much more rapidly in process (23) than in (26). It is evident from Figures 6A and 7 that additions of molecular hydrogen affect the observed rate of hydrogen chloride decomposition much less than do additions of chlorine.

It seems reasonable to conclude that:

(i) reaction (23) is the most important back reaction at all temperatures at which the reactions were studied;

(ii) reaction (26) occurs to a somewhat greater extent than reaction (24), particularly at higher HCl flow rates, because there probably are more hydrogen atoms than molecules in the system;

(iii) most of the hydrogen atoms produced in reactions (21) and (22) react before they recombine whereas chlorine atoms, produced in the same reactions, recombine to a large extent. (It has been shown (118) that the conditions which favour the recombination of chlorine atoms differ from those favouring the recombination of hydrogen atoms);

(iv) recombination of hydrogen atoms, which is certain to occur to some extent, is the main factor responsible for preventing the complete regeneration of HCl, i.e., for permitting the decomposition of HCl by active nitrogen to be observed at all.

The amount of HCl produced in reaction (25) is probably small at all temperatures owing to the infrequency of triple collisions in the gas phase and the number of rapid alternative processes possible for H and Cl before they reach the vessel wall.

To explain the comparable rates of HCl consumption at 310° and 440°C, it must be concluded that changes in the extent of reactions (20), (21), (22) and (26) are just balanced by changes in the amount of HCl regenerated by (23), (24) and (25). This situation would seem to be entirely too coincidental unless it is assumed that there is complete consumption of nitrogen atoms at, or even below, 310°C (i.e., 10 micro-moles per sec. HCl destroyed with the nitrogen atom flow rate 20 micro-moles per sec.). On the basis of this assumption, it can be shown that changes in the extent of the secondary reactions, between 310° and 440°C, are likely to be within experimental error. Reaction (24) probably proceeds at both temperatures until there is complete consumption of available Cl and H_2, the concentrations of which will not differ more than a few percent if the primary decomposition by active nitrogen occurs to essentially the same extent at both temperatures. Extrapolation of the data of Bodenstein et al. (43) indicates that the ratio k_{23}/k_{26} does not change significantly between 310° and 440°C in a flow system. This has been substantiated in the present work by the fact that added chlorine and added hydrogen had the same effects (Figure 6) at 310°C as at 440°C.

The decrease in rate of HCl consumption (see Figure 5) as the temperature is increased from 200° to 310°C and above can be attributed to an increase in the rates of the reactions that regenerate HCl, particularly reaction (23) and perhaps to a lesser extent reaction (24). However, this suggests that there is little or no increase in the rate of destruction of HCl by nitrogen atoms between 200° and 310°C, i.e., that it is approximately 10 micro-moles per sec. over the whole range 200° to 440°C.

The increase in rate of decomposition of HCl as the temperature is increased from 80° to 200°C can be attributed to an increase in the rate of the primary decomposition by nitrogen atoms or to an increase in the rate of reaction (26), or more likely to a combination of the two. Undoubtedly, at 200°C and at higher HCl flow rates, some of the available atomic hydrogen will react according to equation (26) because at that temperature the ratio k_{23}/k_{26} is reduced to approximately 35 (43). However, at the flow rates used in this work, it is probable that most of the observed increase in rate of HCl decomposition is due to an increase in the rate of reactions (20), (21) and (22). This would imply a small temperature coefficient associated with one or more of these reactions.

The energy released (9.76 ev. per mole) when two nitrogen atoms recombine on an HCl molecule can be dissipated in several ways. The particles produced in such an interaction will undoubtedly remove some energy as kinetic energy, but it is difficult to predict the distribution of the remainder. However, it can be said that the more the nitrogen atom in the complex is associated with one of the atoms of HCl (rather than equally with both), the greater will be the percentage of energy available to the vibrational degree of freedom of HCl. It is likely that most, if not all, of the bonding between the nitrogen atom and HCl to form the complex occurs between the electronegative nitrogen atom and the chlorine atom around which the electrons in HCl are concentrated. It is suggested, then, that a large proportion of the recombination energy is available for stretching the H-Cl bond. Thus there is probably sufficient energy (225 kcal. released, 102 kcal. needed) from all nitrogen atom recombinations with HCl as a third body to lead to disintegration of the HCl molecules involved.

In formulating the above mechanism and in using it to explain the results (Figures 5, 6 and 7), it was necessary to make certain assumptions concerning the formation and properties of nitrogen atom-HCl complexes. However, the assumptions do not appear to be unreasonable and they do allow for an explanation of the active nitrogen-hydrogen chloride reaction in terms of atomic nitrogen. Consequently, it may be said that this reaction does not seem to indicate the existence of a second active component.

GENERAL CONCLUSION

It would appear from the foregoing discussion that the reactions of active nitrogen with phosphine and with hydrogen chloride may be reasonably interpreted by assuming atomic nitrogen to be the only reactive species in active nitrogen. Obviously this does not constitute proof that only one reactive species is present. Nevertheless, the corresponding reaction with ammonia remains the only reaction of active nitrogen so far studied for which a satisfactory explanation seems to require the presence of more than one active species. It seems possible that further study of this reaction might reveal some unsuspected feature which would either eliminate or account for the unique position it appears to hold. Such a re-investigation is now in progress in the laboratory.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. A limited examination has been made of the reactions of atomic hydrogen with ethyl chloride, hydrogen iodide and hydrogen bromide. The results indicated that the hydrogen halides reacted to the same extent and therefore that an excess of either consumed the hydrogen atoms completely in the reaction

   $$H + HX \rightarrow H_2 + X.$$

   It was assumed that the plateau value for the rate of hydrogen iodide or hydrogen bromide consumption represented the hydrogen atom flow rate. On this basis the ethyl chloride reaction was 32% complete at 65°C.

2. The atomic hydrogen-phosphine reaction has been studied at 73°, 186° and 286°C; red phosphorus and hydrogen were the only products. The results indicated that an excess of phosphine completely consumed the hydrogen atoms at 73°C since the plateau at that temperature corresponded closely to the maximum amounts of HI and HBr destroyed under similar conditions.

   A mechanism has been proposed in which the primary step, hydrogen abstraction, was followed by combination of PH_2 radicals to give the products. The reaction between red phosphorus and atomic hydrogen to regenerate phosphine has been shown to occur in the system and it has been concluded that this back reaction was important at 286°C.

3. Investigation of the hydrogen atom-hydrogen chloride reaction at 50°, 300° and 440°C over a wide range of HCl flow rates showed that there was no net decomposition of HCl under the conditions of the experiments. It has been concluded that any hydrogen chloride decomposed initially was immediately regenerated in back reactions.

4. The limiting hydrogen cyanide yield in the ethylene-active nitrogen reaction was found to be doubled (from 10 to 20 micro-moles per sec.) when the temperature was raised from 80° to 250°C and then to remain constant, at 20 micro-moles per sec., over the range 250° to 450°C. It was assumed that the temperature dependence was due to recombination of nitrogen atoms catalysed by ethylene at lower temperatures and that the actual active nitrogen flow rate was 20 micro-moles per sec. at all temperatures.

5. The main products of the reaction between active nitrogen and phosphine were found to be molecular hydrogen and the alpha form of phosphorus paranitride, $(PN)_n$. It appeared that the conversion of one molecule of phosphine to phosphorus paranitride required two nitrogen atoms. Hence, it has been suggested that the primary step in the reaction was abstraction of hydrogen by atomic nitrogen and that the resulting PH_2 radicals reacted further with nitrogen atoms to form the nitride. Thus it appeared that the active nitrogen-phosphine reaction was the first one studied in which hydrogen abstraction by nitrogen atoms was of major significance.

6. It was observed that hydrogen atoms reacted with $(PN)_n$ to produce phosphine and a species, presumably nitrogen atoms, which reacted with propane to give HCN. Ammonia was found to react slowly with the nitrogen atoms produced in this way. This is probably the best experimental evidence obtained so far that ammonia does react slowly with atomic nitrogen.

7. The reaction between active nitrogen and hydrogen chloride was investigated at 80°, 200°, 310° and 440°C. There was a three-fold increase in the maximum amount of HCl decomposed as the temperature was raised from 80° to 200°C, followed by a decrease

as the temperature was increased to 310°C, and no further change in the interval 310° to 440°C. The largest rate of HCl decomposition, observed at 200°C, was less than one sixth of the active nitrogen flow rate.

It was suggested that the primary step in the reaction was the formation of a nitrogen atom-HCl complex and that a proportion of the 9.76 ev. recombination energy sufficient to break the H-Cl bond could be derived from the collision of a complex and a nitrogen atom, or from the collision of two complexes, if N_2 were formed.

8. The reactions of HCl-H_2 and HCl-Cl_2 mixtures with active nitrogen were studied with a view to evaluating the contribution of several secondary reactions to the active nitrogen-HCl reaction. Reasons were given to support the conclusion that the reaction of H atoms with molecular chlorine was of predominant importance in determining the net rate of HCl decomposition.

9. There was no indication from the results of the phosphine and hydrogen chloride experiments of a second active species in active nitrogen. Mechanisms were proposed for both reactions in which atomic nitrogen was considered to be the only active species.

It was suggested that perhaps the occurrence of hydrogen abstraction in the phosphine reaction and not in the ammonia reaction partially accounted for the difference in the rates of nitrogen atom attack on these two compounds.

APPENDIX

TABLE VII

Standard Heats of Formation (ΔH_f°) of Gaseous Species at 25°C.

SPECIES	ΔH_f° (kcal.)	SPECIES	ΔH_f° (kcal.)
H	52.089	NH_2	41**
H_2	0	NH	77**
N	112.5***	HCl	-22.063
N_2	0	Cl	29.012
PH_3	2.21	Cl_2	0
PH_2	30*	HBr	-8.66
PH	55*	Br	26.71
P_{red}	-4.4	Br_2	7.34
P_2	33.82	HI	6.20
P	75.18	I	25.482
PN	-20.2	I_2	15.640
NH_3	-11.04		

The above values were taken from ref. (130) unless otherwise noted.

*Estimated values.

**Ref. (133).

***Ref. (61).

TABLE VIII

Bond Dissociation Energy Values

BOND	B.D.E. (kcal.)	REFERENCE
H-H	103.22	(131)
N-N	225	(61)
C_2H_5-Cl	80	(132)
H-I	70.4	(131)
H-Br	86.4	(131)
H-Cl	102.1	(131)
I-I	35.55	(131)
Br-Br	45.44	(131)
Cl-Cl	57.08	(131)
NH_2-H	104	(132)
NH-H	88	(133)
N-H	85	(131)
P-N	138	(131)
P-P	116.0	(131)
PH_2-H	data inadequate	
PH-H		
P-H		

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