# SOLVENT EFFECTS IN CIS-TRANS ISOMERIZATION

by

P. Laner B.Sc. (University of Montreal)

A thesis presented to the Faculty
of Graduate Studies and Research
of McGill University in partial
fulfilment of the requirements for
the Degree of Doctor of Philosophy.

From the Physical Chemistry Laboratory
under the supervision of Dr. C.A. Winkler.

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# SOLVENT EFFECTS IN CIS-TRANS ISOMERIZATION

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# INTRODUCTION

Of the factors that may govern the rate of a homogeneous chemical reaction in solution, probably the least understood is the part played by the solvent. The lack of a clear understanding of solvent effects on reaction rates can be readily appreciated when it is realized that kinetic interpretations in such systems involve merely as one element the difficulties generally inherent in the interpretation of any physico-chemical behaviour in the liquid state or in solutions. Presumably, a general treatment of the problem would require both a general theory of reaction kinetics and a general theory of the liquid state, and neither of these can be said to be available at the present time. Progress has been made, however, by utilizing either the collision or the transition state theories of reaction kinetics, in conjunction with limited theoretical treatments of the liquid state and solutions, to interpret data obtained from studies of different systems involving a variety of solvents. A brief review of certain, though not all, aspects of the previous investigations is necessary for appropriate discussion of the results obtained in the present study.

## REACTION RATE THEORIES

### Collision

The rate of a reaction can be expressed by the well known equation

$$k = Ae^{-E/RT} \qquad .....(1)$$

where k is the specific rate constant of reaction,
A is the frequency factor of the reaction,
E is the activation energy, in calories or kcal. per mole,
R is the molar gas constant,
and T is the absolute temperature.

If log k is plotted against 1/T, a straight line is expected with a slope equal to -E/2.303R. In this way E can readily be determined experimentally. The energy E represents the energy which the reactant must acquire, per mole, to be capable of undergoing reaction. The factor A in a bimolecular reaction is equal to the collision number between the reacting species. In many cases the frequency of collision calculated by kinetic theory agrees with the experimental determination of A. However, there are many reactions in solution which take place at rates much smaller than those calculated on the basis of the simple collision theory. Since in certain gas reactions similar discrepancies are found, (1,2) the anomalies in solution cannot be attributed solely to the solvent. To account for the deviations from the simple collision theory in which the frequency factor A is smaller than the collision number, it was postulated that the number of effective collisions may be less than that given by the collision number multiplied by a simple Boltzmann factor, $e^{-E/RT}$. This has been interpreted to indicate that factors other than acquisition of the necessary energy may be involved in determining the reaction rate (3). Such factors may broadly be termed "steric", representing, for example, a critical orientation, a correct vibrational phase, or a suitable oscillation of groups, at the time of collision. The rate expression may then be written:

$$k = PZ e^{-E/RT}$$

where Z is the collision number and

P the probability or steric factor corresponding to the probability of reaction of molecules endowed with sufficient energy. P thus makes allowance for any effects causing deviations from Equation 1.

Deviations from Equation 1 in which the frequency factor A is much greater than expected, have been explained by assuming (4) that many degrees of freedom of the reacting molecules are involved, instead of the single degree of vibrational freedom taken into account by the simple Boltzmann term in Equation 1. To account for a process that is of the first order kinetically, even though two molecules are involved in the collision, it has been suggested (4) that the rate controlling step in the activation process is not acquisition of the activation energy by molecules through collision, but the intra-molecular distribution of this energy to the reacting bond. In this manner it is possible to explain the high values of A observed in unimolecular reactions and also the fact that the rates of these reactions are independent of the collision number over large concentration ranges.

It has been frequently observed that when a reaction is studied in a series of solvents or when the effect of substitution is studied in the same solvent, a linear relation exists between E and log k with a slope of 2.303RT. When such relations exist the change in the rate is entirely due to changes in the activation energy of the reactions concerned. Another correlation which may emerge, but is by no means always found, when the effect of solvent or substitution on a reaction is studied, is between E and log A (7,8). A linear relation between log A and E has been shown by Evans and Polanyi to be possible on theoretical grounds (9). It has also been correlated with the fluidity of the solvents in which the reactions occur by Waring and Becher (7) and Fairclough and Hinshelwood have interpreted this relation kinetically from the point of view of collision theory (8). In anticipation of the results obtained in this investigation it is appropriate to outline briefly the treatment of Fairclough and Hinshelwood.

If $\theta$ is the average time that elapses between formation of the activated complex and reversal of this process and t is the time for attainment of the right phase for reaction while no reaction occurs, then, according to the principles of statistics, the probability, W, that the activated complex will survive in the interval t is,

$$W = e^{-t/\theta} \qquad .....(2)$$

During the time, $t$, a considerable number of cycles, $n$, of vibration of one of the reacting bonds will usually occur. If the frequency of the latter is $\nu$ , then $t = n/\nu$ . Thus the probability of reaction is proportional to $e^{-n/\nu\theta}$ .

If the structure of the molecules remains constant but the bond strengths are changed by substitution, or by the solvent, $\nu$ and $E$ will also vary. If $\nu = f\ (E)$, then the rate of reaction becomes

$$k = Ae^{-n/\theta\, f(E)}\, e^{-E/RT}$$

$$\log k = \log A - n/\theta\, f(E)\, \frac{-E}{RT}$$

$$= \log PZ - \frac{E}{RT} ,$$

and

$$\log PZ = \text{const.} - n/\theta\, f(E) .$$

When changes in $E$ are small compared with $f(E)$, this approximates to

$$\Delta \log PZ = B\Delta E , \qquad .....(3)$$

where $B$ is a constant. Equation 3 shows that a linear relation between log PZ and E is expected only if $t$ is appreciably greater than $\theta$ in Equation 2. When this condition is not fulfilled a correlation between log A and E cannot be expected.

## The Transition State

In contrast to the collision theory of activation which associates activation solely with the kinetic energy of the molecules (10), the transition state theory focuses its attention on the thermodynamic probability of molecules entering the transition state (Ref. 11, Chap. III). This leads to calculations of the free energy of activation $\underline{\Delta F^{\ddagger}}$ which is related to the heat of activation $\underline{\Delta H^{\ddagger}}$ and the entropy of activation $\underline{\Delta S^{\ddagger}}$ by the well-known thermodynamic equation

$$\Delta F^{*} = \Delta H^{*} - T\Delta S^{*} .$$

By applying the transition state theory to a reaction of the type

$$A \longrightarrow M^{\ddagger} \longrightarrow \text{products}$$

where A is the reactant molecule,
and $M^{\ddagger}$ is the activated complex corresponding to the activated state through which A must pass before it can react,
Eyring and co-workers (5) have derived for the rate of reaction

$$k = K\frac{k'T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \quad .....(4)$$

In this expression,

$k'$ is the Boltzmann constant,

$T$ is the absolute temperature,

$h$ is the Planck's constant,

$\Delta S^{\ddagger}$ is the entropy of activation defined by

$$\Delta S^{\ddagger} = S_{M^{\ddagger}} - S_{A},$$

where $S_{M^{\ddagger}}$ is the molar entropy of $M^{\ddagger}$
and $S_A$ the molar entropy of A,
$\Delta H^{\ddagger}$ is the heat of activation, given by

$$\Delta H^{\ddagger} = H_{M^{\ddagger}} - H_A ,$$

where $H_{M^{\ddagger}}$ and $H_A$ are the molar heat contents of $M^{\ddagger}$ and A respectively and K is the transmission coefficient representing the probability that the activated complex will react to give a molecule of product, rather than return to the initial state. For many reactions $K = 1$.

Comparing Equations 1 and 4 it is seen that

$$\begin{aligned} E &= \Delta H^{\ddagger} \\ A &= K\frac{k'T}{h}\, e^{\Delta S^{\ddagger}/R} \qquad \text{.....(5)} \end{aligned}$$

The frequency factor is thus related to the entropy of activation while the energy of activation is related to the heat of activation.

Equation 4 may be written

$$k = K\,\frac{k'T}{h}\, e^{-\Delta F^{\ddagger}/RT} \qquad \text{.....(6)}$$

where $\Delta F^{\ddagger} = F_{M^{\ddagger}} - F_A$.
Equations 4 and 6 show that the free energy of activation and not necessarily the heat of activation determines the rate of a chemical reaction.

For reactions in solution $\Delta F^{\ddagger}$ can be replaced by $\overline{\Delta F^{\ddagger}}$ defined by

$$\overline{\Delta F}^{\star} = \overline{F}_{M^{\star}} - \overline{F}_{A}$$

where $\overline{F}_{M^{\star}}$ and $\overline{F}_{A}$ are the partial molal free energies of $M^{\star}$ and A. The variation of reaction rates in different solvents may be related to the variation in $\Delta\overline{F}$ and several expressions of such correlations have been derived (12). Most of these expressions relating the free energy of the reactions to some solvent property have been for reactions involving electrostatic forces and for these reactions there is adequate experimental data to confirm the theoretical derivations (Ref. 13, Chap. VIII). However, owing largely to the difficulty involved in estimating the partial molal free energies of non-polar molecules, no complete treatment has been made showing the variation of $\overline{\Delta F}$, or $\overline{\Delta H}$ with any solvent property for non-ionic reactions.

## SOLVENT EFFECTS

### Electrostatic

The reactions of ions and dipoles in solution have received a great deal of attention and it is in this field that the solvent effect has been treated quantitatively with the most success. This part of the subject has been discussed adequately elsewhere (13,14). It would be superfluous to give details of the discussion here, but a summary of the conclusions is relevant to the present investigation. The electrostatic interactions may conveniently be classified and discussed under the following headings.

(i) Reactions between ions.

(ii) Reactions between ions and neutral molecules.

(iii) Reactions between dipoles.

(i) Reactions between ions.

The activity coefficient of an ion in a medium of known ionic strength depends primarily on its charge. By making reasonable assumptions concerning the dimensions of the activated complex formed in a reaction between ions, the activity coefficients have been estimated with good accuracy. (12). Two expressions, depending on the model that is assumed for the activated complex, have been derived relating the rate of a reaction to the electrostatic forces in solution. If two ions involved in a bimolecular reaction come together to form an activated complex and retain the structure of a double sphere, with each part carrying its individual charge, the rate of the reaction between them is given by,

$$\ln k = \ln' k_o + \frac{\varepsilon^2 Z_A Z_B}{k'T\,r}\left(1 - \frac{1}{D}\right) + \frac{Z_A Z_B \varepsilon^2}{D\,k'T}\;\frac{\varkappa}{1 + \varkappa a} \qquad \text{.....(7)}$$

where k is the specific rate constant of the reaction,

$k_o$ is the rate constant in the infinitely dilute, i.e., ideal, gas,

$\varepsilon$ is the unit charge,

$Z_A$ and $Z_B$ are the charges of A and B respectively,

k' is the Boltzmann constant,

T is the absolute temperature,

r is the distance between the ions A and B in the activated complex,

a is the mean distance of closest approach of the two ions,

D is the dielectric constant of the solution,

and $\varkappa$ is the Debye-Hückel term defined in the usual manner. The equation is generally called the Bronsted-Christiansen-Scatchard equation (Ref. 13, Chap. VIII) and relates the specific reaction rate in the given solution to that in an infinitely dilute, i.e. ideal, gas.

Laidler and Eyring (12) assuming an activated complex of a single sphere having a charge equal to the algebraic sum of the two ions concerned, express the relation between the rate of the reaction and the electrostatic forces in solution in the form

$$\ln k = \ln k_o + \frac{\varepsilon^2}{2k'T}\left(\frac{1}{D} - 1\right)\left[\frac{Z_A{}^2}{r_A} + \frac{Z_B{}^2}{r_B} - \frac{(Z_A + Z_B)^2}{r^{*}}\right] + \frac{\varepsilon^2 Z_A Z_B}{Dk'T} \cdot \frac{\varkappa}{1 + \varkappa a} + \frac{\Sigma \Phi}{k'T} \qquad \ldots\ldots(8)$$

where $k, k_o, k', T, D$, $Z_A Z_B$ and $\varkappa$ are previously defined and

$r_A$ and $r_B$ are the radii of the conducting spheres representing the ion on which the charges are assumed to be located,

r is the radius of the spherical activated complex and

$Z_A$ and $Z_B$ is its charge,

$\Sigma\Phi$ is the sum of the non-electrostatic forces contributing to the rate of the reaction.

The only difference between Equations 7 and 8 apart from the nonelectrostatic part involving $\Phi$ 's, is in the second term on the right hand side of each. However, when $r_A = r_B = r^{\ast}$ , the two expressions become identical, indicating that the difference between the two expressions lies in the models rather than in the fundamental theory (12).

Equations 7 and 8 can be tested in two ways. If the dielectric constant of the medium remains unchanged, Equation 7 can be transformed into

$$\log k = \log k_o^s + 1.02\, Z_A Z_B \sqrt{\mu} \ldots\ldots (9)$$

where $k_o^s$ is the rate constant for the infinitely dilute solution,

$\mu$ is the ionic strength of the medium.

Thus it follows from Equation 9 that a plot of log k against $\sqrt{\mu}$ should give a straight line of slope 1.02 $Z_A Z_B$. This equation has been amply confirmed for a variety of processes involving positive or negative ions, or both (Ref 14, Chap IV). Deviations from Equation 9 are sometimes observed at high ionic strengths, especially if ions of high valence are present, which causes the slope of the log k vs. $\sqrt{\mu}$ curve to deviate from that predicted by theory (15). On the other hand, if the ionic strength of the medium is zero, then $\sqrt{\mu}$ is zero and the terms in Equations 7 and 8 involving this quantity disappear. The specific rate constant extrapolated to zero ionic strength becomes a function of the dielectric constant at constant temperature. A plot of ln $k_o$ against 1/D should be linear with a slope, according to Equation 7, of

$$\frac{d \ln k_o}{d(^1/D)} = - \frac{\varepsilon^2 Z_A Z_B}{k' \, Tr}$$

while according to Equation 8, it should be

$$\frac{d \ln k_o}{d(^1/D)} = \frac{\varepsilon^2}{2k' \, T} \left[ \frac{Z_A{}^2}{r_A} + \frac{Z_B{}^2}{r_B} - \frac{(Z_A + Z_B)^2}{r^{\ddagger}} \right] .$$

The preceding theoretical deductions are in harmony with the observed experimental results, but deviations from the straight line plot of log k against 1/D are frequently found for reactions in solvent mixtures of low dielectric constants (16,18). According to Laidler and Eyring (Ref. 13, Chap. VIII) this is due largely to the fact that the solvent is treated as a homogeneous medium of uniform dielectric constant. It is probable that in a mixture of water with a solvent of low dielectric constant the molecules of water will be preferentially orientated around the ions and the dielectric constant in the vicinity of the ion will thus be different from that of the bulk of the medium, which is the value determined experimentally. If the solution contains a large proportion of water, the error will not be significant, but if the dielectric constant of the mixture is low, the difference between the value in the bulk of the solution and that around the ion may be considerable. The observed reaction rates in mixtures of low dielectric constants might thus correspond to those for media of higher dielectric constant.

(ii) Reactions of ions and neutral molecules.

If one of the reactants e.g. B, is a neutral molecule, $Z_B = 0$. Equation 7 is no longer applicable, but according to Equation 8 a straight line of slope

$$\frac{d \ln k}{d(1/D)} = \frac{\varepsilon^2 Z_A}{2 k'T} \left[ \frac{1}{r_A} - \frac{1}{r^{\ast}} \right]$$

should be obtained for the plot of ln k against 1/D. Since $r^{\ast}$ is generally greater than $r_A$ the slope will be positive, so that the rate of the reaction between an ion and a neutral molecule should decrease with increasing dielectric constant of the medium. The reactions between alkyl halides and hydroxyl or halide ions (20,21) and between water and a sulfonium cation are examples of this type of behaviour (22).

(iii) Reactions between dipoles

Kirkwood (23) has calculated the free energy of transfer of a strong dipole $\mu$ from a medium of dielectric constant unity to one of dielectric constant D. This quantity is related to the activity coefficient $\alpha$ , for which the dilute gas D = 1, is the standard state. The result for a single molecule with symmetrical charge distribution within the molecule is

$$\Delta F = k'T \ln \alpha = \frac{\mu^2}{r^3} \cdot \frac{D - 1}{2D + 1}$$

where r is the radius of the molecule,
and $\alpha$ is the activity coefficient.

This equation has been confirmed experimentally by the determination of activity coefficients from the vapour pressures of solutions of polar substances in non-polar solvents (24). However, deviations are sometimes observed in media of low dielectric constants (25). Laidler and Eyring (12) correct the above expression for a non-electrostatic potential and obtain,

$$\ln \alpha = - \frac{1\,\mu^2}{k'T} \cdot \frac{1}{r^3} \cdot \frac{D - 1}{2D + 1} + \frac{\Phi}{k'T} \qquad \ldots\ldots(9)$$

For a reaction

$$A \longrightarrow M^{\ddagger} \longrightarrow \text{products}$$

$$\ln k = \ln k_o + \ln \frac{\varphi_A}{\varphi_{M^{\ddagger}}} \quad . \qquad \ldots\ldots(10)$$

Inserting the values of the activity coefficients given by Equation 9 into Equation 10, the equation,

$$\ln k = \ln k_o - \frac{1}{k'T} \cdot \frac{D-1}{2D+1}\left[\frac{\mu^2_A}{r^3_A} - \frac{\mu^2_{M^{\ddagger}}}{r^3_{M^{\ddagger}}}\right] + \frac{\Sigma\Phi}{k'T} \qquad .....(11)$$

is obtained where $\mu_A$ is the dipole moment of the reactant,

$\mu_{M^{\ddagger}}$ is the dipole moment of the activated complex,

$r_A$ is the radius of the reactant molecule,

$r_{M^{\ddagger}}$ is the radius of the activated complex,

$\Sigma\Phi$ is the difference in the non-electrostatic potentials arising from the reactant and activated complex,

D, $k_o$, $k'T$, have the usual significance.

Provided that the non-electrostatic terms in Equation 11 are small enough to be neglected, a plot of ln k versus D-1/2D+1 should, as an approximation, yield a straight line. Since the dielectric constants of dilute solutions do not differ greatly from those of the corresponding pure solvents, the dielectric constants of the latter may be used in making the plots. Laidler and Eyring (12) have made such plots for the formation of quaternary ammonium salts in alcohol-benzene mixture , for the hydrolysis of tertiary butyl chloride, for the acid catalysed hydrolysis of ortho formic ester, and for the alkaline hydrolysis of ethyl benzoate, the last three in alcohol-water mixtures. In these five cases the agreement with theory was satisfactory.

When the quaternary ammonium salt formation was studied in benzene-nitrobenzene solvents the linear relation between log k vs. (D-1)/(2D + 1) expected for such a reaction was found not to hold at higher dielectric constants of the solvent mixtures. A plot of log k against D-1/2D + 1 for the reaction between triethyamine and benzyl bromide and between pyridine and benzyl bromide in benzene-nitrobenzene mixtures at 29°C. is shown in Figure 1. Laidler and Eyring attribute the deviation from a straight line to specific solvent effects and formulate these in terms of the non-electrostatic potentials $\Phi$ . For a bimolecular reaction of the type

$$A + B \longrightarrow M^{\ddagger} \longrightarrow X + Y$$

Equation 11 may be written as

$$\ln k = \ln k_0 - \frac{1}{k'T} \cdot \frac{D-1}{2D+1} \left[ \frac{\mu^2_A}{r^3_A} + \frac{\mu^2_B}{r^3_B} - \frac{\mu^2_{M^{\ddagger}}}{r^3_{M^{\ddagger}}} \right] + \frac{\Phi_A + \Phi_B - \Phi_{M^{\ddagger}}}{k'T} .$$

In the formation of quaternary ammonium salts the activated complex has a considerable dipole moment and resembles the product in general properties. Thus in nitrobenzene the activated complex is solvated and consequently has a low activity coefficient. This causes the reaction velocity to be high. In terms of the $\Phi$ functions, $\Phi_A$ and $\Phi_B$ are normal, but owing to solvation, $\Phi_{M^{\ddagger}}$ is very small, and

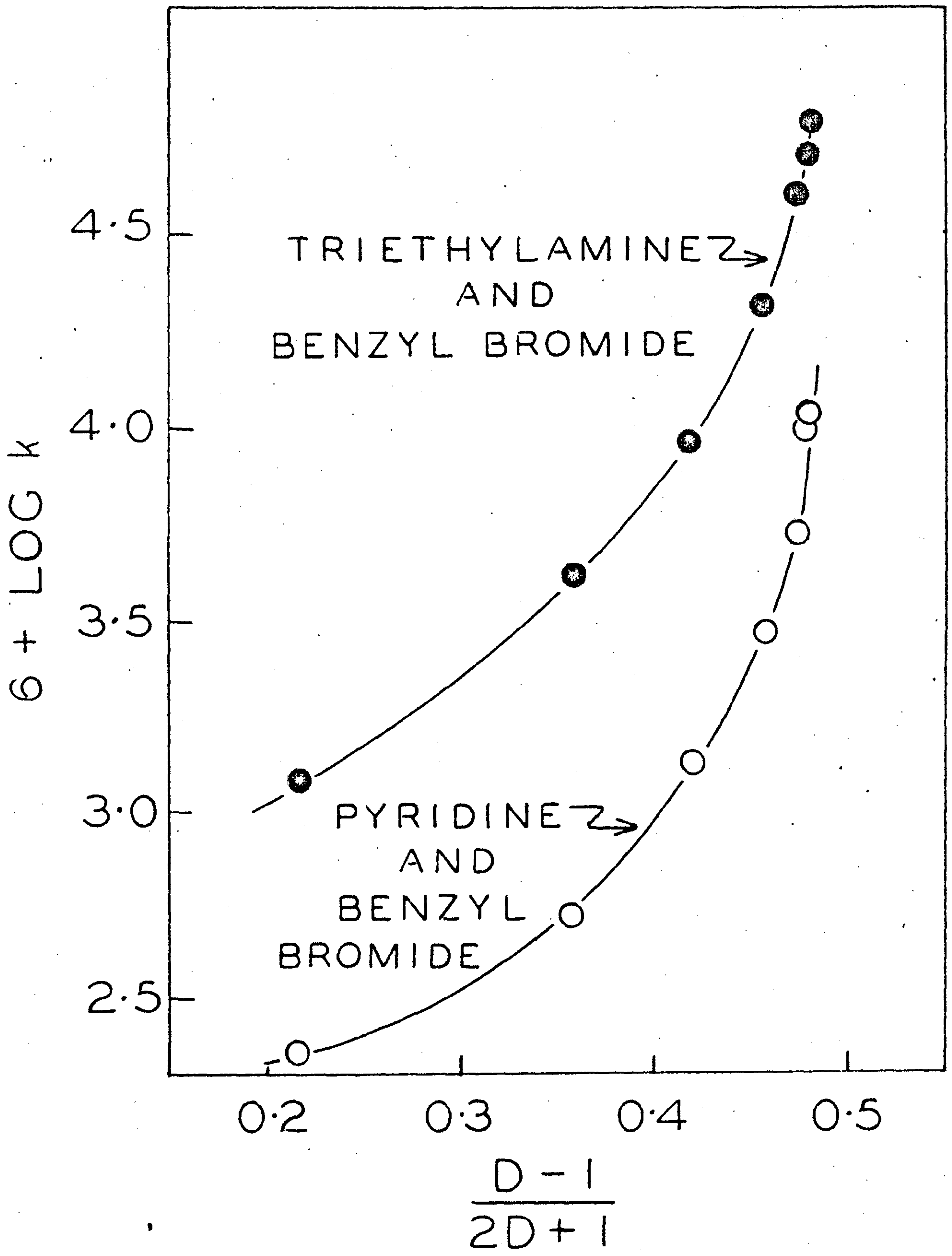


Fig. 1. Dependence of specific reaction rates on dielectric constant in benzene-nitrobenzene mixtures

and consequently the reaction velocity is higher. With benzene as solvent the activated complex is not solvated, $\gamma_{M^{\ddagger}}$ and $\Phi_{M^{\ddagger}}$ are consequently large and the reaction slow.

Non-electrostatic

As with a gas reaction , the rate of a reaction in solution can be expressed in terms of partition functions for the reacting species and the activated state, but these partition functions should now contain terms for the influence of the solvent environment. Since there is much uncertainty about partition functions in solution, owing to the difficulty of what constitutes the reacting species in solution, the rates of reaction in solution have been treated in a less fundamental way, by the use of activity coefficients.

Laidler and Eyring (12), using the transition state theory, express the rate of a unimolecular reaction in solution as,

$$k = K \frac{k'T}{h} \cdot K_o^{\#} \frac{\gamma_A}{\gamma_{M^{\ddagger}}}$$

where k is the specific rate constant of the reaction,

k' is the Boltzmann constant,

h is the Planck's constant,

$K_o^{\#}$ is the ratio of the partition functions of the activated state complex to that of the reactant,

$\gamma_A$ is the activity coefficient of the reactant, and $\gamma_{M^\ddagger}$ is the activity coefficient of the activated complex. If, in the above expression the activity coefficients are defined with reference to the dilute gas, the rate is given by

$$k_{(gas)} = K \frac{k'T}{h} \cdot K_o^{\#}$$

since in a dilute gas the activity coefficients are equal to unity. The rate of a reaction in solution is therefore

$$k = k_{(gas)} \frac{\gamma_A}{\gamma_{M^\ddagger}} \qquad .....(12)$$

if the mechanism of the reaction in the gas phase is the same as that in solution. This equation can be used to relate the rate constant in solution not only to that in the gas phase but also to that in very dilute solution , where the substances behave ideally. It can be seen from Equation 12 that if the reactant and the activated complex have similar structures, $\gamma_A$ and $\gamma_{M^*}$ will not differ greatly, and the rate of reaction in solution will be similar to that in the gas phase. The rate of decomposition of nitrogen pentoxide in a number of solvents has been found to be the same as in the gas phase (Ref. 11, Chap. V). This implies that the reactant and the activated complex have similar structures. The abnormally slow rates of its decomposition in nitric acid and propylene chloride and the corresponding high energies of activation have been explained on the assumption that a complex is formed between the reactant and the solvent. Such a complex formation decreases $\alpha_A$ and consequently the rate of reaction. Replacing the activity coefficient $\alpha$, by $\gamma$ in Equation 12, which now relates the ideal behaviour of a solute to its behaviour in an ideal solution, the rate of reaction can be written

$$RT \ln k_s = RT \ln k_o + RT \ln \gamma_A - RT \ln \gamma_{M^{\ddagger}} \qquad .....(13)$$

The rates of reaction in solution can therefore be evaluated in terms of thermodynamic quantities. Owing to the present lack of knowledge of the intermolecular forces in the liquid phase no complete treatment of a reaction in solution has been made. However, if suitable approximations are made, expressions relating the rate of a reaction to solvent properties can be derived.

Hildebrand (26) has defined as "regular" those solutions in which the distribution and orientation of the different molecular species are completely random. This means that the molecules can rotate freely and that there is no combination or association. In a regular solution therefore, the entropy of mixing has the ideal value of

$$\Delta S = - RN_1 \ln N_1 - RN_2 \ln N_2$$

where $N_1$ and $N_2$ are the mole fractions of the liquids.

For a regular solution the activity coefficient $\gamma$, of a solute can be expressed as

$$RT \ln\gamma_1 = v_1\left[\frac{N_2v_2}{N_1v_1 + N_2v_2}\right]^2\left[-\frac{2E_{12}}{(v_1v_2)^{1/2}} + \frac{E_{11}}{v_1} + \frac{E_{22}}{v_2}\right] \qquad .....(14)$$

where v is the molar volume and N the mole fraction of the species designated by the subscripts 1 and 2. The E terms are the potential energies related to the attractive forces between the molecules; $E_{11}$ and $E_{22}$ refer to attraction between molecules of the same kind, and $E_{12}$ refers to that between molecules of different kinds. This formula was derived by Scatchard (27) and by Hildebrand and Wood (28) by regarding the attraction between molecules as entirely of the van der Waals type. They further assumed that the repulsive potentials could be neglected and that the molecules possessed spherical symmetry. If it is assumed that for van der Waals forces

$$E_{12} = (E_{11}\,E_{22})^{1/2}$$

Equation 14 becomes

$$RT \ln\gamma_1 = v_1\left[\frac{N_2v_2}{N_1v_1 + N_2v_2}\right]^2\left[\left(\frac{E_{11}}{v_1}\right)^{1/2} - \left(\frac{E_{22}}{v_2}\right)^{1/2}\right]^2 \qquad .....(15)$$

The deviations from Raoult's law for these solutions are regarded as due to heat of mixing and not to entropy effects. For liquids which are not entirely miscible such an assumption is not entirely valid (12) and it is necessary to modify such theories of solution as that of Hildebrand and Wood (28), and a similar equation of Scatchard (27), in which random distribution of the molecules is assumed. Kirkwood (29) has calculated values of the energies and the entropies under various conditions and has shown that the entropy terms due to ordering are always comparatively small, their contribution to the free energy term $\Delta F$ being of the order of only 15%, when the departure from random distribution is so large that the liquid system is on the point of separating into two phases. In dilute solutions they are therefore often negligible. This shows that in the majority of cases the treatment of Hildebrand and Wood is adequate.

Treatments of solutions which take more accurate account of molecular "ordering" are those of Rushbrooke(30) and Kirkwood (31) who have modified and improved an earlier treatment due to Guggenheim (32).

If the solution is dilute, $N_1v_1$ in Equation 15 may be neglected in comparison with $N_2v_2$ and the expression reduces to

$$RT \ln \gamma_1 = v_1\left[\left(\frac{E_{11}}{v_1}\right)^{1/2} - \left(\frac{E_{22}}{v_2}\right)^{1/2}\right]^2 \qquad .....(16)$$

By inserting the values of $RT \ln \gamma_1$ given by Equation 16 into Equation 13, the following expression results,

$$RT \ln k = RT \ln k_0 + v_1 \left[ \frac{E_{11}}{v_1} + \frac{E_{22}}{v_2} - 2 \left[ \frac{E_{11} E_{22}}{v_1 v_2} \right]^{1/2} \right]$$

$$- v_m \left[ \frac{E_{mm}}{v_m} + \frac{E_{22}}{v_2} - 2 \left( \frac{E_{mm} E_{22}}{v_m v_2} \right)^{1/2} \right]$$

$$= \text{constant} + (E_{11} - E_{mm}) + (v_1 - v_m) \left( \frac{E_{22}}{v_2} \right)$$

$$- 2\, v_m \left( \frac{E_{22}}{v_2} \right)^{1/2} \left[ \left( \frac{E_{11}}{v_1} \right)^{1/2} - \left( \frac{E_{mm}}{v_m} \right)^{1/2} \right] \quad ..(17)$$

Since $\left(E_{11} - E_{mm}\right)$ is constant, and if solvation effects are excluded, it is reasonable to assume that there is no volume change when the reactant passes into the activated state. Then $v_1 = v_m$ and Equation 17 reduces to

$$RT \ln k = J - K \left( \frac{E_{22}}{v_2} \right)^{1/2} \quad .....(18)$$

where J and K are constants. This equation relates the rate of a reaction in different solvents to the square root of the cohesive energy density, $\frac{E_{22}}{v_2}$, of the solvent. In the preceding deduction only the short range forces are assumed to be operative. In many solutions there are contributions from other types of forces which invalidate the assumptions made in deriving Equation 18.

Halpern, Brady and Winkler (33) using existing theories of solutions and of chemical kinetics, have derived relations for the solvent effect on the rate of a unimolecular non-ionic reaction. Their arguments leading to these relations are outlined below.

For a reaction in solution, the thermodynamic functions, H and S, can be replaced by the corresponding partial molal quantities $\overline{H}$ and $\overline{S}$, which lead to the following relations

$$\begin{aligned} \Delta H^{\ddagger} &= \overline{H}_{M^{\ddagger}} - \overline{H}_{X} \\ &= (H^{o}_{M^{\ddagger}} + \overline{H}_{M^{\ddagger}}) - (H^{o}_{X} + \overline{H}_{X}) \\ &= \Delta H^{\ddagger}_{o} + (\overline{\Delta H}_{M^{\ddagger}} - \overline{\Delta H}_{X}) \qquad .....(19) \end{aligned}$$

where $H^{o}_{M^{\ddagger}}$ and $H^{o}_{X}$ are the heat content of $M^{\ddagger}$ and X respectively in their standard states, which are taken for convenience as being the pure liquids,

and $\overline{\Delta H}_{M^{\ddagger}}$ and $\overline{\Delta H}_{X}$ are their partial molal heats of solution.

$\Delta H^{\ddagger}_{o}$ represents the activation energy of the reaction when X and $M^{\ddagger}$ are in their standard states.

The entropy of activation of a reaction in solution may be similarly expressed,

$$\Delta S^{\ddagger} = \Delta S^{\ddagger}_{o} + (\overline{\Delta S}_{M^{\ddagger}} - \overline{\Delta S}_{X}) \qquad .....(20)$$

where all the symbols are analogously defined.

Hildebrand (26, 28) has shown that for dilute regular solutions of $X_1$ in $X_2$, the partial molal heat of solution of $X_1$ is given by the expression,

$$\overline{\Delta H_1} = v_1 \left[ (P_1)^{1/2} - (P_2)^{1/2} \right]^2$$

where $v_1$ is the molar volume of $X_1$

and $P_1$ and $P_2$ are the internal pressures of $X_1$ and $X_2$ respectively.

Halpern, Brady and Winkler applying the above to a unimolecular reaction of the type

$$X \longrightarrow M^{\star} \longrightarrow Y,$$

obtain for the heat of solution of the reactant X

$$\Delta \overline{H}_X = v_X \left[ (P_X)^{1/2} - (P_S)^{1/2} \right]^2$$

where $v_X$ is the molar volume,

$P_X$ is the internal pressure of the reactant,

and $P_S$ is the internal pressure of the solvent.

The heat of solution of the activated complex, $M^{\star}$, is given by a similar expression,

$$\Delta \overline{H}_{M^{\star}} = v_{M^{\star}} \left[ (P_{M^{\star}})^{1/2} - (P_S)^{1/2} \right]^2$$

Inserting these expressions in Equation 19 and assuming $v_X = v_{M^{\star}}$, they obtained the relation,

$$E - RT = \Delta H^{\star} = \Delta H_0^{\star} + v_X \left[ \left\{ (P_X)^{1/2} - (P_{M^{\star}})^{1/2} \right\} 2 (P_S)^{1/2} - ( P_X - P_{M^{\star}}) \right] \qquad .....(21)$$

which corresponds to a linear relation between E and $(P_S)^{1/2}$, since $P_M^*$ and $P_X$ are constants for a given reaction.

To derive an expression for the solvent effect on the frequency factor, these investigators used the semi-empirical relation,

$$\frac{\Delta\overline{S}}{R} = \rho\,\Delta\overline{H} + C \qquad .....(22)$$

first established by Evans and Polanyi (9) which relates the heats and entropies of solution, where

$\Delta\overline{S}$ is the partial molal entropy of solutions,

$\Delta\overline{H}$ is the partial molal heat of solution,

and $\rho$ and C are constants for a given solute. Substituting expressions of this form for $\Delta\overline{S}_{M^\ddagger}$ and $\Delta\overline{S}_X$ in Equation 20 and taking $\rho_M^* = \rho_X$ the expression,

$$\frac{\Delta S^\ddagger}{R} = \left(\frac{\Delta S_o^\ddagger}{R} - \rho_X\,\Delta H_o^\ddagger + \Delta C\right) + \rho_X\,\Delta H^\ddagger \qquad .....(23)$$

where $\Delta C^\ddagger = C_{M^\ddagger} - C_X$, was obtained. Taking logarithms of Equation 5 and substituting for $\Delta S^\ddagger$, a linear relation between log A and E or $\Delta H^\ddagger$ for the reaction in different solvents was obtained,

$$\log A = \log\left(e_K\,\frac{k'T}{h}\right) + \frac{+1}{2.303}\left(\frac{\Delta S_o^\ddagger}{R} - \rho_X\,\Delta H_o^\ddagger + \Delta C^\ddagger\right) + \frac{\rho_X\,\Delta H^\ddagger}{2.303} \qquad .....(24)$$

By substituting the values of $\Delta H^{\ddagger}$ and log A given by Equations 21 and 24 respectively into the expression

$$\log k = \log A - \frac{\Delta H^{\ddagger}}{2.303RT}$$

the following expression was obtained.

$$\log k = \log\left(K\frac{k'T}{h}\right) + \frac{1}{2.303}\left(\frac{\Delta S_0^{\ddagger}}{R} - \rho_X\,\Delta H_0^{\ddagger} + \Delta\,C^{\ddagger}\right)$$

$$+ \frac{1}{2.303}\left(\rho_X - \frac{1}{RT}\right)\left\{\Delta H_0^{\ddagger} + 2v_X\left[\left\{(P_X)^{1/2} - (P_M^{\ddagger})^{1/2}\right\}.\right.\right.$$

$$\left.\left.(P_S)^{1/2} - (P_X - P_M^{\ddagger})\right]\right\} \qquad .....(25)$$

This relation may be written in the form

$$\log k = J - L\,(P_S)^{1/2} \qquad .....(26)$$

where J and L are functions of T only, for a given reaction. This corresponds to a linear relation between log k and $(P_S)^{1/2}$. While Equation 21, expressing the effect of solvent on the activation energy, was derived by considering the solution as regular, this restriction was dropped in deriving Equation 24 and the entropy of the solution was estimated, using empirical properties of real solutions. Besides predicting linear relations between the internal pressure of the solvent and the activation energy or the rate, Equations 17 and 25 give the sign of the slope depending on the relative magnitude of $(P_X)^{1/2}$ and $(P_M)^{1/2}$. Thus, if the internal pressure of the activated complex is larger than that of the reactant, an increase in the rate of the reaction would be expected with an increase in the internal pressure of the solvent, while the reverse effect would be expected if the internal pressure of the reactant is larger than that of the activated complex.

To test the above relations the kinetics of the cis-trans isomerization of azobenzene was investigated in sixteen pure solvents by the same authors (33). They found a linear relation between the activation energy, E, and the internal pressure of the solvent, $(P_S)^{1/2}$, in agreement with the deductions. Linear relations between log A and E, and between log k and $(P_S)^{1/2}$ were also found, but the results for the reaction in highly polar solvents deviated significantly from these relations.

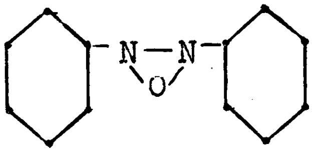
The effect of solvent on the rate of a non-ionic unimolecular reaction is thus related entirely to the heats and entropies of solution (Equations 21 and 24) or alternatively to the activity coefficients of the reactant and activated complex, (Equation 12) and the calculation of the solvent effect was reduced to the thermodynamic problem of estimating these properties.

A survey of the effect of solvent on reaction rates (34) reveals that the smallest solvent effects are observed for non-ionic reactions. However, Halpern, Brady and Winkler(33) have shown that the isomerization of cis azobenzene which is a non-ionic unimolecular reaction, shows an appreciable solvent effect. Since Müller (35) and Reissert (36) have shown that the azoxy compounds isomerize completely to their trans forms, it is reasonable to assume isomerization of the azoxy compounds, by analogy with azobenzene would be subject to solvent effects. The cis and trans isomers of azoxybenzene and p,p'-azoxytoluene were therefore chosen to investigate further the role of the solvent in a non-ionic unimolecular reaction.

Most of the data that have been presented (12,14) to show the effect of solvent have been for mixed solvents. Studies in mixed solvents are often complicated by preferential solvation of some component in solution, microscopic immiscibility of the solvents, or by compound formation between some constituent of the solvent and solute. Reactions occurring in mixed solvents are consequently complicated and a clear interpretation of the role of the solvent in such reactions is often difficult to obtain. The isomerization reactions in this investigation were therefore studied in pure solvents only.

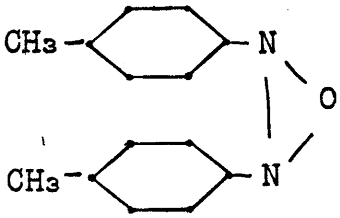
## AZOXYBENZENES

Azoxybenzene was first prepared by Zinin (37) in 1841 by reducing nitrobenzene with alcoholic potassium hydroxide. It was shown by him to be an intermediate product in the reduction of nitrobenzene to aniline, and was given the formula $C_{12}H_{10}N_2O$. Since its discovery a large number of derivatives have been prepared and their chemical properties studied (38). Considering the nature of the other products of the reduction of nitrobenzene, nitrosobenzene, phenyhydroxylamine, azobenzene, hydrazobenzene, the stable nature of the azoxy compounds is remarkable. They are not attacked by dilute nitric, sulfuric or hydrochloric acid, nor by sodium hydroxide. Kekule (39) represented the azoxybenzene molecule as,

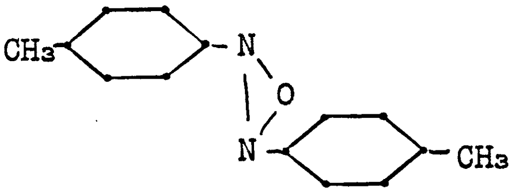


Hantzsch and Werner (40) suggested that the azoxy compounds might illustrate stereoisomerism of the geometric type closely analogous to the suggested isomerism of the azobenzenes. They represented the two isomeric p,p'-azoxytoluenes by the formulae

syn (cis)



anti (trans)



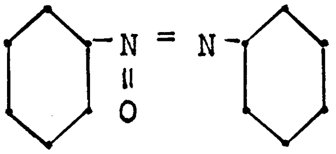
At that time there was much confusion in assigning structures to substituted azoxybenzenes, due to the fact that the possibility of structural isomerism was not recognized for these compounds. This possibility was admitted later by Angeli (41) who assigned a new structure to azoxybenzene. In 1909 Reissert (36) undertook a further study of azoxy compounds with the possibility of stereoisomerism in view. He assumed that compounds made at an elevated temperature would give only the isomers stable at that temperature, while at lower temperatures he might obtain pairs of such isomers. With this in view he treated nitrosobenzene in alcohol with a water solution of sodium hydroxide while the reaction mixture was cooled to 10°C. He obtained ordinary azoxybenzene melting at 36°C. and in small quantities an isomeric form melting at 84°C. By condensation of phenylhydroxylamine with nitrosobenzene he obtained no trace of the new isomer. With o-nitrosotoluene, reduced as above he obtained the usual o-azoxytoluene, melting at 59°C, and an isomeric iso-azoxytoluene melting at 82°C. while with the p-nitrosotoluene he obtained only the usual p-azoxytoluene melting at 70°C. The higher melting isomers of azoxybenzene and o-azoxytoluene when heated transformed into the better known isomers as identified by their melting points. He further found that the higher the temperature the higher the rate of transformation.

In 1932 Muller and Kreutzman (35) repeated the work of Reissert (36) and found his results to be entirely reproducible. They extended his work to include several symmetrical cis and trans derivatives and found a general procedure for their preparation. This consisted of reacting the nitroso compound, R N O, with the corresponding hydroxylamine derivative, R N H O H, in an alkali-dioxane solution at about 10°C. In this manner, they also obtained the cis isomer of p-azoxytoluene which Reissert was unable to prepare. Furthermore they showed that in these condensation reactions equimolar ratios of the reactants were essential to obtain the cis isomers, since they found that an excess of the hydroxylamine will react with the cis form to give the trans isomer. This observation probably explains the failure of Reissert to obtain cis azoxybenzene when he attempted to condense phenylhydroxylamine with nitrosobenzene in an alkali solution. Attempts to prepare these isomers in either alcohol or dioxane alone or to increase the yield of the cis isomer by increasing the alkali concentration were not effective.

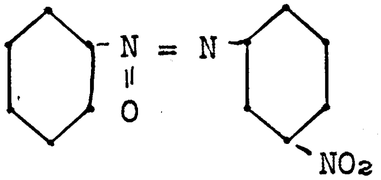
The absorption spectra of several symmetrical azoxy compounds in their isomeric forms prepared in the above manner were obtained by Müller and co-workers (42,43) and by comparison with the known spectra of cis and trans isomers of aromatic azo and ethylenic compounds they concluded that the two forms of these azoxy compounds corresponded to cis and trans isomers. Measurements of the dipole moments of the two forms of azoxybenzene and several of its derivatives conform with the structure expected for cis and trans isomers

(44,45).

Angeli and co-workers (41,46) studied the structural isomerism of the azoxy compounds. By postulating the structure of the azoxybenzene to be

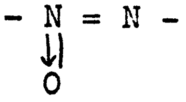


they recognized that no isomerism is to be expected with symmetrical compounds, but with compounds of the type,



two isomers might be expected if the oxygen were attached only to one nitrogen atom, which was pentavalent. The isomers correspond to location of the substituent group in the ring adjacent either to the trivalent or to the pentavalent nitrogen. The isomer containing the unsubstituted ring attached to a trivalent nitrogen is the $\beta$ form while the other is the $\alpha$ form (38).

Auwers and Heinke (47) have shown that the molecular refractions of several derivatives of azoxybenzene are little different in their $\alpha$ and $\beta$ forms, and conclude from these observations that a triple ring structure for the azoxy group is quite improbable. A limited number of determinations of the parachors of these compounds favours the formula suggested by Angeli (41), modified by the introduction of a semi-polar bond as required by the octet theory



$$-\underset{\underset{O}{\downarrow}}{N}=N- \quad .$$

Extensive studies by Szego (48,49) of the absorption spectra of $\alpha$ and $\beta$ azoxybenzenes in the ultra violet have shown that the two isomers are also similar in this respect, which further supports the formula suggested by Angeli. They also observed that the absorption spectra of azoxy compounds strongly resembled those of the azo compounds, from which they inferred that the structures of the azoxy and azo compounds were closely related.

## DIAZOCYANIDES

While the effect of solvent on the azoxy compounds was being investigated, a similar study by LeFevre and Northcott (50) on the cis-trans isomerization of the diazocyanides appeared. These investigators studied the effect of structure and solvent on the thermal transformation of the diazocyanides by measuring changes in the dielectric constants of the solutions. They failed to find any correlation between k or E with any solvent property in the cis-trans isomerization of p-chlorobenzenediazocyanide. For the various diazocyanides isomerizing in benzene, the influence of substituents was best expressed by the equation

$$E = E_0 + 2.9\ RT\ (\mu + 0.209\mu^2)$$

where $\mu$ is the dipole moment of the appropriate $C_6H_5X$ compound,

and $E_0$ is the activation energy observed for benzenediazocyanide.

A calculation of the internal pressure of the solvents used in their investigation revealed that a very limited range of internal pressures was employed. In view of the satisfactory agreement obtained between theory and experiment for the solvent effect in the cis-trans isomerization of azobenzene (33) where a wide range of internal pressures was used, it was thought that a reinvestigation of the isomerization of p-chlorbenzenediazocyanide using a spectrophotometric method of analysis and an extension of the range of internal pressures of the solvents used by LeFevre would be useful in elucidating the role of the solvent in this reaction.

Hantzsch (51) in his classical investigations on the diazo compounds, postulated the existence of a syn and anti form for the diazocyanides. He argued by analogy with the isomers of ethylenic compounds and recognized the less stable form of the diazotates, cyanides and sulfonates as cis (syn) and the more stable forms as the trans (anti). His views on the subject were accepted only after long controversy which has been revived recently. Orton (52) first suggested that the syn and anti forms were really the iso cyanide and normal cyanide respectively. Hodgson and Marsden (53) revived these views in 1944 and attempted to support their arguments by the reaction of the cis diazocyanides with Grignard Reagent. Meanwhile the existence of cis and trans forms in azobenzene was definitely established by dipole moment measurements (54) and X-ray diffraction (55), and the existence of geometrical isomerism of the N = N double bond could no longer be discounted. From studies of the dipole moments of several cis and trans derivatives LeFevre and Vine (56) were able to provide definite physical evidence for the correctness of the configuration given to these compounds by Hantzsch. These investigators further showed that the cis forms isomerize spontaneously and in a first order manner to the trans forms.

Infra-red spectral analysis of several isomeric diazocyanides by Sheppard and Sutherland (57) gave conclusive evidence that the isomers are not related as cyanide and isocyanide but that they are both cyanides. An examination of the magnetic rotary powers and the diamagnetic susceptibilities of several isomeric aromatic diazocyanides in solution and in the solid state (58), further indicated both the isomers to be cyanides. The absorption spectra of these isomeric diazocyanides were studied by LeFevre and co-workers (56,59) who found that the differences between the two forms was not great, such differences as do exist being more in the relative absorption of light than in the wave length at maximum absorption.

# EXPERIMENTAL

## PREPARATION OF CIS AND TRANS ISOMERS

### cis p-Chlorobenzenediazocyanide

This isomer was prepared according to the procedure of Anderson, Bedwell and LeFevre (58). A tenth mole p-chloroaniline was dissolved in 50 ml. of 6 N hydrochloric acid, the solution placed in an ice bath and a solution containing 6.5 gm. of sodium nitrate in 50 ml. of water added dropwise. When the diazotization was complete, the solution was filtered, 50 ml. of alcohol and 200 ml. of light petroleum were added, and the resulting mixture cooled to -25°C. With careful exclusion of light, a solution containing 13 gm. of potassium cyanide in 50 ml. of water was added dropwise to this cold mixture with continuous stirring. The temperature of the mixture was then raised to 0°C. by allowing it to stand at room temperature. The hydrocarbon layer was separated, dried with sodium sulphate, and cooled in the dark to -30°C. The cis compound crystallized and was separated from the mother liquor by filtering in a dry atmosphere. According to Anderson and co-workers (58) recrystallizations are unnecessary when the cis isomer is prepared in this way. The isomer was stored at 0°C. in a vacuum desiccator, which was covered to exclude light. The cis p-chlorobenzenediazocyanide prepared in this way remained stable for several weeks.

### trans p-Chlorobenzenediazocyanide

The trans isomer was obtained by crystallization of a concentrated solution of the mother liquor.

### cis Azoxybenzene

cis Azoxybenzene is formed when nitrosobenzene is condensed in an alkaline medium (36). The cis isomer is then separated from the cis-trans mixture by extracting the trans with petroleum ether.

The nitrosobenzene was prepared according to the procedure described in Organic Syntheses (60). To a solution containing 75 gm. of ammonium chloride in 2.5 l. of water was added 125 ml. commercial nitrobenzene. With vigorous stirring 186 gm. of zinc dust (90% pure) was added in small portions over a period of 5 minutes. When the temperature of the reaction mixture reached 65°C., enough ice was added to lower the temperature to 50-55°C. Twenty minutes after the introduction of the zinc, the solution was filtered and the zinc oxide residue washed with 2 l. of boiling water. The filtrate and washings were combined and immediately cooled by the addition of sufficient ice to lower the temperature to 0°C., leaving about 1 Kg. of ice unmelted. To this cold solution of β-phenylhydroxylamine was added 375 ml. of concentrated sulfuric acid cooled to -5°C. An ice cold solution of 85 gm. of sodium dichromate dihydrate in 350 ml. water was then poured as rapidly as possible into this mixture. The nitrosobenzene was collected, washed with 1 l. of water, and the crude nitrosobenzene steam-distilled. The product was then crystallized from alcohol and dried over calcium chloride.

The cis azoxybenzene was then prepared according to Reissert (36). Fifteen grams of the nitrosobenzene was dissolved in 300 ml. of 95% ethanol and cooled to 9°C. A solution of 30 ml. NaOH (2 N) mixed with 40 ml. ethanol was slowly added to the nitrosobenzene with continuous stirring. The mixture, which remained standing for 1.5 hours, was then neutralized with 6 N HCl and diluted with 3 l. of water. An oil, which separated on dilution, solidified when placed in a refrigerator overnight. This solid (cis-trans mixture) was filtered off, dried and ground in a mortar. Since trans azoxybenzene is more soluble in petroleum than the cis isomer, the former was separated from the cis-trans mixture by repeatedly (12 times) shaking the residue with 25 ml. portions of petroleum ether and filtering. The final residue was dissolved in methanol, shaken with charcoal, and filtered. The cis azoxybenzene was recrystallized twice from methanol by the addition of water and stored at 0°C.

### trans Azoxybenzene

The trans isomer was obtained by recrystallization of the petroleum ether filtrates.

### cis p,p'-Azoxytoluene

A mixture of cis and trans p,p'-azoxytoluene is obtained when p-nitrosotoluene reacts with p-tolylhydroxylamine in an alkaline medium (35). The cis isomer is separated from the trans by their different solubilities in petroleum ether. The p-tolylhydroxylamine and p-nitrosotoluene were prepared by conventional procedures (61,62).

To prepare p-tolylhydroxylamine, 75 gm. of nitrotoluene was dissolved in 75 ml. of hot ether and poured into a flask containing 38 gm. of ammonium chloride in 1200 ml. of water. Maintaining the temperature at 16°C., 90 gm. of zinc dust was added to this reaction mixture over a period of 40 min. with continuous stirring. Forty-five minutes after the zinc was added, the zinc oxide was filtered off, and washed first with water, then with ether. Since the p-tolylhydroxylamine is slightly soluble in water, the aqueous layer of the filtrate and the washings were saturated with sodium chloride and extracted three times with ether. The ether extracts were combined, dried overnight with sodium sulphate and then carefully concentrated. When the concentrated ether solution of p-tolylhydroxylamine was diluted with 175 ml. ligroin, the p-tolylhydroxylamine precipitated in flaky white crystals.

To prepare p-nitrosotoluene, a mixture of 120 ml. of a 20% sulphuric acid and a saturated aqueous solution containing 22 gm. of sodium dichromate was cooled to freezing and to it was added as rapidly as possible a cold ether solution containing 24.6 gm. of p-tolylhydroxylamine. The p-nitrosotoluene was steam-distilled and the product was collected in a flask cooled by standing in ice-water. Flaky white crystals of p-nitrosotoluene were obtained by crystallizing the crude product from benzene.

The cis p,p'-azoxytoluene was then prepared by reaction of 10 gm. of p-nitrosotoluene, dissolved in 200 ml. dioxane and 100 ml. of 0.4 N sodium hydroxide, with a solution containing 10 gm. of p-tolylhydroxylamine in 100 ml. dioxane which was added dropwise to the solution of p-nitrosotoluene at 10°C. After remaining at room temperature for six hours, the mixture was neutralized with 2 N HCl, diluted with 4 l. water and placed in a refrigerator for 24 hr. The solution was then filtered and the residue of the cis and trans isomers dried. The cis isomer was separated from the cis-trans mixture by repeatedly (12 times) shaking the residue with 25 ml. portions of petroleum ether and filtering. The final residue was dissolved in cold methanol and the cis isomer precipitated by the addition of water and cooling. The cis p,p'-azoxytoluene was filtered, dried and stored at 0°C.

### trans p,p'-Azoxytoluene

This isomer was prepared by recrystallization of the petroleum ether filtrates.

## ANALYTICAL PROCEDURE

All the optical density measurements were made on a Beckman model "DU" spectrophotometer. A tungsten filament lamp was used as a light source for the visible region and a hydrogen lamp for the ultra-violet region. In the region above 350 $m\mu$, the measurements were made in corex absorption cells of 1 cm. ± 0.002 light path, while silica absorption cells were used below 350 $m\mu$. In each case, one cell was used as a standard in calibrating the other cells of that group. The appropriate corrections were then applied to the cells. The extinction coefficients were calculated from the formula

$$D = \epsilon cd$$

where D is the optical density,

$\epsilon$ is the extinction coefficient,

c is the concentration of the solution in moles/l.,

and d is the length of the light path.

The cis and trans isomers of azoxybenzene and p,p'-azoxytoluene in methanol were characterized by their ultraviolet absorption spectra. These are recorded in Tables I and II and shown graphically in Figures 2 and 3, where the logarithms of the extinction coefficient, $\epsilon$, are plotted as a function of the wave length. The cis and trans isomers of both compounds show a strong absorption in the region of 3300 Å,

## TABLE I

## ABSORPTION SPECTRA OF AZOXYBENZENE IN METHANOL

Concentration = 0.025 g./l.

| | Cis Isomer | | Trans Isomer | |
|---|---|---|---|---|
| Wave Length (Å) | Optical Density | log $\epsilon$ | Optical Density | log $\epsilon$ |
| 3500 | 0.345 | 3.436 | 0.976 | 3.887 |
| 3400 | 0.400 | 3.501 | 1.434 | 4.058 |
| 3300 | 0.425 | 3.526 | 1.765 | 4.144 |
| 3200 | 0.424 | 3.526 | 1.893 | 4.176 |
| 3100 | 0.395 | 3.496 | 1.765 | 4.145 |
| 3000 | 0.353 | 3.446 | 1.470 | 4.066 |
| 2900 | 0.326 | 3.412 | 1.146 | 3.958 |
| 2800 | 0.384 | 3.483 | 0.920 | 3.862 |
| 2700 | 0.540 | 3.630 | 0.895 | 3.851 |
| 2600 | 0.810 | 3.807 | 1.005 | 3.900 |
| 2500 | 1.187 | 3.972 | 1.007 | 3.899 |

## TABLE II

## ABSORPTION SPECTRA OF p,p'-AZOXYTOLUENE IN METHANOL

Concentration = 0.025 g./l.

| | Cis Isomer | | Trans Isomer | |
|---|---|---|---|---|
| Wave Length (Å) | Optical Density | log ε | Optical Density | log ε |
| 3500 | 0.500 | 2.490 | 1.697 | 3.020 |
| 3400 | 0.532 | 2.516 | 2.040 | 3.100 |
| 3300 | 0.525 | 2.511 | 2.125 | 3.117 |
| 3200 | 0.487 | 2.479 | 1.940 | 3.079 |
| 3100 | 0.435 | 2.430 | 1.595 | 2.993 |
| 3000 | 0.392 | 2.384 | 1.254 | 2.889 |
| 2900 | 0.398 | 2.391 | 1.000 | 2.791 |
| 2800 | 0.495 | 2.486 | 0.872 | 2.732 |
| 2700 | 0.680 | 2.623 | 0.850 | 2.720 |
| 2600 | 0.980 | 2.782 | 0.785 | 2.686 |
| 2500 | 1.393 | 2.936 | 0.710 | 2.643 |
| 2400 | 1.555 | 2.982 | 0.993 | 2.788 |
| 2300 | 1.360 | 2.924 | 1.006 | 2.792 |

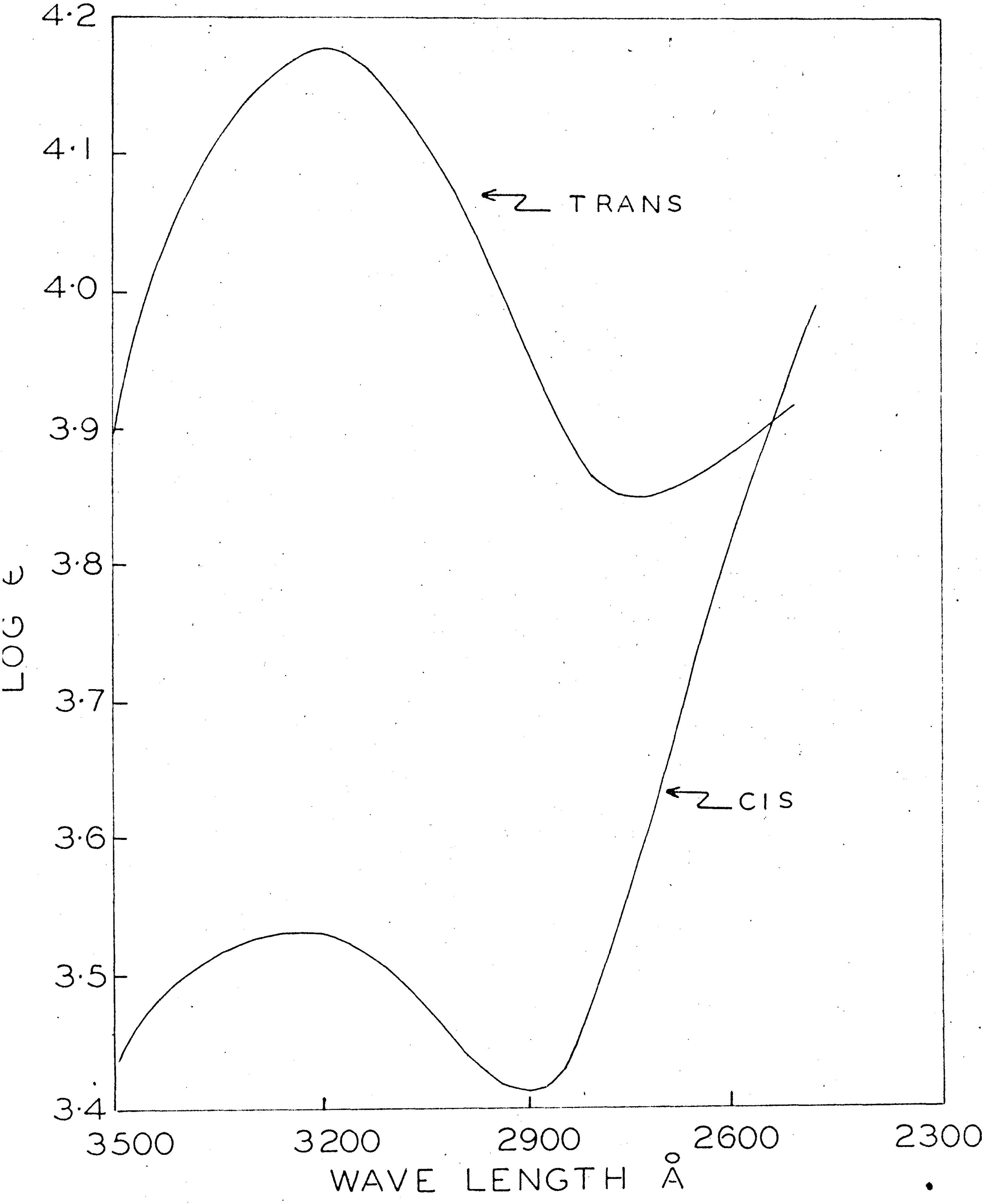


Fig. 2 Absorption Spectra of Azoxybenzene in Methanol

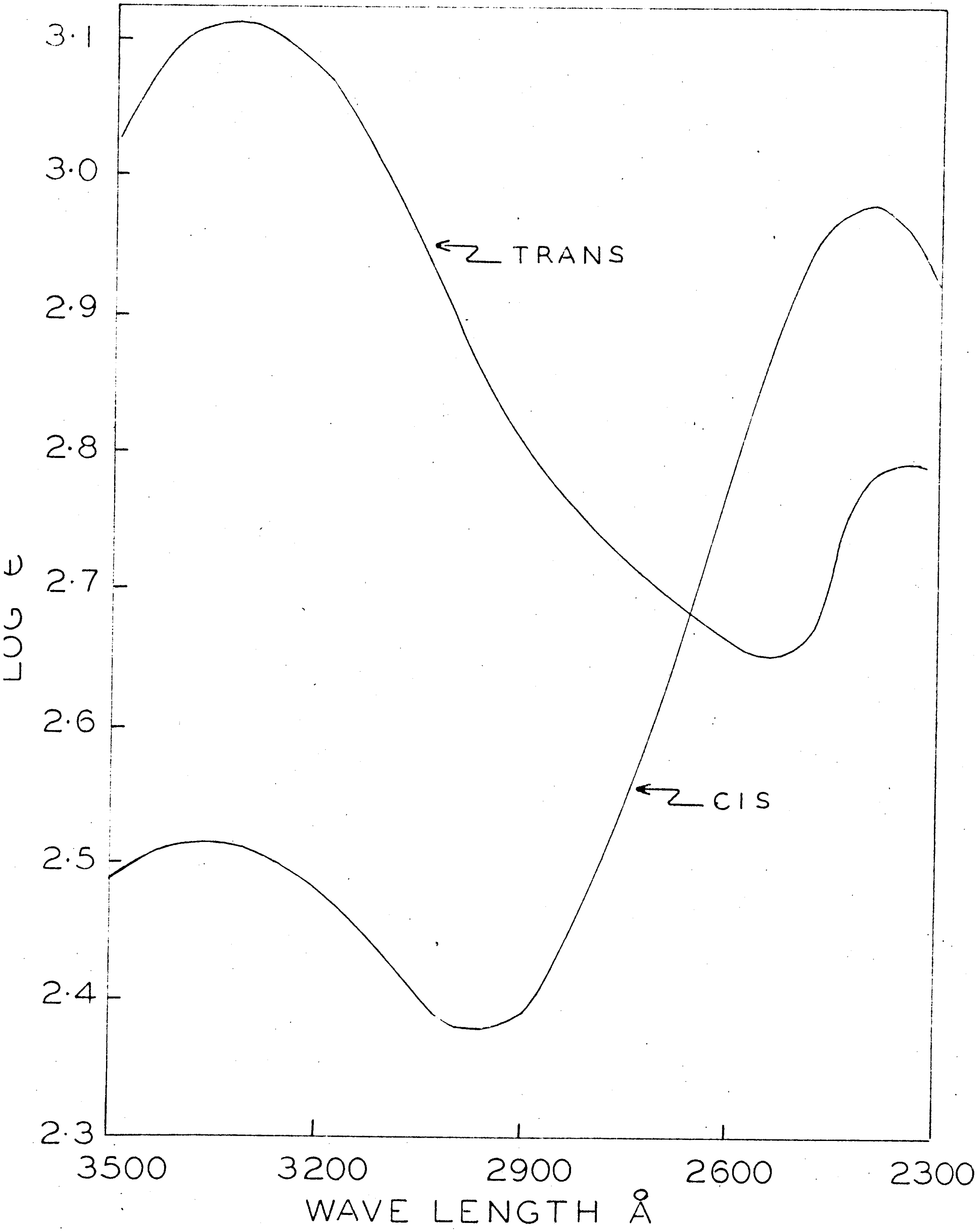


Fig. 3. Absorption Spectra of p,p'-Azoxytoluene in Methanol

the absorption of trans isomer being considerably stronger however, than that of the cis isomer. These results are in agreement with those of Müller (43). The large difference in extinction coefficients of the two isomers at 3300 Å indicated that the concentrations of these isomers in solution can be measured accurately at this wave length. Preliminary experiments showed that the initial concentrations of the cis isomers could not be determined accurately in all solvents owing to the fast rate of isomerization. No attempt, therefore, was made to determine the purity of the cis isomers or to establish a calibration curve for the determination of the rate constants.

Since isomerization reactions are first order, rate constants may be obtained from the slope of a plot of log ( $\Upsilon$ - T) against time,

i.e.
$$k = \pm 2.303 \frac{\log (\Upsilon - T)}{\Delta t} \qquad \text{.....(27)}$$

where the plus sign is used if the cis isomer absorbs more strongly than the trans, and the minus sign if the trans isomer absorbs more strongly than the cis,

k is the specific rate constant of the reaction,

$\Upsilon$ is the optical density of the solution x $10^3$ at time t,

T is the optical density of the solution x $10^3$ at time $t_\infty$ after isomerization is complete, and $\Delta t$ is the time interval corresponding to the change in optical density $(\Upsilon - T.)$

This relation is valid only if impurities in the isomeric compounds do not interfere with the optical densities of the solutions, and if linear relations exist between the optical densities and the total concentrations of the cis-trans mixtures. Using the above equation, experiments with two different preparations of cis-azoxybenzene showed that the reaction was consistently first order and that the rate constants were reproducible, indicating that the foregoing assumptions are valid for determining the rate constants of the isomerization reaction. After isomerization was complete the solutions gave the same absorption maxima at 3300 Å as methanol solutions prepared from pure trans azoxybenzene or trans p,p'-azoxytoluene. This is shown in Figures 4 and 5 where the logarithms of the optical densities are plotted as a function of the wave length for a few typical solvents. This further substantiates that the rate constants obtained from Equation 27 are true measures of the rates of cis-trans isomerization.

The absorption spectra for a series of substituted benzenediazocyanides have been determined by LeFevre and Wilson (59). They observed a strong absorption band for p-chlorobenzenediazocyanide at 4500 Å, with the cis isomer absorbing more strongly than the trans in this region. Experiments with p-chlorobenzenediazocyanide, similar to

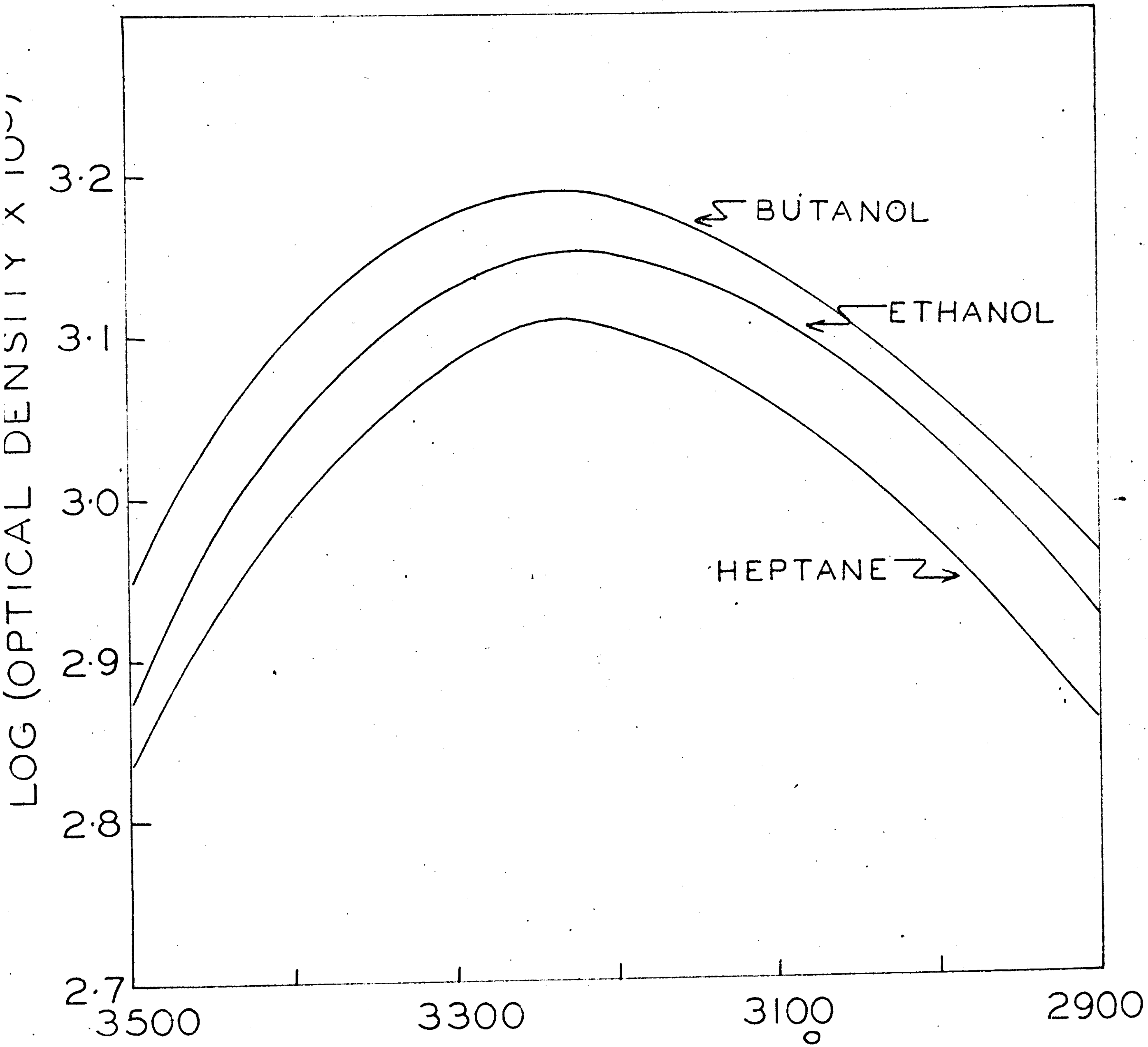


Fig. 4. Absorption Spectra of Some Completely Isomerized Solutions of Azoxybenzene

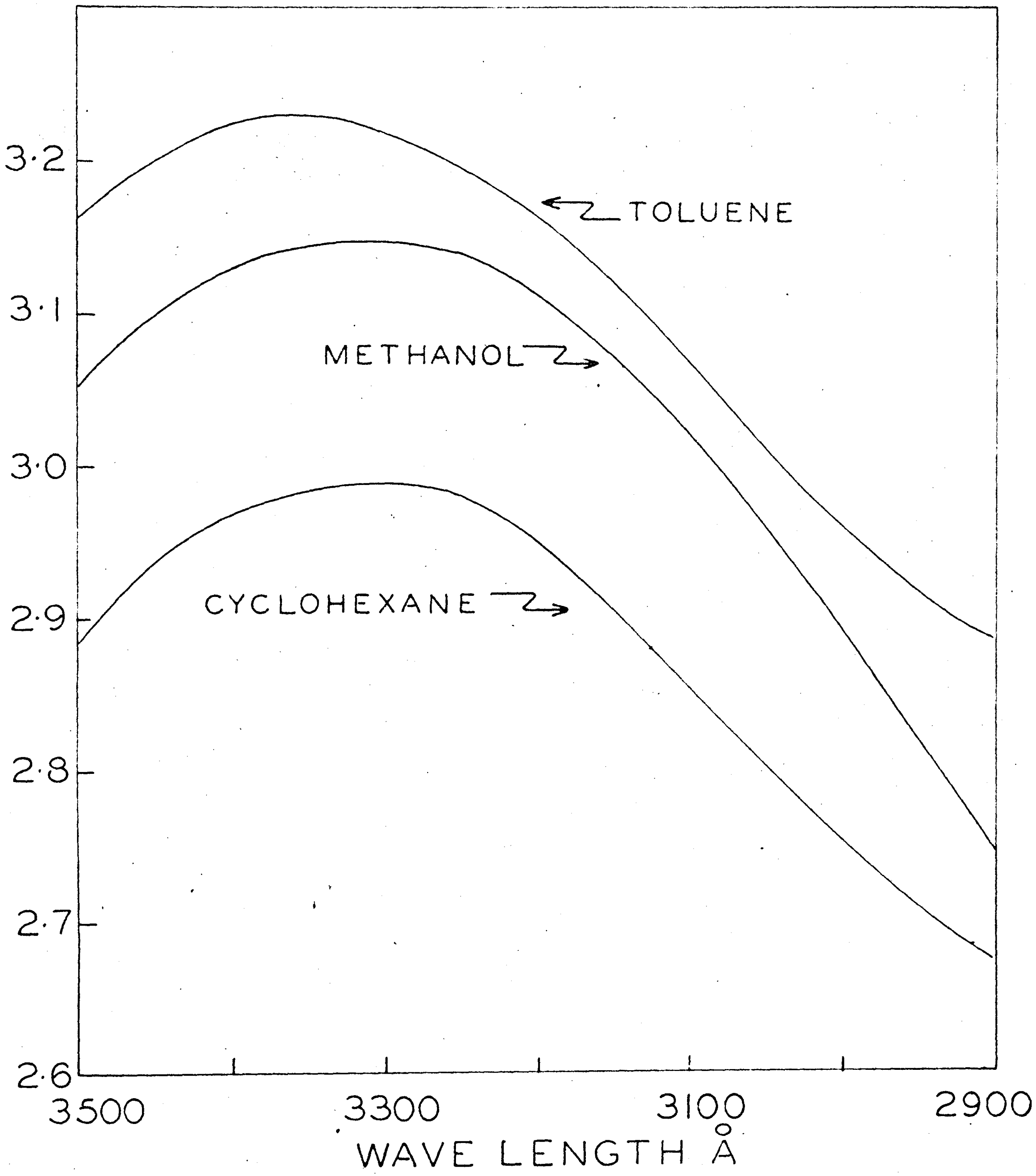


Fig. 5. Absorption Spectra of Some Completely Isomerized Solutions of p,p'-Azoxytoluene

those described with azoxybenzene, showed that the specific rate constant can be obtained using Equation 27.

## DETERMINATION OF THE RATE OF ISOMERIZATION

The solvents used in all the isomerization reactions were supplied by Brickman and Co., Montreal. They were dried with the appropriate desiccants, distilled, and the middle fractions of the correct boiling points were collected. Solutions of the cis isomer were diluted to an optical density suitable for accurate readings on the spectrophotometer. When the cis isomer was slightly soluble, an excess of the isomer was added, the solution stirred and then filtered. Approximately 10 ml. of the solutions were placed in half-ounce amber bottles and tightly closed with screw-caps fitted with aluminum gaskets. In each experiment the reaction mixtures were placed simultaneously in thermostats controlled to $0 \pm .03$°C. with mercury regulators. The reaction bottles were withdrawn at different time intervals, cooled rapidly to room temperature by immersion in ice-water and the optical densities of the solutions measured at the appropriate wave length against the corresponding pure solvent as a blank. The isomerization of p-chlorobenzenediazocyanide was studied in a darkened room to avoid errors due to photochemical isomerization (63).

In most solvents the rates of the isomerization reactions were slow enough at room temperature to permit accurate spectrophotometric readings to be taken. However, in cyclohexane and heptane the isomerization of azoxybenzene and p,p'-azoxytoluene proceeded at appreciable rates even at room temperature and it would have been necessary to take readings at temperatures ranging from -10°C. to 20°C. to obtain the same accuracy as with the other solvents. This was not possible, since the spectrophotometer was not equipped with a low temperature thermostat. As a consequence, a somewhat greater error had to be accepted in the measurements with these solvents.

Zero time for the reaction was assumed to be the time of immersion of the reaction mixture in the thermostat plus one half the time required for it to attain the thermostat temperature. The times for attaining thermostat temperature were evaluated experimentally as 1.5 min. at 60°C., one min. at 45°C. and 0.5 min. at 35°C. At 25°C. and 30°C. no corrections to the zero times were necessary since the reactions were all quite slow at these temperatures except when heptane or cyclohexane were used as solvents.

## EXPERIMENTAL RESULTS

### ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE

Following the experimental procedure outlined previously the rate of isomerization of p-chlorobenzenediazocyanide was investigated in six pure solvents at temperatures of 30, 45, and 60°C. The data for these reactions are recorded in Tables III-VIII, and plotted in Figures 6-11. The linearity of the plots indicates that the reaction is consistently first order. The rate constants k, were obtained from the expression

$$k = 2.303 \times \log \frac{(\tau - T)}{\Delta t}$$

and are extimated to be accurate within ±1.5%. In Figure 12 the logarithms of the rate constants, k, for the reaction in different solvents are plotted as a function of $\frac{1}{T}$. The activation energies, E, were obtained from the expression

$$E = 2.303\ R\ (\text{slope of the Arrhenius line})$$

and are estimated to be accurate within 250 calories. The "frequency factors", A, were calculated utilizing the expression

$$\log k = \log A - \frac{E}{2.303RT} \quad .$$

A summary of the kinetic data for p-chlorobenzenediazocyanide is tabulated in Table IX. A comparison of the results obtained in this investigation with those of LeFevre for the same reaction will be made later.

## ISOMERIZATION OF AZOXYBENZENE AND p,p'-AZOXYTOLUENE

The rates of isomerization of azoxybenzene and p,p'-azoxytoluene in nine solvents were similarly determined. The rate data for these two isomerization reactions in toluene, hexanol, and acetonitrile are shown in Tables X-XII and XIV-XVI and plotted in Figures 13-15 and 17-19. The specific rate constants, k, the activation energies, E, and the frequency factors, A, were obtained as before and recorded in Tables XIII and XVII.

The probable error in the activation energy for each isomerization reaction was estimated as the deviation of the temperature coefficients calculated for successive temperature intervals from their mean value, represented by $E_{calc.}$, and are included in Tables XIII and XVII with the activation energy determined from the Arrhenius line. Arrhenius lines for azoxybenzene and p,p'-azoxytoluene in toluene hexanol and acetonitrile are shown in Figures 16 and 20.

## TABLE III

## CIS-TRANS ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE IN HEPTANE

| Temp. (°C.) | Time (Min.) | log ($\Upsilon$ - T) |
|---|---|---|
| 29.93 | 60 | 2.418 |
| | 188 | 2.362 |
| | 305 | 2.320 |
| | 450 | 2.274 |
| | 628 | 2.199 |
| | 663 | 2.193 |
| | 810 | 2.110 |
| 45.80 | 5 | 2.415 |
| | 15 | 2.408 |
| | 30 | 2.366 |
| | 45 | 2.328 |
| | 70 | 2.258 |
| | 112 | 2.173 |
| | 180 | 2.029 |
| 58.57 | 6 | 2.367 |
| | 10 | 2.330 |
| | 15 | 2.280 |
| | 20 | 2.240 |
| | 30 | 2.155 |
| | 45 | 2.000 |
| | 62 | 1.826 |

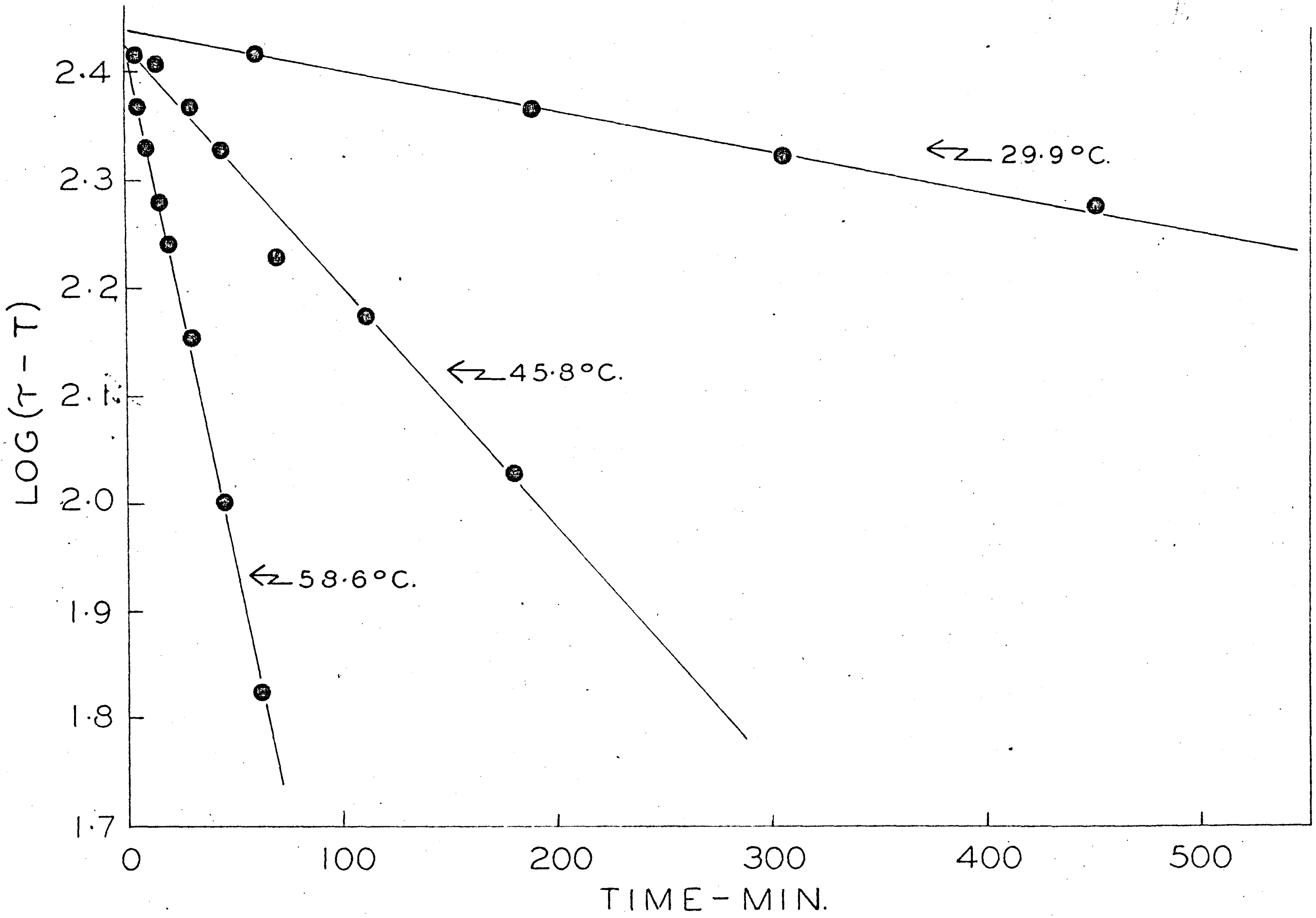


Fig. 6. Isomerization of p-Chlorobenzenediazocyanide in Heptane

## TABLE IV

## CIS-TRANS ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE IN CYCLOHEXANE

| Temp. (°C.) | Time (min.) | log ($\tau$ - T) |
|---|---|---|
| 29.93 | 120 | 2.441 |
| | 240 | 2.428 |
| | 420 | 2.380 |
| | 600 | 2.318 |
| | 825 | 2.246 |
| 45.80 | 15 | 2.509 |
| | 30 | 2.471 |
| | 51 | 2.438 |
| | 120 | 2.272 |
| | 180 | 2.140 |
| | 308 | 1.839 |
| 58.56 | 10 | 2.459 |
| | 20 | 2.352 |
| | 30 | 2.258 |
| | 40 | 2.170 |
| | 60 | 1.996 |
| | 70.5 | 1.863 |

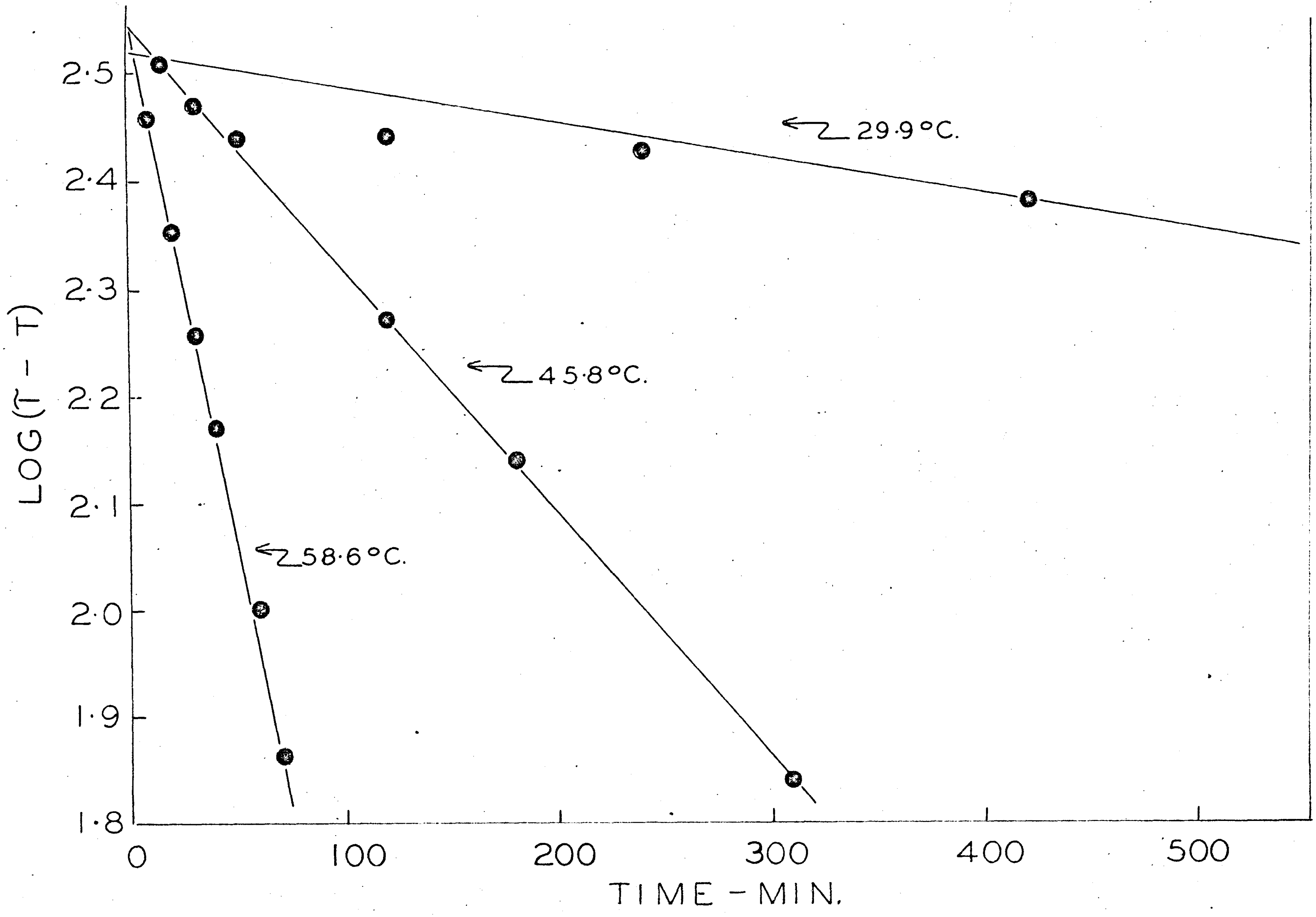


Fig. 7. Isomerization of p-Chlorobenzenediazocyanide in Cyclohexane

## TABLE V

## CIS-TRANS ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE IN BENZENE

| Temp. (°C.) | Time (Min.) | log ($\tau$ - T) |
|---|---|---|
| 29.93 | 120.00 | 2.316 |
| | 240.00 | 2.223 |
| | 360.00 | 2.143 |
| | 480.00 | 2.068 |
| | 560.00 | 1.991 |
| | 720.00 | 1.869 |
| 45.80 | 10.00 | 2.342 |
| | 20.25 | 2.303 |
| | 30.25 | 2.250 |
| | 50.00 | 2.161 |
| | 70.00 | 2.057 |
| | 100.00 | 1.914 |
| 58.57 | 10.00 | 2.228 |
| | 20.00 | 2.041 |
| | 30.00 | 1.832 |
| | 45.00 | 1.505 |
| | 60.00 | 1.230 |

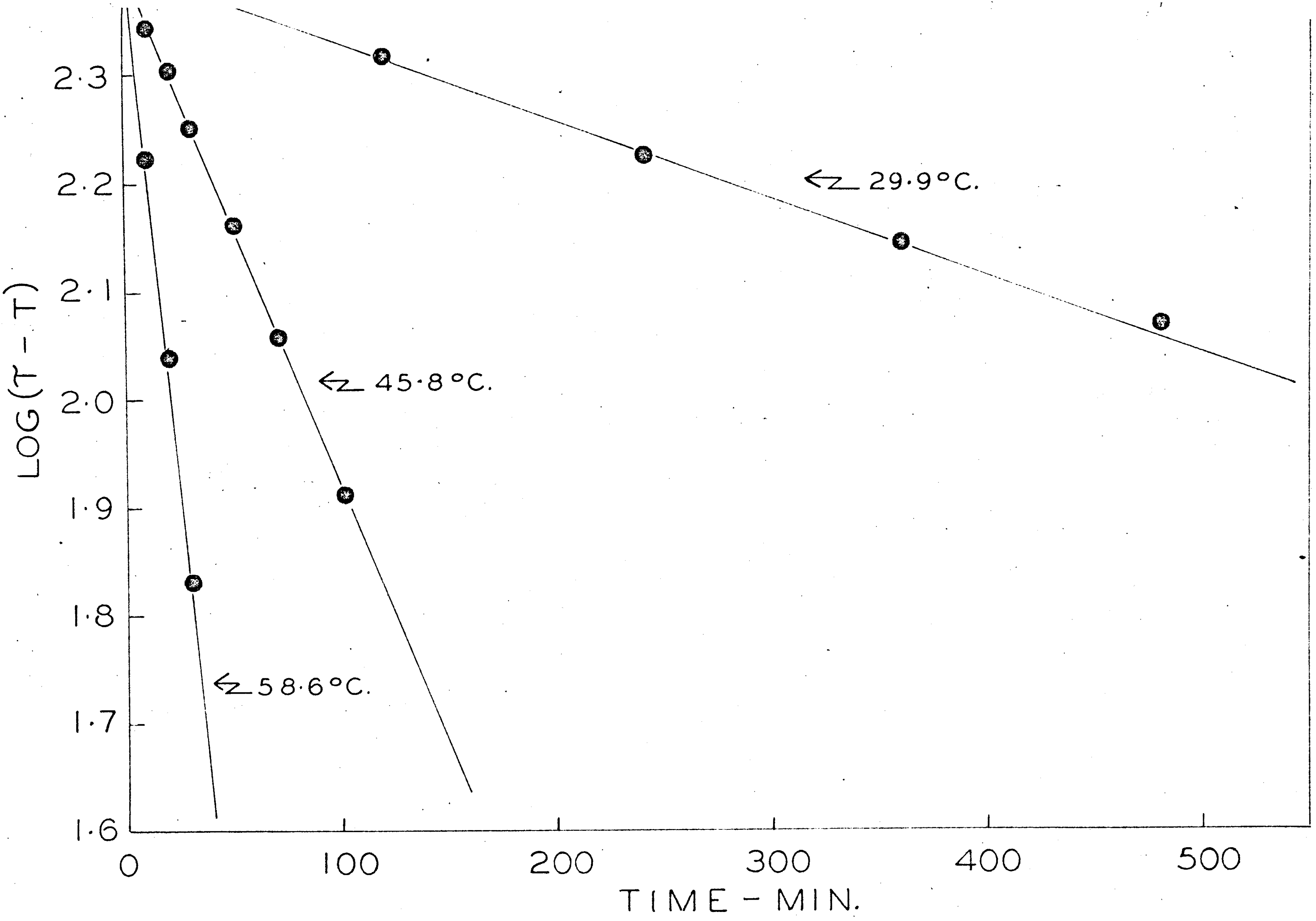


Fig. 8. Isomerization of p-Chlorobenzenediazocyanide in Benzene

## TABLE VI

## CIS-TRANS ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE IN CHLOROBENZENE

| Temp. (°C.) | Time (Min.) | log ($\Upsilon$ - T) |
|---|---|---|
| 29.93 | 60 | 2.507 |
| | 145 | 2.423 |
| | 220 | 2.342 |
| | 305 | 2.255 |
| | 390 | 2.176 |
| | 518 | 2.049 |
| 45.80 | 20 | 2.436 |
| | 30.5 | 2.371 |
| | 45 | 2.272 |
| | 80 | 2.033 |
| | 105 | 1.887 |
| | 130.5 | 1.724 |
| 58.57 | 6 | 2.428 |
| | 10 | 2.326 |
| | 17 | 2.146 |
| | 22 | 2.033 |
| | 30 | 1.820 |

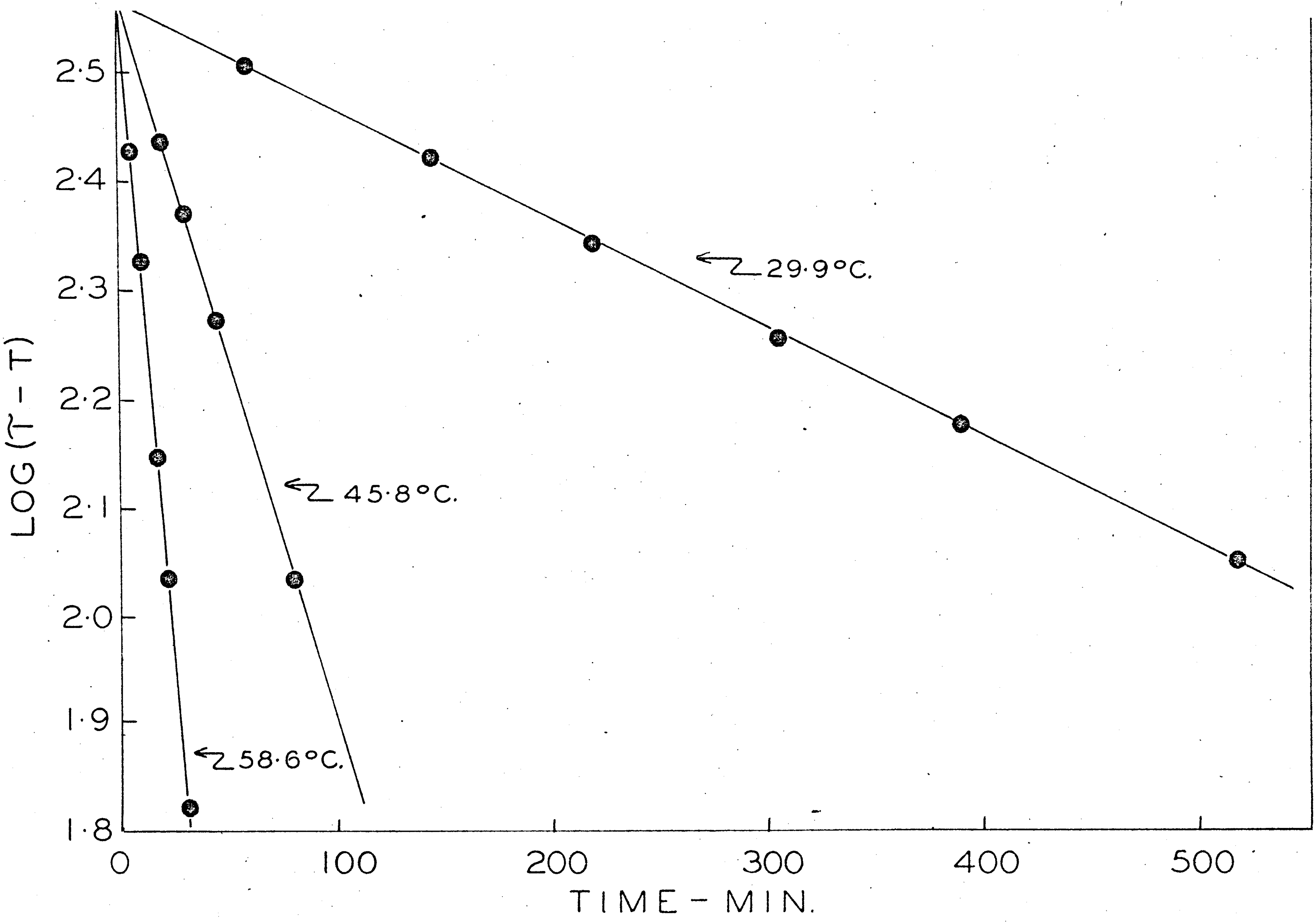


Fig. 9. Isomerization of p-Chlorobenzenediazocyanide in Chlorobenzene

## TABLE VII

## CIS-TRANS ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE IN O-DICHLOROBENZENE

| Temp. (°C.) | Time (Min.) | log ($\tau$ - T) |
|---|---|---|
| 29.93 | 65 | 2.431 |
| | 120 | 2.362 |
| | 195 | 2.265 |
| | 275 | 2.161 |
| | 360 | 2.068 |
| | 465 | 1.954 |
| 45.80 | 16.5 | 2.396 |
| | 30 | 2.295 |
| | 47 | 2.140 |
| | 60 | 2.045 |
| | 90 | 1.799 |
| 58.57 | 5 | 2.396 |
| | 10 | 2.238 |
| | 15.5 | 1.987 |
| | 20.0 | 1.914 |
| | 30 | 1.653 |

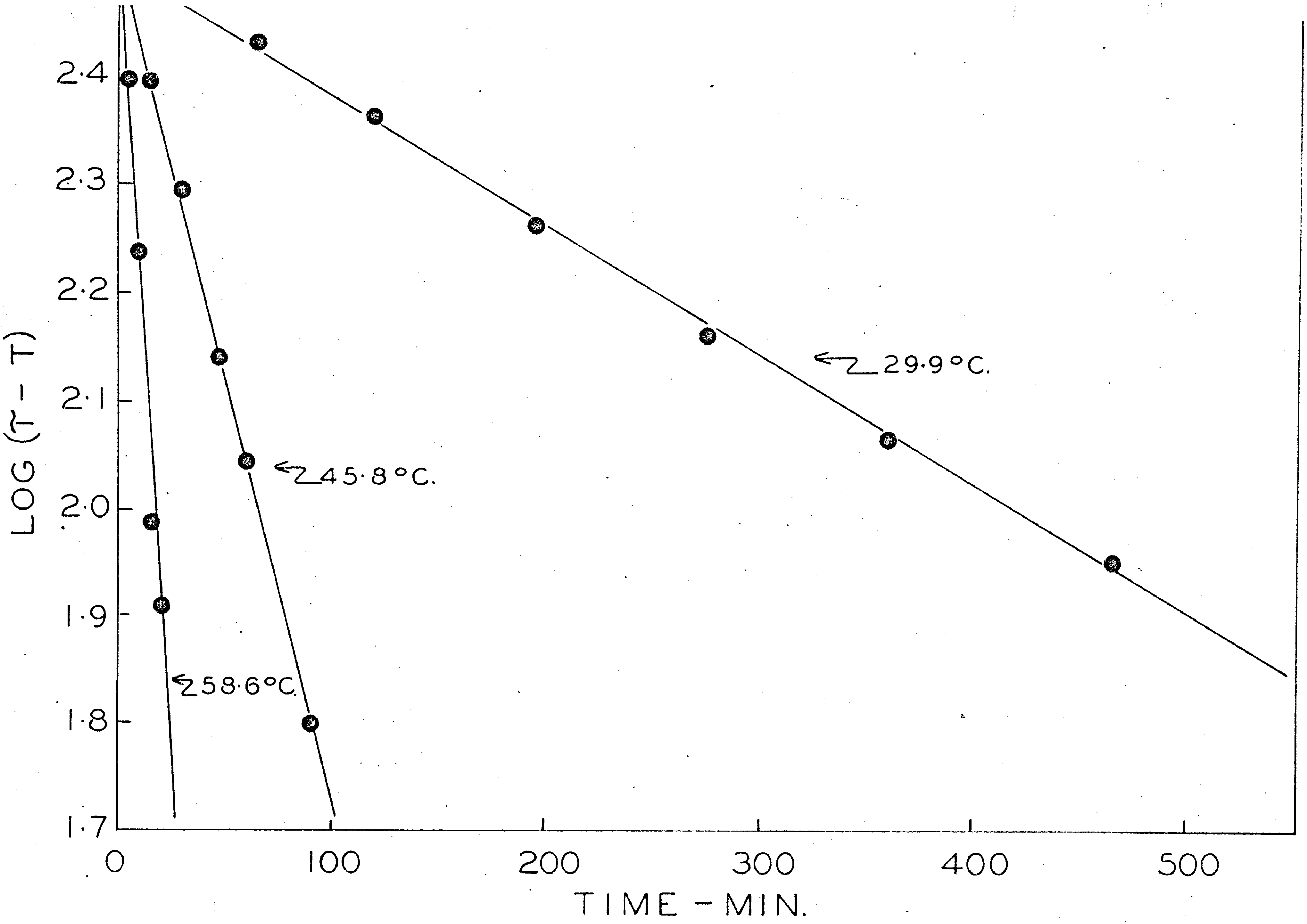


Fig. 10. Isomerization of p-Chlorobenzenediazocyanide in o-Dichlorobenzene

## TABLE VIII

## CIS-TRANS ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE IN CHLOROFORM

| Temp. (°C.) | Time (Min.) | log ($\Upsilon$ - T) |
|---|---|---|
| 29.93 | 120 | 2.380 |
| | 210 | 2.201 |
| | 305 | 1.996 |
| | 375 | 1.863 |
| | 530 | 1.568 |
| | 695 | 1.230 |
| 45.80 | 10 | 2.420 |
| | 25 | 2.346 |
| | 63 | 1.924 |
| | 90 | 1.672 |
| | 130 | 1.204 |
| | 190 | 0.602 |
| 58.57 | 10 | 2.236 |
| | 15 | 2.057 |
| | 20 | 1.820 |
| | 30 | 1.491 |
| | 45 | 0.699 |
| | 60.5 | 0.301 |

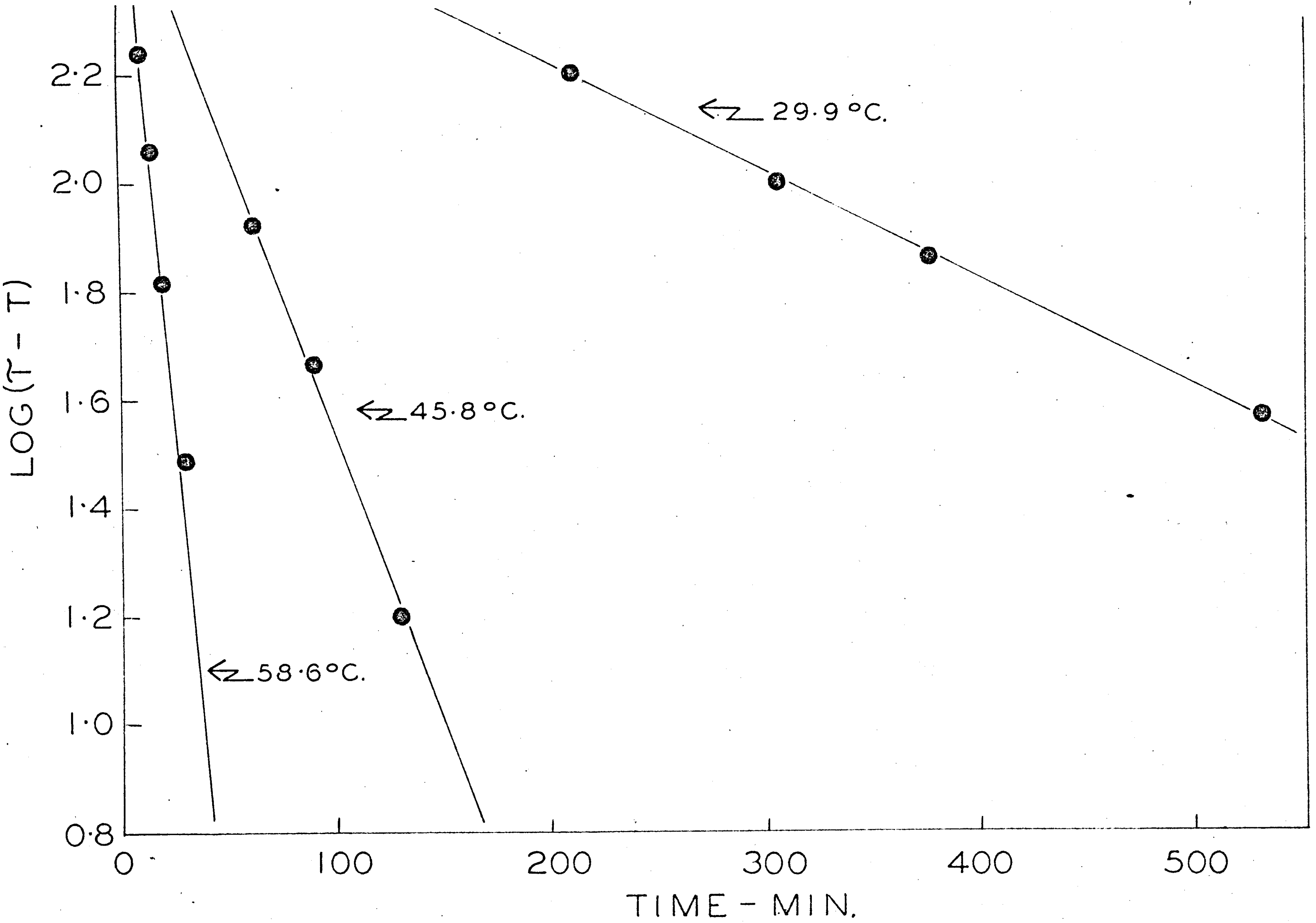


Fig. 11. Isomerization of p-Chlorobenzenediazocyanide in Chloroform

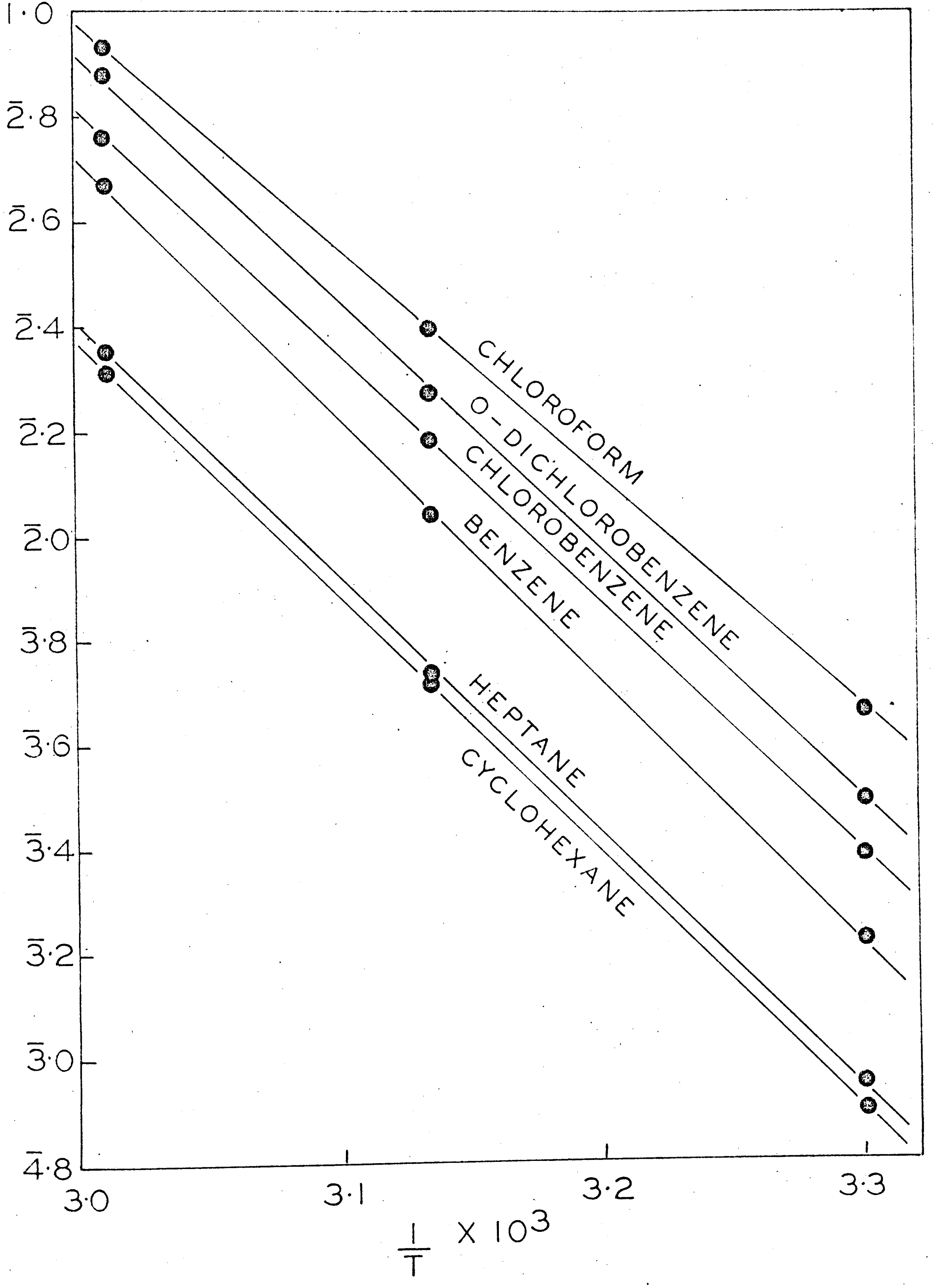


Fig. 12. Arrhenius Lines for the Isomerization of p-Chlorobenzenediazocyanide

## TABLE IX

## ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE IN VARIOUS SOLVENTS

### SUMMARY OF KINETIC DATA

| Solvent | Temp. (°C.) | k ($\text{min}^{-1}$) | log k | E (k.cal./mole) | log A |
|---|---|---|---|---|---|
| Heptane | 29.93 | 0.0008831 | $\bar{4}.946$ | 22.40 | 13.12 |
|  | 45.80 | 0.005346 | $\bar{3}.728$ |  |  |
|  | 58.57 | 0.02244 | $\bar{2}.351$ |  |  |
| Cyclohexane | 29.93 | 0.0007816 | $\bar{4}.893$ | 22.51 | 13.18 |
|  | 45.80 | 0.005284 | $\bar{3}.723$ |  |  |
|  | 58.57 | 0.02061 | $\bar{2}.314$ |  |  |
| Benzene | 29.93 | 0.001656 | $\bar{3}.219$ | 22.92 | 13.77 |
|  | 45.80 | 0.01091 | $\bar{2}.038$ |  |  |
|  | 58.57 | 0.04656 | $\bar{2}.668$ |  |  |
| Chlorobenzene | 29.93 | 0.002432 | $\bar{3}.386$ | 21.92 | 13.23 |
|  | 45.80 | 0.01517 | $\bar{2}.181$ |  |  |
|  | 58.57 | 0.005754 | $\bar{2}.760$ |  |  |
| O-dichloro-benzene | 29.93 | 0.003055 | $\bar{3}.485$ | 21.80 | 13.25 |
|  | 45.80 | 0.01879 | $\bar{2}.274$ |  |  |
|  | 58.57 | 0.07516 | $\bar{2}.876$ |  |  |
| Chloroform | 29.93 | 0.004560 | $\bar{3}.659$ |  |  |
|  | 45.80 | 0.02438 | $\bar{2}.387$ |  |  |
|  | 58.57 | 0.08453 | $\bar{2}.927$ | 20.05 | 12.18 |

## TABLE X

## CIS-TRANS ISOMERIZATION OF AZOXYBENZENE IN TOLUENE

| Temp. (°C.) | Time (min.) | log(T - $\tau$) |
|---|---|---|
| 45.94 | 5 | 2.932 |
| | 8 | 2.851 |
| | 12 | 2.752 |
| | 17 | 2.610 |
| | 25 | 2.407 |
| | 30 | 2.295 |
| 35.33 | 10 | 2.591 |
| | 20 | 2.517 |
| | 30 | 2.444 |
| | 45 | 2.330 |
| | 65 | 2.188 |
| | 93 | 2.000 |
| 25.03 | 16 | 2.467 |
| | 46 | 2.412 |
| | 80 | 2.339 |
| | 120 | 2.263 |
| | 180 | 2.158 |
| | 240 | 2.021 |

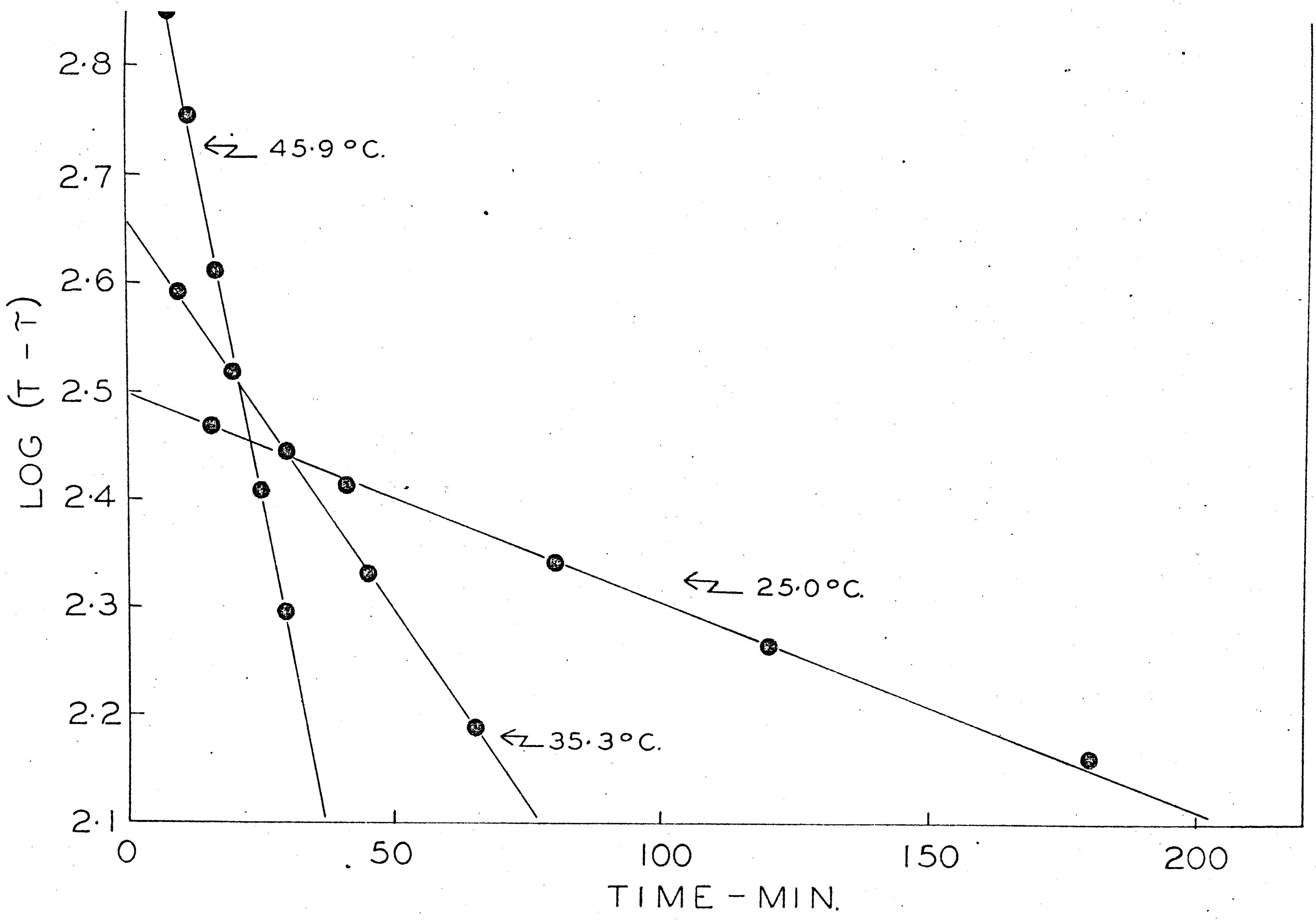


Fig. 13. Isomerization of Azoxybenzene in Toluene

## TABLE XI

## CIS-TRANS ISOMERIZATION OF AZOXYBENZENE IN HEXANOL

| Temp. (°C.) | Time (min.) | log (T - $\hat{T}$) |
|---|---|---|
| 45.97 | 10 | 2.756 |
| | 18 | 2.637 |
| | 26 | 2.542 |
| | 41 | 2.352 |
| | 56 | 2.170 |
| | 86 | 1.863 |
| 35.35 | 21 | 2.801 |
| | 41 | 2.732 |
| | 70 | 2.634 |
| | 100 | 2.520 |
| | 129 | 2.420 |
| | 162 | 2.318 |
| 25.03 | 112 | 2.847 |
| | 177 | 2.783 |
| | 258 | 2.703 |
| | 294 | 2.674 |
| | 348 | 2.630 |
| | 415 | 2.565 |

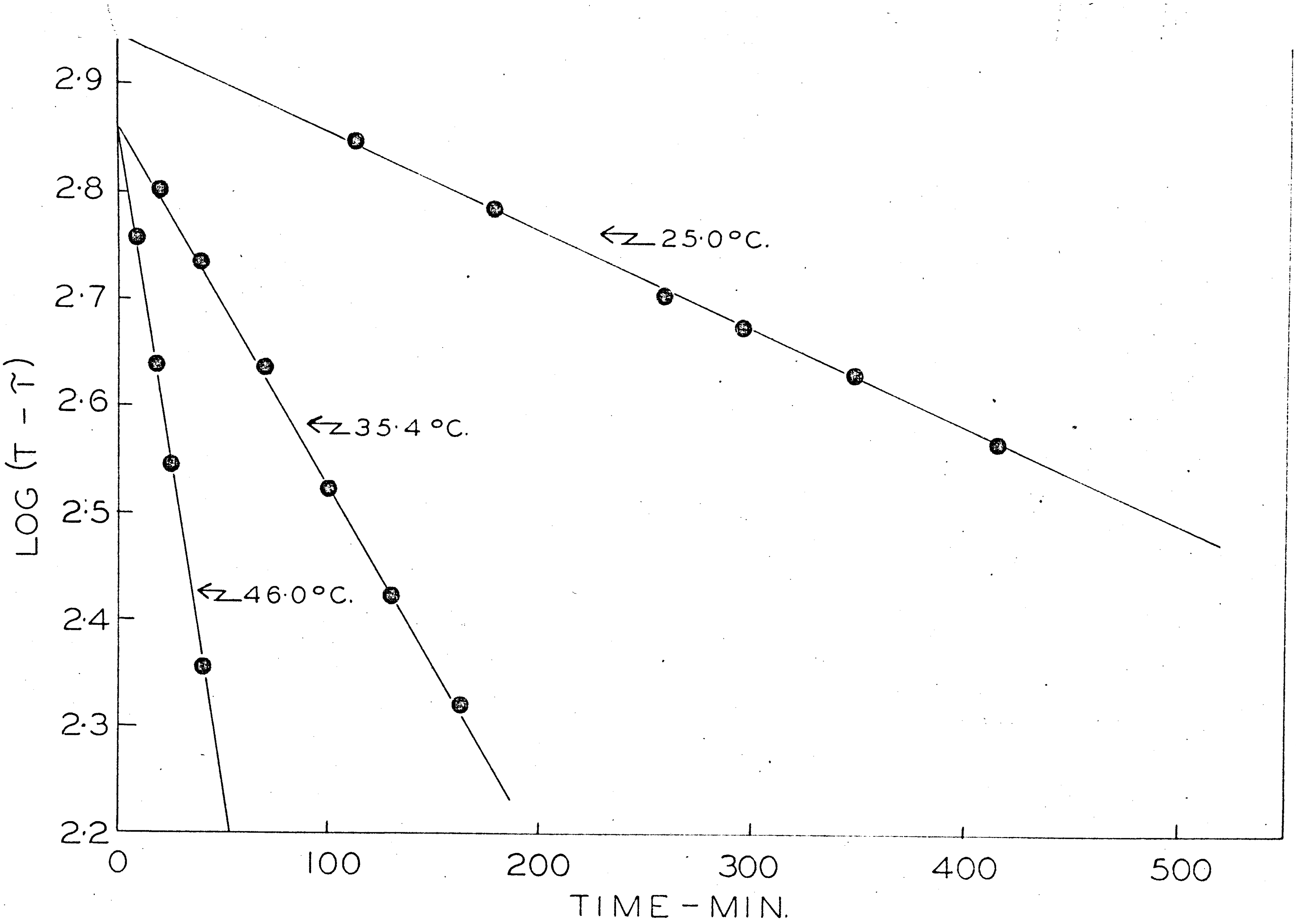


Fig. 14. Isomerization of Azoxybenzene in Hexanol

## TABLE XII

### CIS-TRANS ISOMERIZATION OF AZOXYBENZENE IN ACETONITRILE

| Temp. (°C.) | Time (min.) | $\log (T - \tau)$ |
|---|---|---|
| 58.68 | 3 | 2.957 |
| | 6 | 2.910 |
| | 9 | 2.853 |
| | 13.5 | 2.766 |
| | 19 | 2.688 |
| | 25 | 2.554 |
| 45.92 | 6 | 3.057 |
| | 13.5 | 3.025 |
| | 24.5 | 2.977 |
| | 36 | 2.927 |
| | 56 | 2.851 |
| 29.50 | 55 | 3.021 |
| | 150 | 2.969 |
| | 260 | 2.914 |
| | 395 | 2.842 |
| | 545 | 2.763 |
| | 650 | 2.703 |

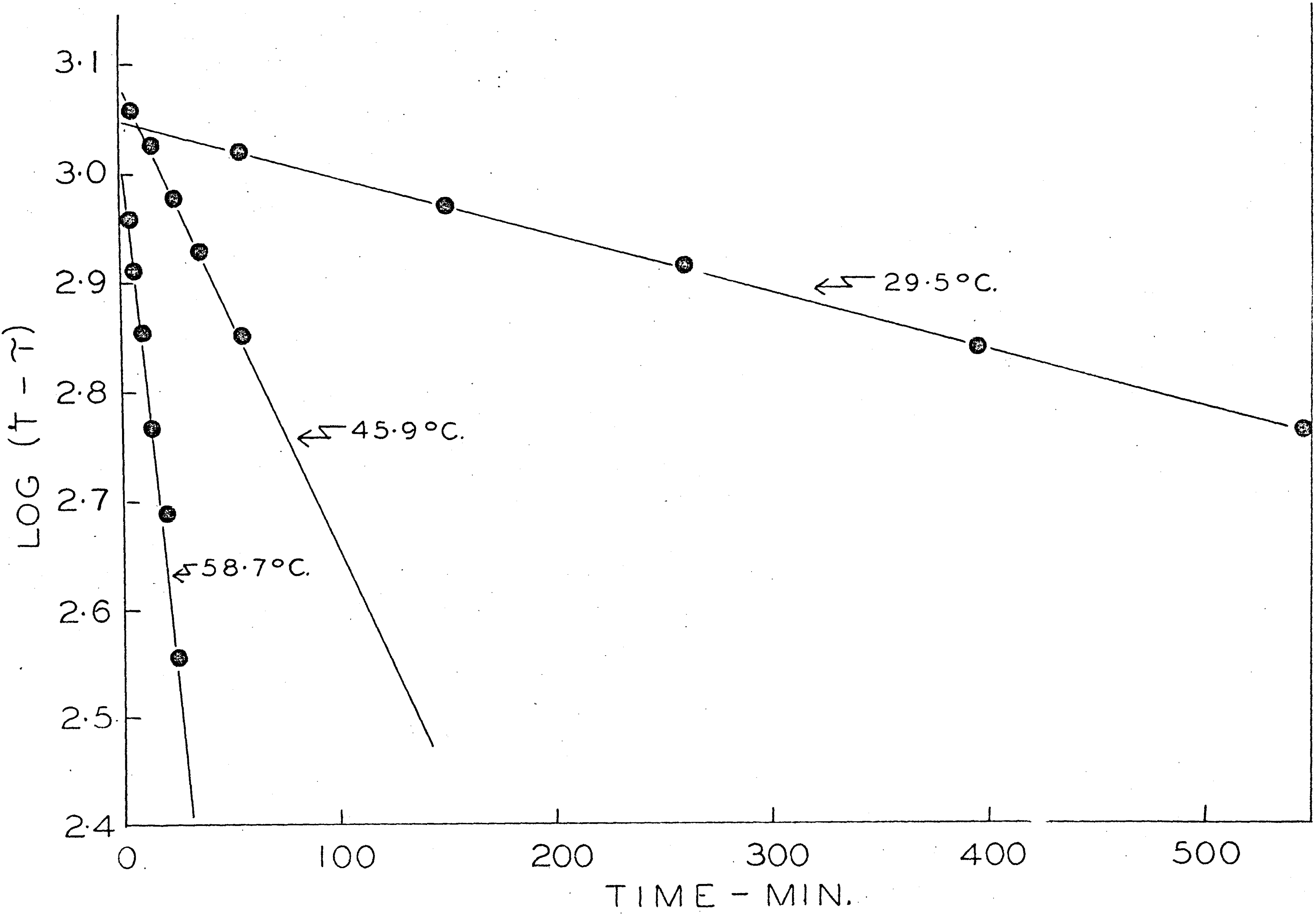


Fig. 15. Isomerization of Azoxybenzene in Acetonitrile

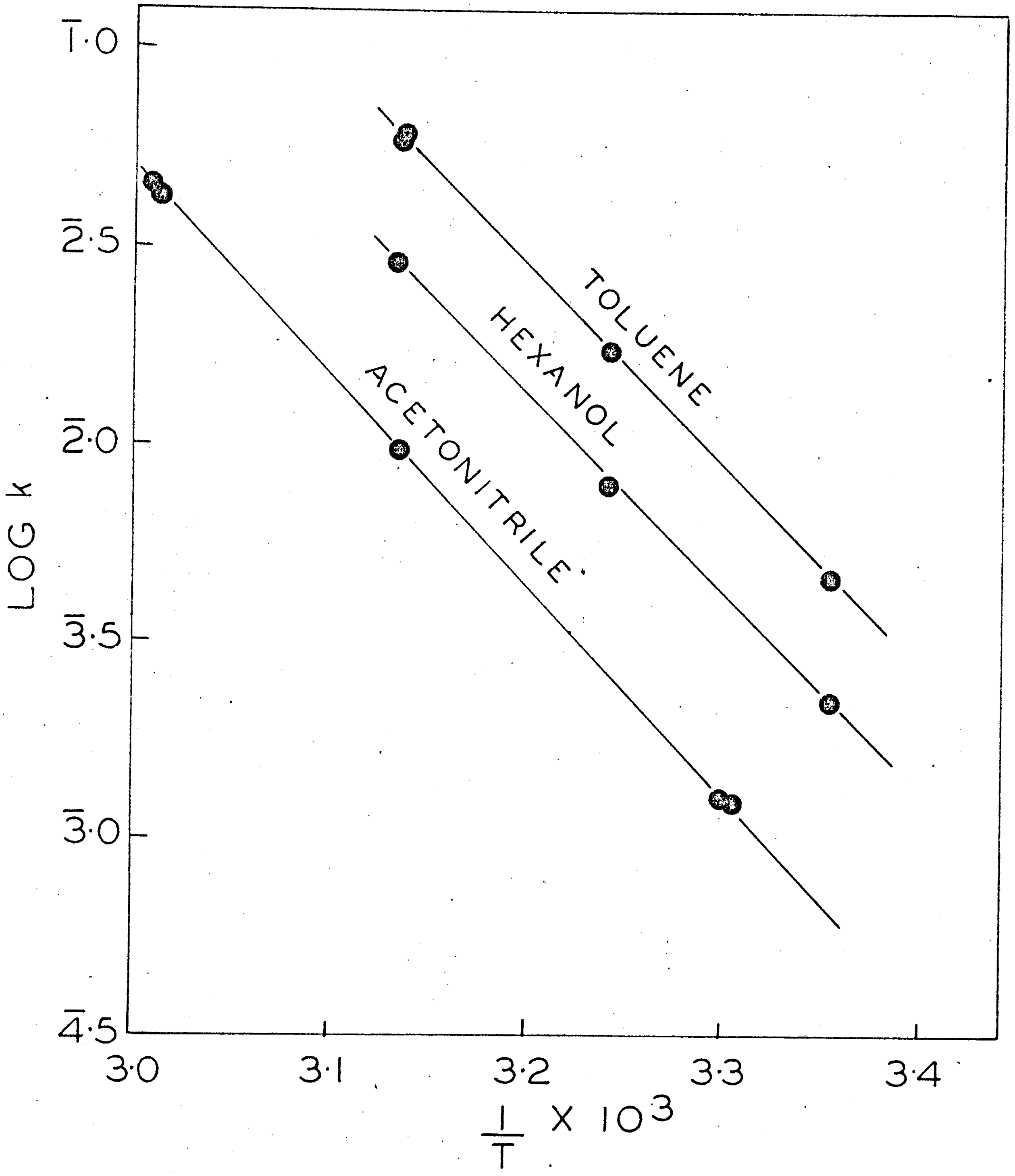


Fig. 16. Typical Arrhenius Lines for the Isomerization of Azoxybenzene in Different Solvents

## TABLE XIII

## ISOMERIZATION OF AZOXYBENZENE IN VARIOUS SOLVENTS

| Solvent | Temp. °C. | k min.$^{-1}$ | log k | $E_{calc.}$ k.cal/ mole | Probable Error in E k.cal/ mole | $E_{graphical}$ | log A |
|---|---|---|---|---|---|---|---|
| Methanol | 58.68 | 0.0295 | $\bar{2}.470$ | 22.08 | 0.16 | 22.25 | 13.05 |
| | 45.85 | 0.00777 | $\bar{3}.890$ | | | | |
| | 29.50 | 0.00115 | $\bar{3}.060$ | | | | |
| Ethanol | 59.3 | 0.0550 | $\bar{2}.741$ | 22.89 | 0.57 | 22.9 | 13.86 |
| | 58.68 | 0.0526 | $\bar{2}.721$ | | | | |
| | 46.04 | 0.0130 | $\bar{2}.114$ | | | | |
| | 45.92 | 0.01442 | $\bar{2}.160$ | | | | |
| | 45.75 | 0.0123 | $\bar{2}.090$ | | | | |
| | 29.93 | 0.00185 | $\bar{3}.267$ | | | | |
| | 29.50 | 0.00186 | $\bar{3}.269$ | | | | |
| Heptane | 35.35 | 0.0452 | $\bar{2}.665$ | 22.40 | 0.51 | 22.4 | 14.58 |
| | 29.50 | 0.0228 | $\bar{2}.358$ | | | | |
| | 25.03 | 0.0131 | $\bar{2}.117$ | | | | |
| | 15.49 | 0.00359 | $\bar{3}.556$ | | | | |
| Acetonitrile | 59.3 | 0.0460 | $\bar{2}.663$ | 24.27 | 0.12 | 24.3 | 14.82 |
| | 58.68 | 0.0422 | $\bar{2}.626$ | | | | |
| | 58.58 | 0.0420 | $\bar{2}.624$ | | | | |

## TABLE XIII, continued

| Solvent | Temp. °C. | k min.$^{-1}$ | log k | $E_{calc.}$ k.cal./ mole | Probable Error in E k.cal./ mole | $E_{graphical}$ | log A |
|---|---|---|---|---|---|---|---|
| Acetonitrile, cont. | 45.92 | 0.00962 | $\bar{3}.982$ | | | | |
| | 29.93 | 0.001265 | $\bar{3}.102$ | | | | |
| | 29.50 | 0.00123 | $\bar{3}.090$ | | | | |
| Butanol | 46.02 | 0.02053 | $\bar{2}.312$ | 22.81 | 0.86 | 23.2 | 14.00 |
| | 45.94 | 0.0221 | $\bar{2}.344$ | | | | |
| | 45.75 | 0.0214 | $\bar{2}.330$ | | | | |
| | 29.93 | 0.00301 | $\bar{3}.478$ | | | | |
| | 29.50 | 0.003035 | $\bar{3}.482$ | | | | |
| | 25.03 | 0.001735 | $\bar{3}.239$ | | | | |
| Hexanol | 45.97 | 0.0285 | $\bar{2}.455$ | 22.8 | 0.37 | 22.7 | 14.11 |
| | 35.35 | 0.00789 | $\bar{3}.897$ | | | | |
| | 25.03 | 0.00222 | $\bar{3}.346$ | | | | |
| Benzene | 46.00 | 0.0489 | $\bar{2}.689$ | 22.22 | 0.48 | 22.8 | 13.93 |
| | 35.35 | 0.01345 | $\bar{2}.129$ | | | | |
| | 29.50 | 0.00662 | $\bar{3}.821$ | | | | |
| | 25.03 | 0.03875 | $\bar{3}.583$ | | | | |
| Toluene | 45.94 | 0.0583 | $\bar{2}.766$ | 23.29 | 0.49 | 22.8 | 14.78 |
| | 45.75 | 0.0613 | $\bar{2}.787$ | | | | |
| | 35.33 | 0.01695 | $\bar{2}.229$ | | | | |
| | 25.03 | 0.00460 | $\bar{3}.663$ | | | | |

## TABLE XIII, continued

| Solvent | Temp. °C. | k min.$^{-1}$ | log k | $E_{calc.}$ k.cal./ mole | Probable error in E k.cal./ mole | $E_{graphical}$ | log A |
|---|---|---|---|---|---|---|---|
| Cyclohexane | 35.35 | 0.0433 | $\bar{2}.637$ | 22.35 | 0.57 | 22.4 | 14.63 |
|  | 29.50 | 0.0219 | $\bar{2}.340$ |  |  |  |  |
|  | 15.49 | 0.00351 | $\bar{3}.545$ |  |  |  |  |

## TABLE XIV

### CIS-TRANS ISOMERIZATION OF p,p'-AZOXYTOLUENE IN TOLUENE

| Temp. (°C.) | Time (min.) | log (T - $\tau$) |
|---|---|---|
| 45.85 | 3 | 3.016 |
| | 6 | 2.979 |
| | 12 | 2.897 |
| | 17 | 2.825 |
| | 24 | 2.726 |
| | 35 | 2.594 |
| 36.13 | 10 | 3.083 |
| | 20 | 3.043 |
| | 30 | 3.002 |
| | 45.5 | 2.934 |
| | 60 | 2.872 |
| | 80.5 | 2.794 |
| 29.52 | 25 | 2.880 |
| | 60.5 | 2.815 |
| | 100 | 2.744 |
| | 145 | 2.666 |
| | 211 | 2.558 |
| | 300 | 2.420 |
| 25.03 | 70 | 2.968 |
| | 122 | 2.919 |
| | 190 | 2.851 |
| | 262 | 2.783 |
| | 340 | 2.708 |
| | 400 | 2.653 |

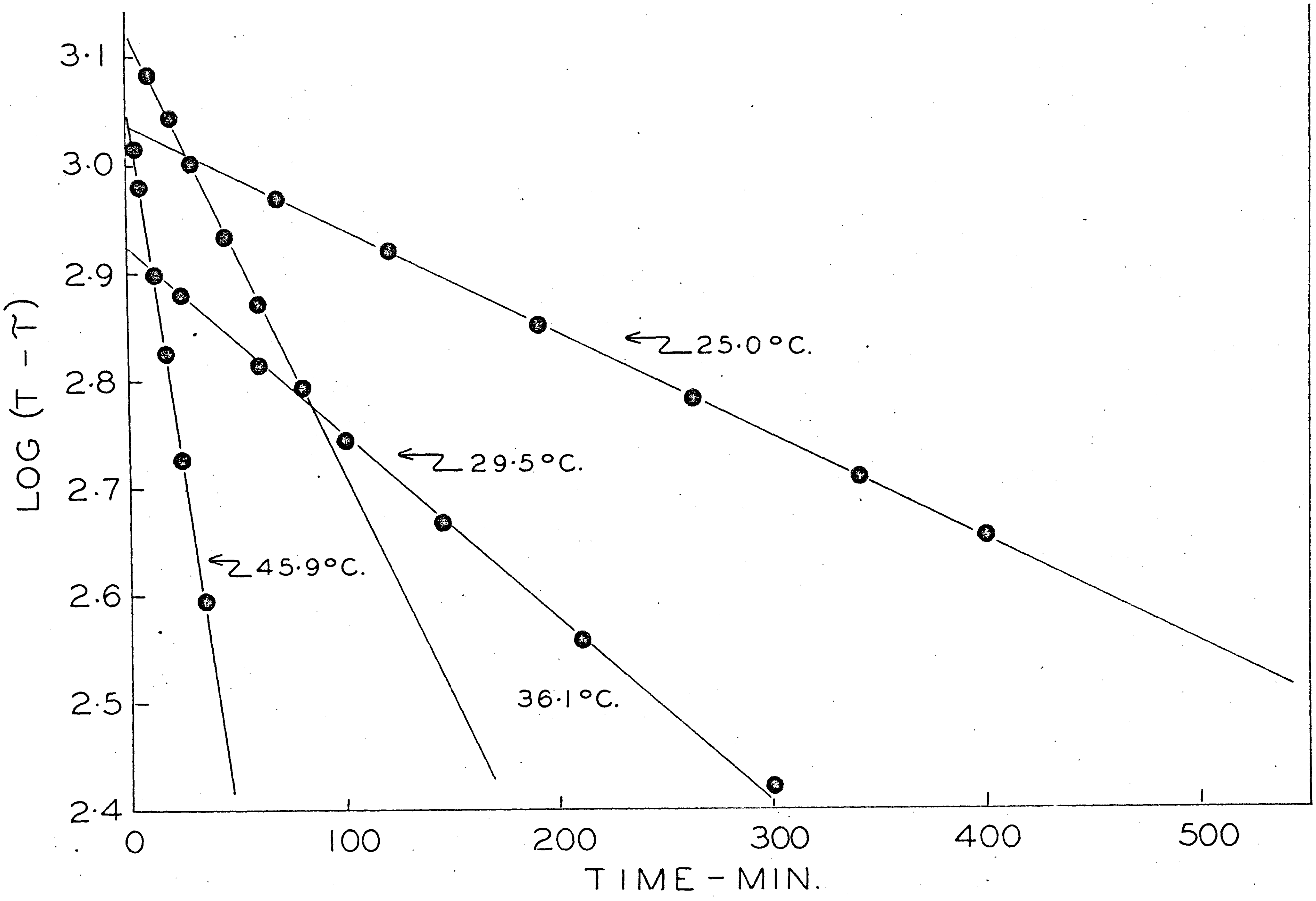


Fig. 17. Isomerization of p,p'-Azoxytoluene in Toluene

## TABLE XV

## CIS-TRANS ISOMERIZATION OF p,p'-AZOXYTOLUENE IN HEXANOL

| Temp. (°C.) | Time (min.) | log (T - τ) |
|---|---|---|
| 45.97 | 5 | 2.776 |
| | 30 | 2.586 |
| | 45 | 2.468 |
| | 65 | 2.316 |
| | 96 | 2.000 |
| 35.35 | 15 | 2.785 |
| | 35 | 2.743 |
| | 65 | 2.683 |
| | 102 | 2.579 |
| | 141 | 2.384 |
| 25.03 | 120 | 2.812 |
| | 240 | 2.750 |
| | 290 | 2.714 |
| | 365 | 2.685 |
| | 458 | 2.644 |
| | 620 | 2.559 |

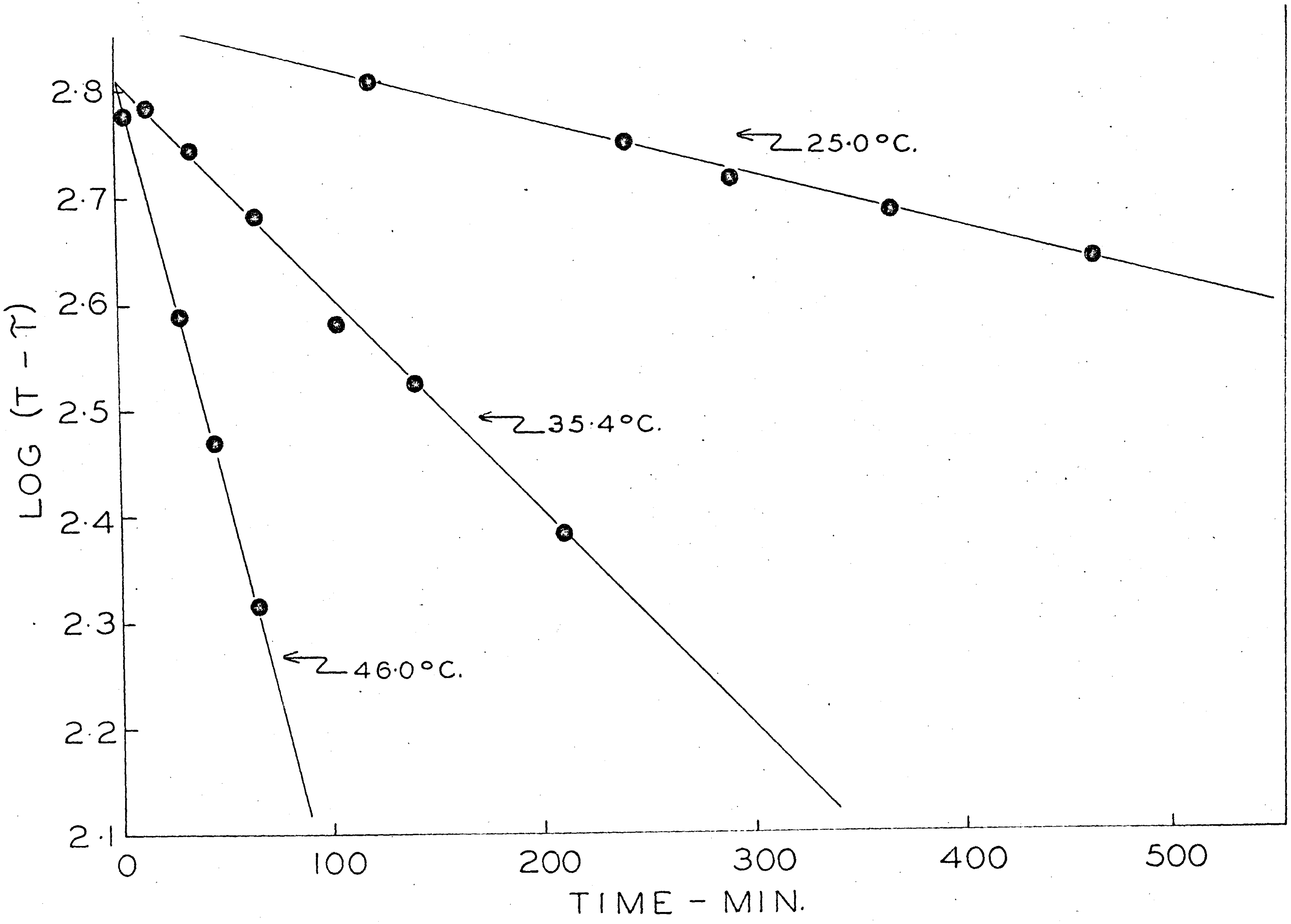


Fig. 18. Isomerization of p,p'-Azoxytoluene in Hexanol

## TABLE XVI

## CIS-TRANS ISOMERIZATION OF p,p'-AZOXYTOLUENE IN ACETONITRILE

| Temp. (°C.) | Time (min.) | log(T-$\tau$) |
|---|---|---|
| 58.65 | 5.50 | 2.958 |
| | 11.50 | 2.880 |
| | 18.50 | 2.801 |
| | 27.50 | 2.697 |
| | 35.50 | 2.594 |
| 45.85 | 12 | 2.979 |
| | 30 | 2.934 |
| | 45 | 2.887 |
| | 70 | 2.818 |
| | 100 | 2.747 |
| | 130 | 2.666 |
| 35.35 | 70 | 2.954 |
| | 135 | 2.917 |
| | 255 | 2.829 |
| | 357 | 2.760 |
| | 477 | 2.668 |
| | 638 | 2.551 |
| 29.50 | 100 | 2.982 |
| | 205 | 2.945 |
| | 350 | 2.898 |
| | 486 | 2.857 |
| | 652 | 2.799 |
| | 799 | 2.760 |

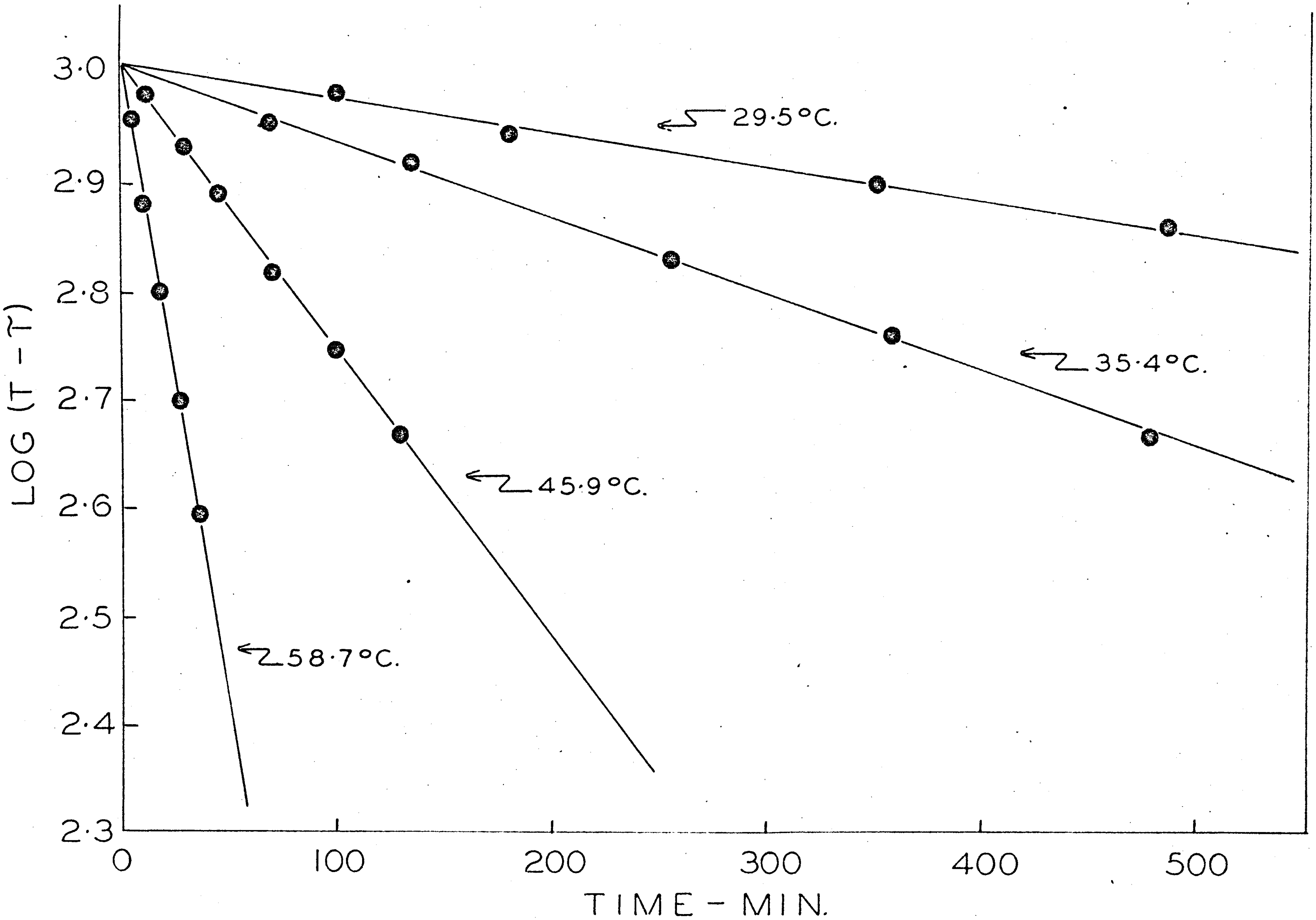


Fig. 19. Isomerization of p,p'-Azoxytoluene in Acetonitrile

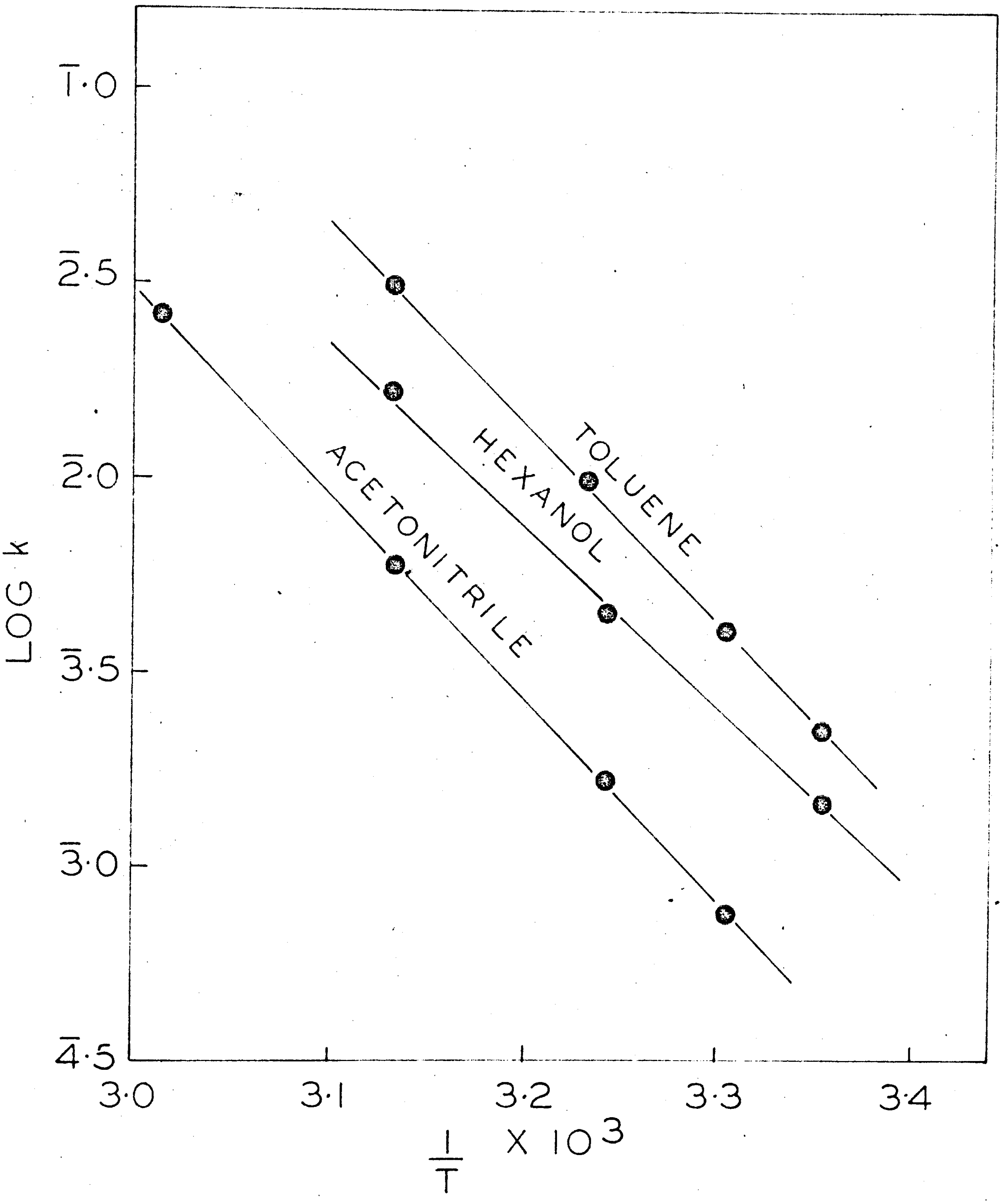


Fig. 20. Typical Arrhenius Lines for the Isomerization of p,p'-Azoxytoluene in Different Solvents

## TABLE XVII

## ISOMERIZATION OF p,p'-AZOXYTOLUENE IN VARIOUS SOLVENTS

## SUMMARY OF KINETIC DATA

| Solvent | Temp. °C. | k min.$^{-1}$ | log k | $E_{calc.}$ k.cal./mole | Probable Error in E k.cal./mole | $E_{graphical}$ | log A |
|---|---|---|---|---|---|---|---|
| Methanol | 59.0 | 0.0173 | $\bar{2}.238$ | 23.88 | 0.29 | 23.8 | 14.03 |
| | 45.85 | 0.004085 | $\bar{3}.611$ | | | | |
| | 29.50 | 0.000524 | $\bar{4}.719$ | | | | |
| Ethanol | 58.65 | 0.0294 | $\bar{2}.468$ | 23.21 | 0.87 | 23.4 | 13.84 |
| | 45.95 | 0.00777 | $\bar{3}.891$ | | | | |
| | 45.85 | 0.00756 | $\bar{3}.879$ | | | | |
| | 29.50 | 0.000980 | $\bar{4}.991$ | | | | |
| Acetonitrile | 58.65 | 0.0260 | $\bar{2}.415$ | 24.12 | 0.17 | 24.1 | 14.36 |
| | 45.85 | 0.00601 | $\bar{3}.779$ | | | | |
| | 35.35 | 0.001655 | $\bar{3}.219$ | | | | |
| | 29.50 | 0.000759 | $\bar{4}.880$ | | | | |
| Hexanol | 45.97 | 0.0167 | $\bar{2}.223$ | 23.85 | 0.17 | 23.5 | 14.60 |
| | 35.35 | 0.00442 | $\bar{3}.648$ | | | | |
| | 25.03 | 0.00116 | $\bar{3}.064$ | | | | |
| Benzene | 45.85 | 0.0241 | $\bar{2}.381$ | 23.44 | 0.10 | 23.4 | 14.50 |
| | 36.13 | 0.0753 | $\bar{3}.877$ | | | | |
| | 29.53 | 0.00320 | $\bar{3}.505$ | | | | |

## TABLE XVII, continued

| Solvent | Temp. °C. | k min.$^{-1}$ | log k | $E_{calc.}$ k.cal./ mole | Probable Error in E k.cal./ mole | $E_{graphical}$ | log A |
|---|---|---|---|---|---|---|---|
| Benzene, cont. | 25.03 | 0.00178 | $\bar{3}.251$ | | | | |
| Toluene | 45.85 | 0.0308 | $\bar{2}.489$ | 23.68 | 0.48 | 23.6 | 14.75 |
| | 36.13 | 0.00967 | $\bar{3}.985$ | | | | |
| | 29.52 | 0.00394 | $\bar{3}.596$ | | | | |
| | 25.03 | 0.00223 | $\bar{3}.349$ | | | | |
| Butanol | 46.04 | 0.0118 | $\bar{2}.072$ | 23.22 | 0.57 | 23.1 | 14.01 |
| | 45.85 | 0.0119 | $\bar{2}.076$ | | | | |
| | 35.35 | 0.00323 | $\bar{3}.509$ | | | | |
| | 29.50 | 0.00155 | $\bar{3}.190$ | | | | |
| | 25.03 | 0.000875 | $\bar{4}.942$ | | | | |
| Cyclohexane | 35.31 | 0.0256 | $\bar{2}.408$ | 22.12 | 0.41 | 22.9 | 14.14 |
| | 25.03 | 0.007495 | $\bar{3}.875$ | | | | |
| | 15.49 | 0.002155 | $\bar{3}.333$ | | | | |
| Heptane | 35.35 | 0.0273 | $\bar{2}.436$ | 22.67 | 0.66 | 22.9 | 14.54 |
| | 25.03 | 0.00792 | $\bar{3}.899$ | | | | |
| | 15.49 | 0.002162 | $\bar{3}.335$ | | | | |

## DISCUSSION

The effect of solvent on the rate of isomerization of p-chlorobenzenediazocyanide will be discussed first, followed by a discussion of the isomerization studies with azoxybenzene and p,p'-azoxytoluene. This arrangement is convenient since the solvents used in the isomerization of p-chlorobenzenediazocyanide were different from the solvents used with the other two compounds. In the isomerization reaction of p-chlorobenzenediazocyanide the solvents used were non-ionizing. While the same series of solvents was used for the studies with azoxybenzene and p,p'-azoxytoluene they varied widely within the series in respect of physical properties. The results of these three isomerization reactions will then be compared and contrasted with other similar studies.

The internal pressures of the solvents used were calculated using the equation $P_S = E/V$ where E is the energy of vaporization and V is the molar volume. The data employed in calculating the internal pressures at 35°C. are given in Table XVIII. The heat of vaporization ($H_{vap.}$) and the molar volume (V) of the liquids were obtained from the International Critical Tables and the Landolt-Bornstein Tables. Where the value of $H_{vap.}$ for a solvent at 35°C. was not available, it was estimated from vapour pressure data. The energy of vaporization, E, was

## TABLE XVIII

## INTERNAL PRESSURE DATA AT 35°C.

| Solvent | $H_{vap.}$ (cal./ mole) | E (cal./ mole) | V (cc.) | $P_S$ (cal./ cc.) | $(P_S)^{1/2}$ |
|---|---|---|---|---|---|
| Heptane | 8525 | 7912 | 149.6 | 52.9 | 7.27 |
| Cyclohexane | 7550 | 6937 | 110.0 | 63.0 | 7.94 |
| Butanol | 12580 | 11967 | 92.6 | 129.2 | 11.35 |
| Ethanol | 9985 | 9372 | 59.2 | 158.5 | 13.60 |
| Hexanol | 16340 | 15727 | 126.6 | 124.3 | 11.14 |
| Acetonitrile | 7980 | 7367 | 53.5 | 137.8 | 11.73 |
| Methanol | 8830 | 8217 | 41.1 | 200.0 | 14.14 |
| Chloroform | 7382 | 6769 | 81.7 | 82.8 | 9.10 |
| Chlorobenzene | 10080 | 9467 | 103.0 | 91.0 | 9.54 |
| O-dichlorobenzene | 9610 | 9690 | 113.1 | 85.8 | 9.26 |
| Benzene | 8000 | 7387 | 90.75 | 81.4 | 9.02 |
| Toluene | 9230 | 8617 | 108.2 | 79.6 | 8.92 |

then calculated using the approximate relation, $E = H_{vap.} - RT$.

The dielectric constants of the different solvents obtained from the International Critical Tables are summarized in Table XIX. The values for the dielectric constants are recorded for temperatures of 20°C. or 25°C., but since the dielectric constant varies only slightly with temperature (6), no corrections were applied when comparing them with rate data at 35°C.

## ISOMERIZATION OF p-CHLOROBENZENEDIAZOCYANIDE

When solutions of the cis isomer were dissolved in cyclohexanone, pyridine, or nitromethane, the change in optical density of the solutions at 4500 Å were so rapid that measurements could not be made. After several minutes these solutions became highly coloured. On the other hand, the absorption spectra of trans p-chlorobenzenediazocyanide in cyclohexanone and pyridine are shown in Figures 21 and 22 where the log of the optical density is plotted as a function of the wave length. The characteristic absorption maxima at 4500 Å, as well as the lack of colour formation, are indications that decomposition of the trans isomer did not occur in these solvents. When solutions containing 0.08 gm./l. of the cis isomer were made in cyclohexane, chlorobenzene, o-dichlorobenzene, heptane or chloroform, the initial optical densities were observed to be approximately the same and no colour formation occurred. These observations

## TABLE XIX

## DIELECTRIC CONSTANTS

| Solvent | Dielectric Constants | |
|---|---|---|
| | D | D-1/2D+1 |
| Heptane | 1.9 | 0.183 |
| Cyclohexane | 2.05 | 0.206 |
| Butanol | 17.0 | 0.457 |
| Ethanol | 25.0 | 0.471 |
| Hexanol | 10.1 | 0.428 |
| Acetonitrile | 37.0 | 0.479 |
| Methanol | 33.0 | 0.477 |
| Chloroform | 5.05 | 0.650 |
| Chlorobenzene | 5.9 | 0.383 |
| O-dichlorobenzene | 7.5 | 0.465 |
| Benzene | 2.28 | 0.230 |
| Toluene | 2.39 | 0.241 |

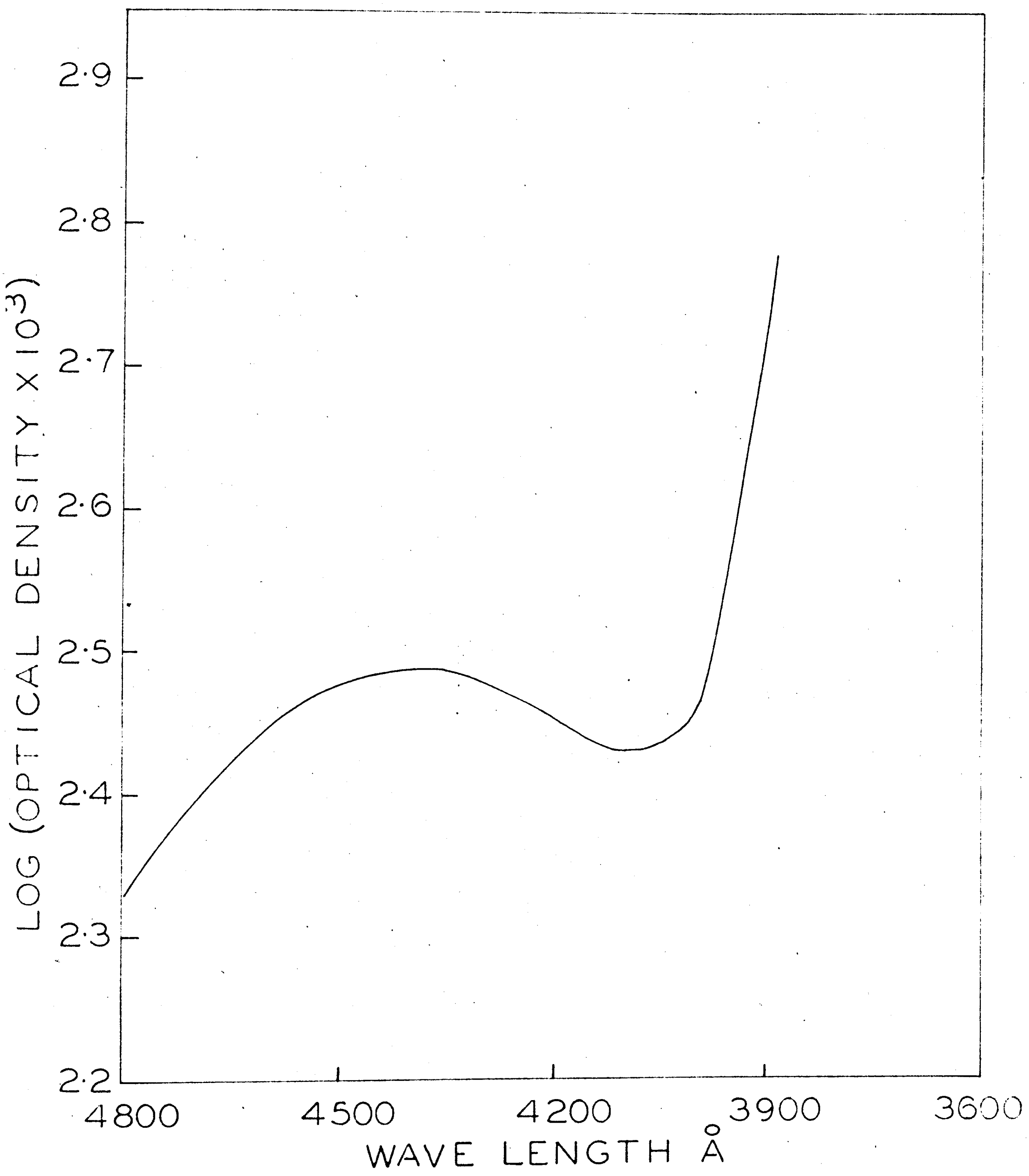


Fig. 21 Absorption Spectra of Trans-p-Chlorobenzenediazocyanide in Cyclohexanone

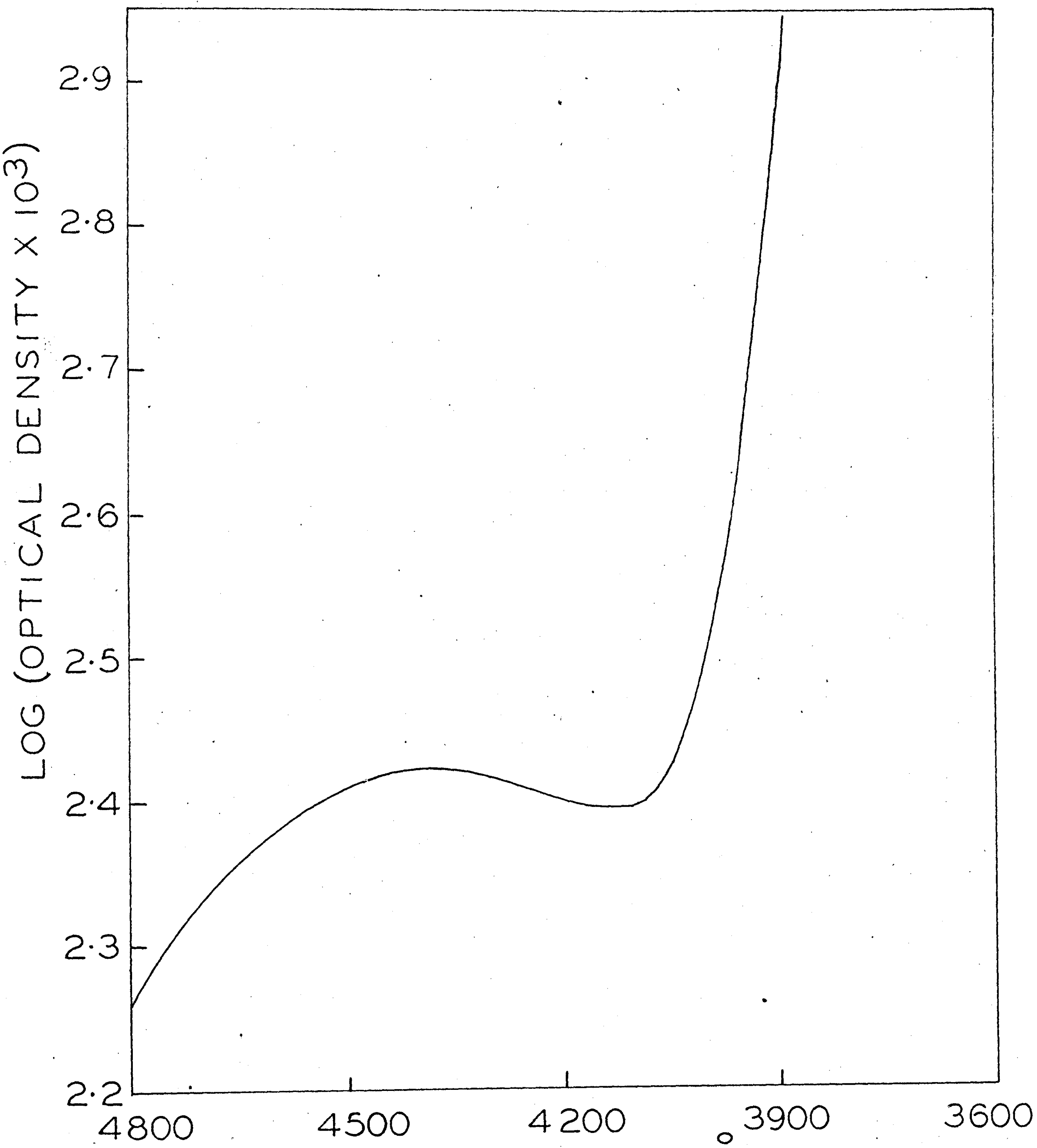
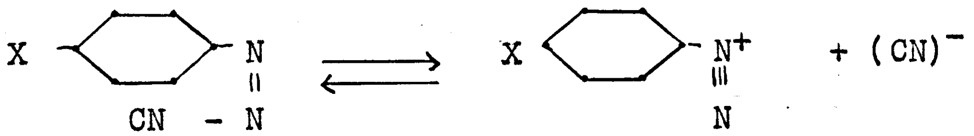


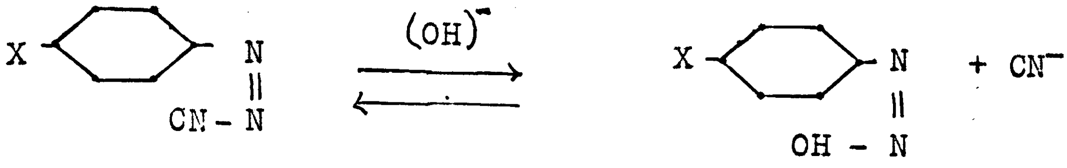
Fig. 22. Absorption Spectra of Trans p-Chlorobenzenediazocyanide in Pyridine

suggest that the cis isomer decomposes in ionizing solvents, while the trans isomer is stable both in ionizing and non-ionizing solvents.

Stephenson and Waters (17), have studied the decomposition of several cis and trans derivatives of benzenediazocyanide in a variety of solvents. They observed that while the cis isomer in acetone and methanol decomposes spontaneously in the dark, the trans isomer decomposes only slightly in the same solvents. This slight decomposition was attributed to oxidation in the solutions. The cis diazocyanides dissolved in carbon tetrachloride and benzene isomerized completely to the trans form in the dark and in the presence of light. Stephenson and Waters account for the difference in behaviour of the cis diazocyanides in ionizing and non-ionizing solvents on the basis that there is a tautomeric equilibrium with the unstable salt, the diazoniumcyanide



Because the cis diazocyanides, in contrast to the trans form, yield conducting solutions, and the decomposition of the cis isomers is not inhibited by the presence of considerable quantities of nitric acid, Waters distinguishes the above tautomeric equilibrium from a hydrolysis reaction of the type,



As mentioned in the introduction, the cis-trans isomerization of p-chlorobenzenediazocyanide was investigated kinetically in a variety of solvents by LeFevre and Northcott (50) who followed the progress of the reaction by the changes in the dielectric constants of the solutions. It is interesting to compare their results with those obtained by the spectrophotometric method used in the present investigation.

They observed first order kinetics with frequency factors between $10^{12}$ and $10^{15}$ $sec^{-1}$ and activation energies ranging from 21 to 26 Kcal./mole. No regular correlations of solvent properties with k or E were discerned. The relative order of the rate constants in the different solvents at 45°C. were: chlorobenzene > cyclohexane > carbon tetrachloride > chloroform > benzene > o-dichlorobenzene pyridine > cyclohexanone. This order changed somewhat at 25°C. By assuming that the internal pressure of the activated complex exceeds the internal pressure of the products, LeFevre and Northcott succeed in achieving a qualitative correlation between the rate of the isomerization and the internal pressure of the solvents.

The kinetic data obtained by the spectrophotometric method for the cis-trans isomerization of p-chlorobenzene-diazocyanide in six solvents have been summarized in Table IX. In this group of solvents the rate increased five fold in passing from cyclohexane to chloroform. The activation energy varied from 22.5 to 20 K.cal./mole., while the frequency factor ranged from $1.5 \times 10^{12}$ to $1.5 \times 10^{13}$ $\text{min.}^{-1}$. The relative magnitude of the rate constants for the solvents used were: chloroform $>$ o-dichlorobenzene $>$ chlorobenzene $>$ benzene $>$ heptane $>$ cyclohexane, and this order was maintained over a 30° temperature interval.

Not only are there serious discrepancies between the data from the present study and those of LeFevre in the relative rates in the same series of solvents, but rate data for the isomerization reaction in pyridine and cyclohexanone could not be obtained at all spectrophotometrically. Since Stephenson and Waters (17) have shown that the decomposition of the cis diazocyanides in ionizing media is a general behaviour, it appears that measuring the rates of these reactions by following the changes in dielectric constant of the solutions is not an entirely reliable method.

The activation energies in the two studies are in reasonable agreement, considering that two of the three solvents in which the activation energy is in excess of 25 K.cal. in the work of LeFevre were omitted from the present investigation.

Theoretically it has been shown that quantitative relations for the effect of solvent on the rate of a unimolecular reaction can be derived for two different cases. (a) When the van der Waals forces predominate, the rate of the reaction is determined by the internal pressure of the solvent and from Equation 25, it is apparent that the direction in which the change occurs depends upon the relative internal pressures of the activated complex and reactant. In many cases the properties of the activated complex can be estimated a priori and the sense in which the rate changes with a change in internal pressure of the solvent can be predicted. If the activation energies for unimolecular reactions in regular solutions which show solvent effects can be determined accurately, the relations between the Arrhenius parameters, A and E, and the internal pressure, $(P_S)^{1/2}$ will apply.

(b) When the forces in solution which determine the rate of reaction are electrostatic in nature, the expression relating the rate to these forces in a reaction of the type

$$A \longrightarrow M^{\ddagger} \longrightarrow \text{products}$$

is given by Equation 11 and a plot of log k against D-1/2D+1 should give a straight line.

In practice, there is with certain solvents a parallelism between internal pressure and dielectric constant (19) in which case it is not possible to ascribe the influence on rate to a particular type of force. However, even if Equations 11 and 25 are not obeyed exactly they may be utilized to indicate qualitatively the influence of a solvent in terms of the internal pressure and the dielectric constant.

In Figure 23 log k for the isomerization of p-chlorobenzenediazocyanide at 35°C. is plotted as a function of the internal pressures of the solvents $(P_S)^{1/2}$, while in Figure 24 log k at 35°C. is plotted as a function of D-1/2D+1. Figure 23 shows that there is a trend towards increased rate of isomerization with increase in the internal pressure of the solvent. Unfortunately, owing to the limited type of solvents that could be used, it was not found possible to extend the range of internal pressure values sufficiently to evaluate adequately the possible significance of this trend. On the other hand, the linear relation obtained between log k and D-1/2D+1 in Figure 24 would seem to indicate that the forces which primarily determine the rate are electrostatic in nature. The discrepancies in the rates of reaction in heptane and cyclohexane should probably not be considered to invalidate the relation since the range of dielectric constants in which the reaction rates were measured was large, and Bell (64) has shown theoretically that Equation 11 does not hold for solvents of low dielectric constants. Nevertheless, since the dielectric constant of

## KEY TO SOLVENTS

1. Heptane
2. Cyclohexane
3. Butanol
4. Ethanol
5. Hexanol
6. Acetonitrile
7. Methanol
8. Chloroform
9. Chlorobenzene
10. o-Dichlorobenzene
11. Benzene
12. Toluene

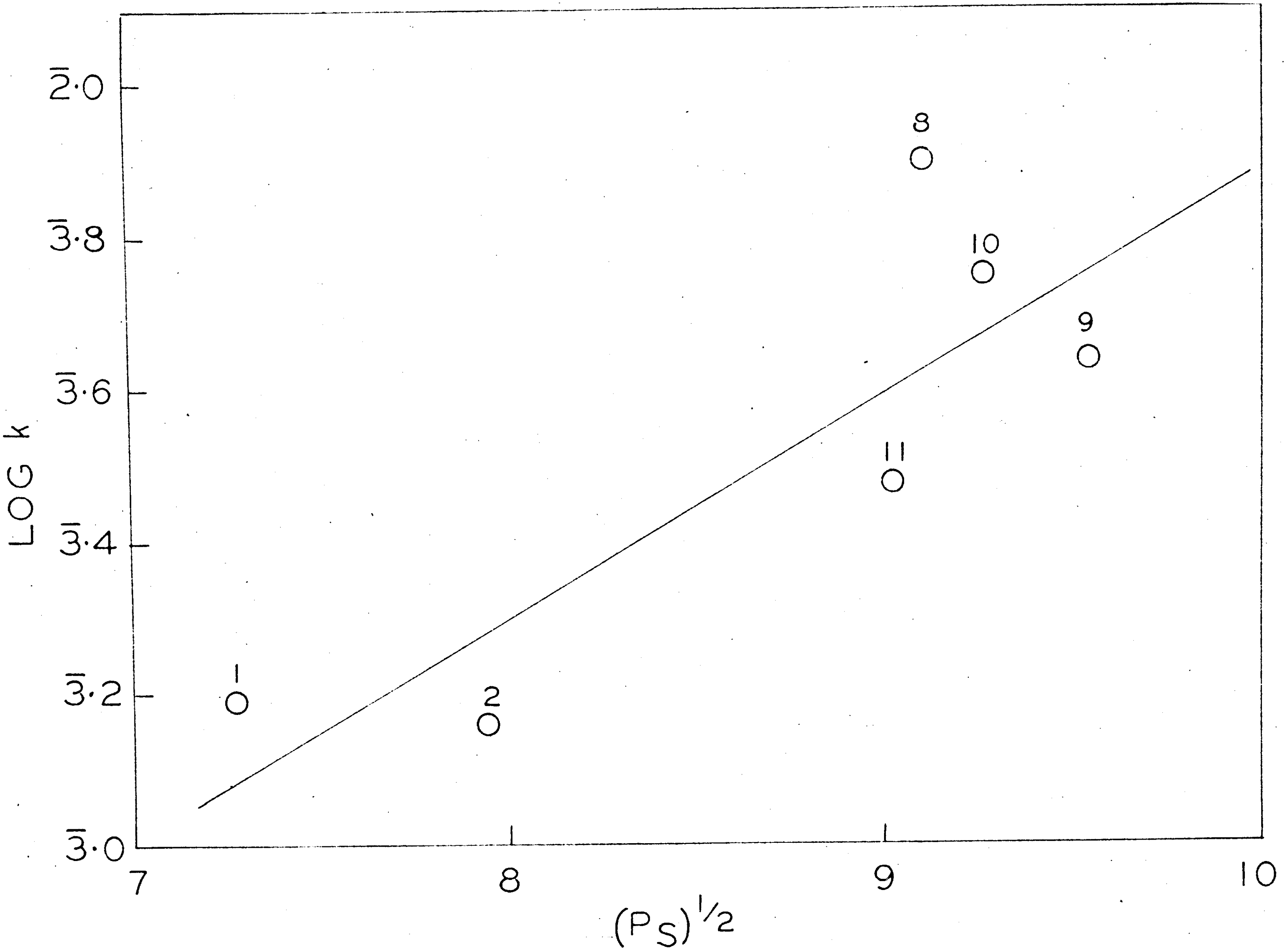


Fig. 23. Relation between log k and $(P_S)^{1/2}$ at 35°C. for the Isomerization of p-Chlorobenzenediazocyanide in Different Solvents

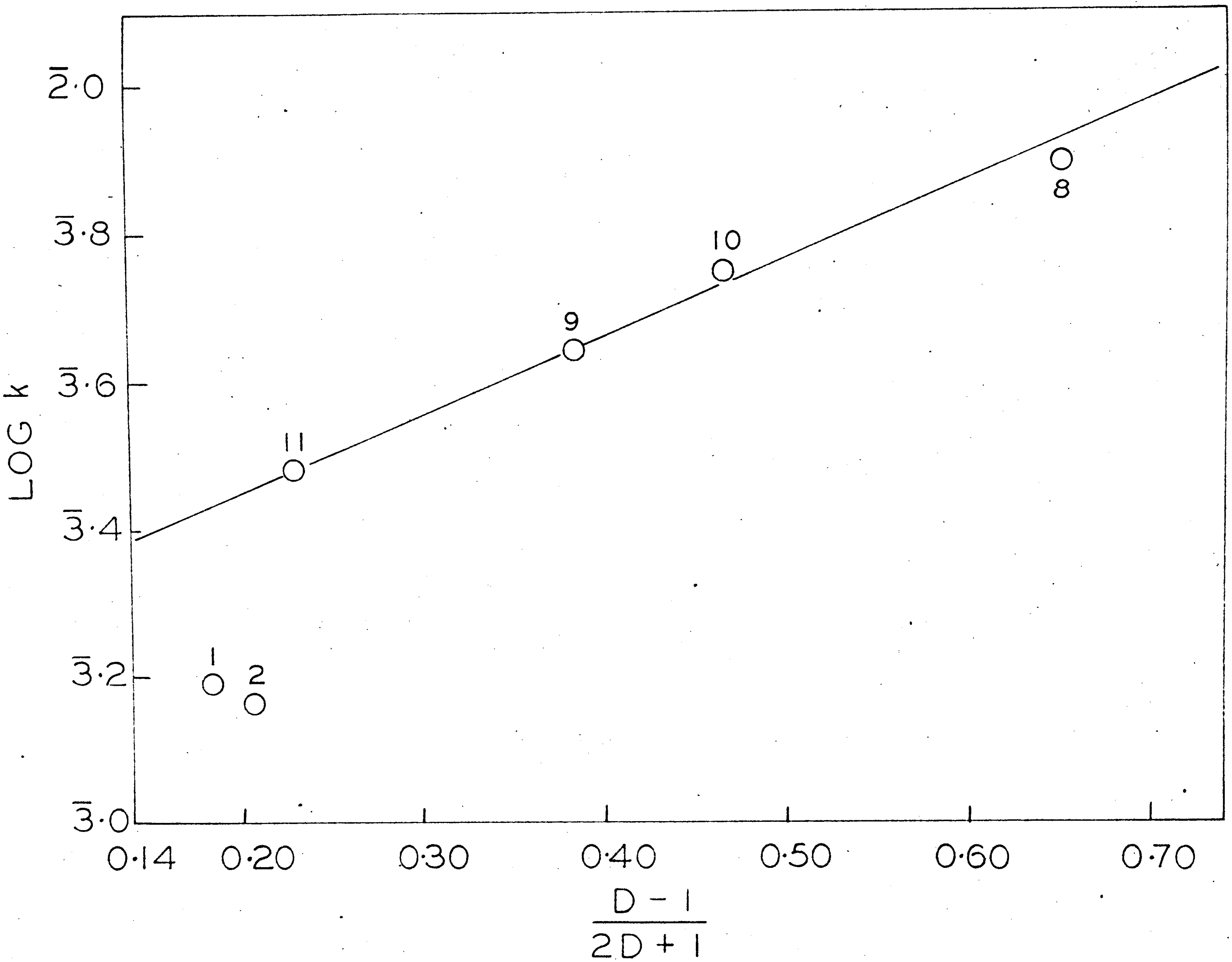


Fig. 24. Relation between log k and $\frac{D-1}{2D+1}$ at 35°C. for the Isomerization

benzene is only slightly higher than that of heptane or of cyclohexane, the different behaviour of the reaction in the latter two solvents appears to be real.

A possible explanation for the different behaviour of the reaction in heptane and cyclohexane may be suggested. When log k is plotted against E for the reaction in various solvents as shown in Figure 25, and approximate linear relation is obtained except for reaction in heptane and cyclohexane. It seems possible that in these two solvents the degree of solvation of the reactant is low compared with the other solvents, as a consequence of which the activation energies for the reactions are less in these two solvents.

The slope of the plot of log k against D-1/2D+1 is given by the expression

$$\frac{d \ln k}{d\ (D-1/2D+1)} = -\frac{1}{k'T}\ \frac{\mu^2{}_A}{r^3{}_A} - \frac{\mu^2{}_{M^\ddagger}}{r^3{}_{M^\ddagger}} ,$$

where the quantities are as previously defined. The slope of the line may be positive or negative according as the dipole moment of the activated complex is larger or smaller than the dipole of the reactant. The slope of the line in Figure 24 is positive from which it might be inferred that the dipole moment of the activated complex is larger than that of the reactant.

Consideration of the dipole moments of the reactant (2.39 Debye units) and the product (3.73 Debye units) leads

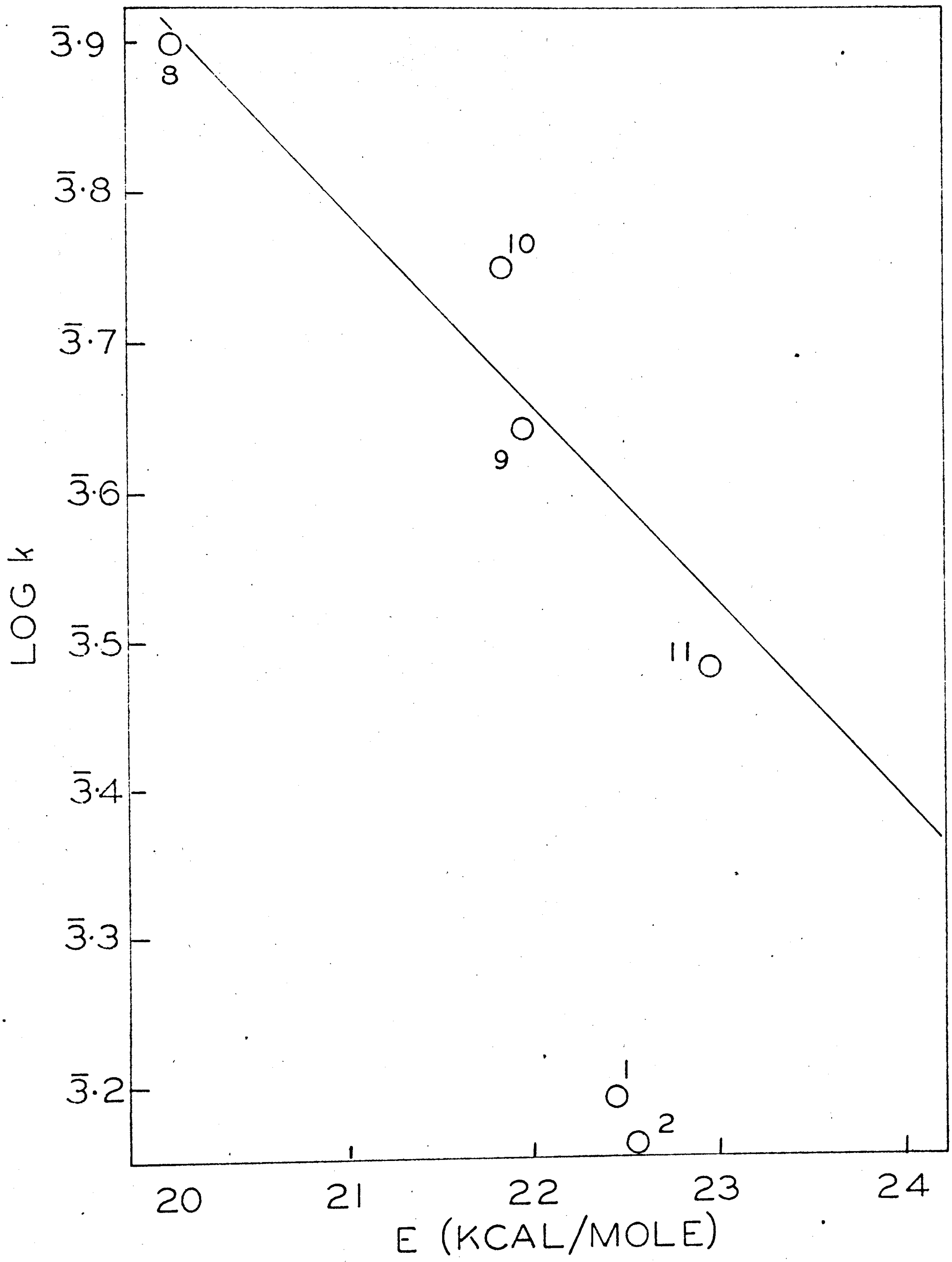


Fig. 25. Relation between log A and E for the Isomerization of p-Chlorobenzenediazocyanide in Different Solvents

to the same conclusion. The activated complex presumably has properties intermediate between the cis and the trans form, hence its dipole moment would be expected to be greater than that of the reactant. This, in turn presumably means that the internal pressure of the activated complex is greater than that of the reactant, since the internal pressure generally increases with polarity (19).

A comparison of the slope of the line in Figure 23 with Equation 25 agrees with the inference just made that the internal pressure of the activated complex is greater than that of the reactant.

For Equation 25 to hold exactly, the distribution and orientation of the molecular species must be completely random (28), but as shown in Figure 24, the rate of the reaction strongly depends upon the polar forces in solution and Equation 25 can hardly be expected to hold rigorously under these conditions.

As a further indication that the rate of isomerization of p-chlorobenzenediazocyanide is not largely governed by the van der Waals forces, the relations between log A and $(P_S)^{1/2}$ or between E and $(P_S)^{1/2}$ did not even approximate to the linearity expected if these forces alone governed the isomerization reaction (33).

Additional information about the role of the solvent in a reaction can be obtained by interpreting the manner in which the Arrhenius parameters, k, A and E vary when a reaction is studied in a series of solvents. In view of a lack of such data for non-ionic unimolecular reactions (7), any correlation between log A and E for the isomerization of p-chlorobenzenediazocyanide is of particular interest.

Figure 26 shows a linear relation between log A and E for the isomerization of p-chlorobenzenediazocyanide in six solvents. The small deviations in heptane and cyclohexane are not serious since, in calculating the frequency factor from the expression

$$\log A = \log k + \frac{E}{2.303\ RT}$$

a small error in E will produce a relatively large error in log A. Because of a possible error of 250 calories in a total variation of E of approximately 2,500 calories, the linear relation between log A and E can be considered satisfactory.

The conditions, according to Fairclough and Hinshelwood (8), for a linear relation between log A and E have been outlined in the introduction. A possible interpretation of these conditions has been suggested by Remick (Ref. 67, Chap. VII).

The increase in activation energy in Figure 26 which is attributable to a change in the solvent, presumably corresponds to an increase in the - N = N - bond strength. This in turn would mean an increase in the vibrational

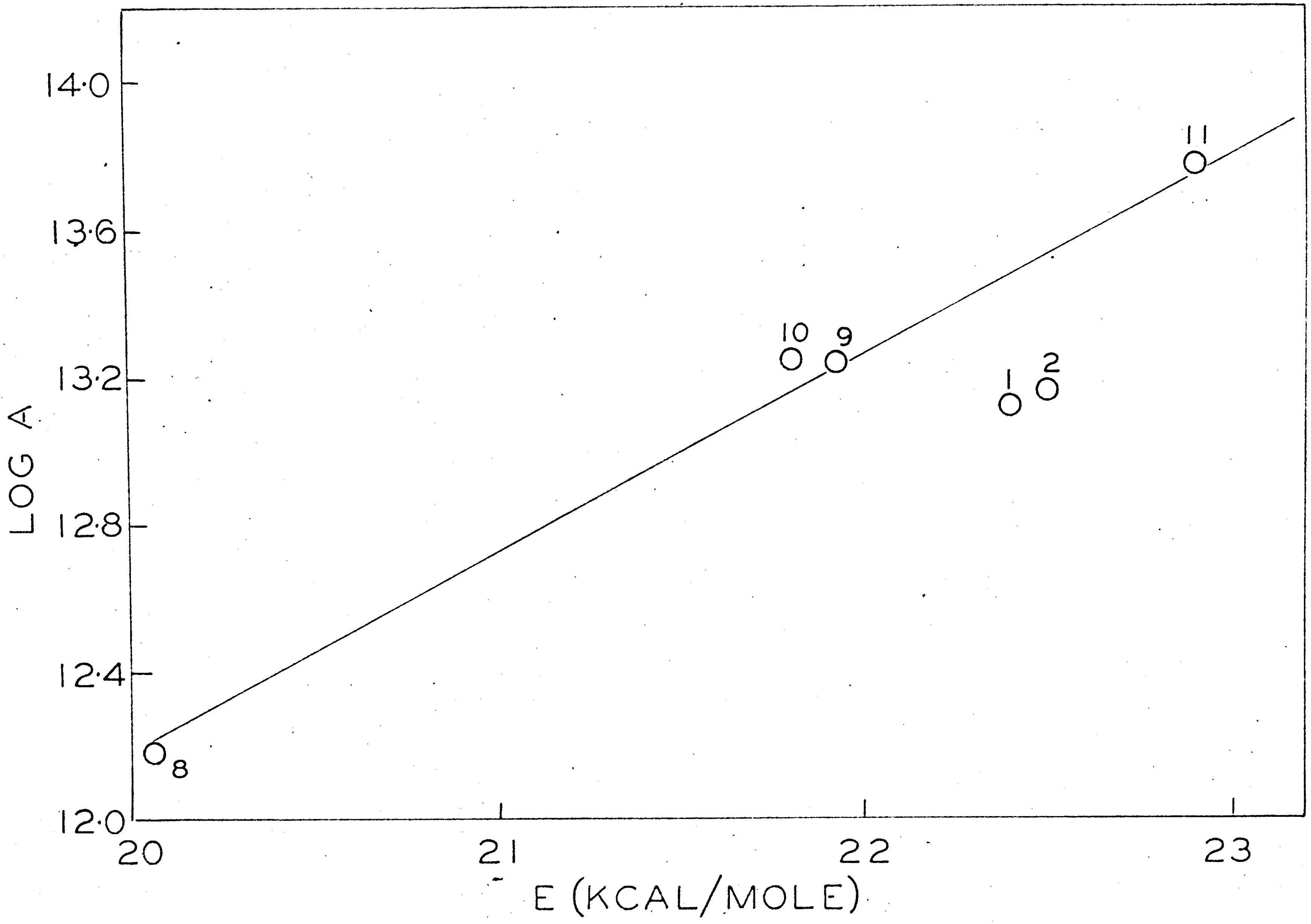


Fig. 26. Relation between log k at 35°C. and E for p-Chlorobenzenediazocyanide in Different Solvents

frequency of this bond. Remick points out that an increase in the vibrational frequency of the molecule increases the probability that the energy in the activated complex will find its way into the reacting bond before deactivation occurs, since the value of t, in the Fairclough-Hinshelwood probability term $e^{-t/\theta}$ is decreased. Hence, an increase in $e^{-t/\theta}$ of Equation 2, corresponding to an increase in log A, would be expected to accompany the increase in activation energy.

In more general terms Ogg and Rice (66) account for the variation in A and E as due to internal volume and solvation effects. According to their interpretation, if the reactants are solvated, an increase in A and E and a decrease in the rate would be expected as solvation is increased, while solvation of the activated complex should have the reverse effect. The linear relation between log A and E (Figure 26) and between log k and E (Figure 25) conform to an interpretation on the Ogg-Rice basis that in the isomerization reaction of p-chlorobenzenediazocyanide the reactant is solvated.

In Figure 27 the activation energy, E, is plotted as a function of $D-1/2D+1$. It is seen that the activation energy decreases as the dielectric constant of the solvent increases. From Figure 24 it was inferred that the dipole moment of the activated complex is larger than that of the reactant. Consequently the electrostatic and dipole interactions are greater between solvent and activated complex

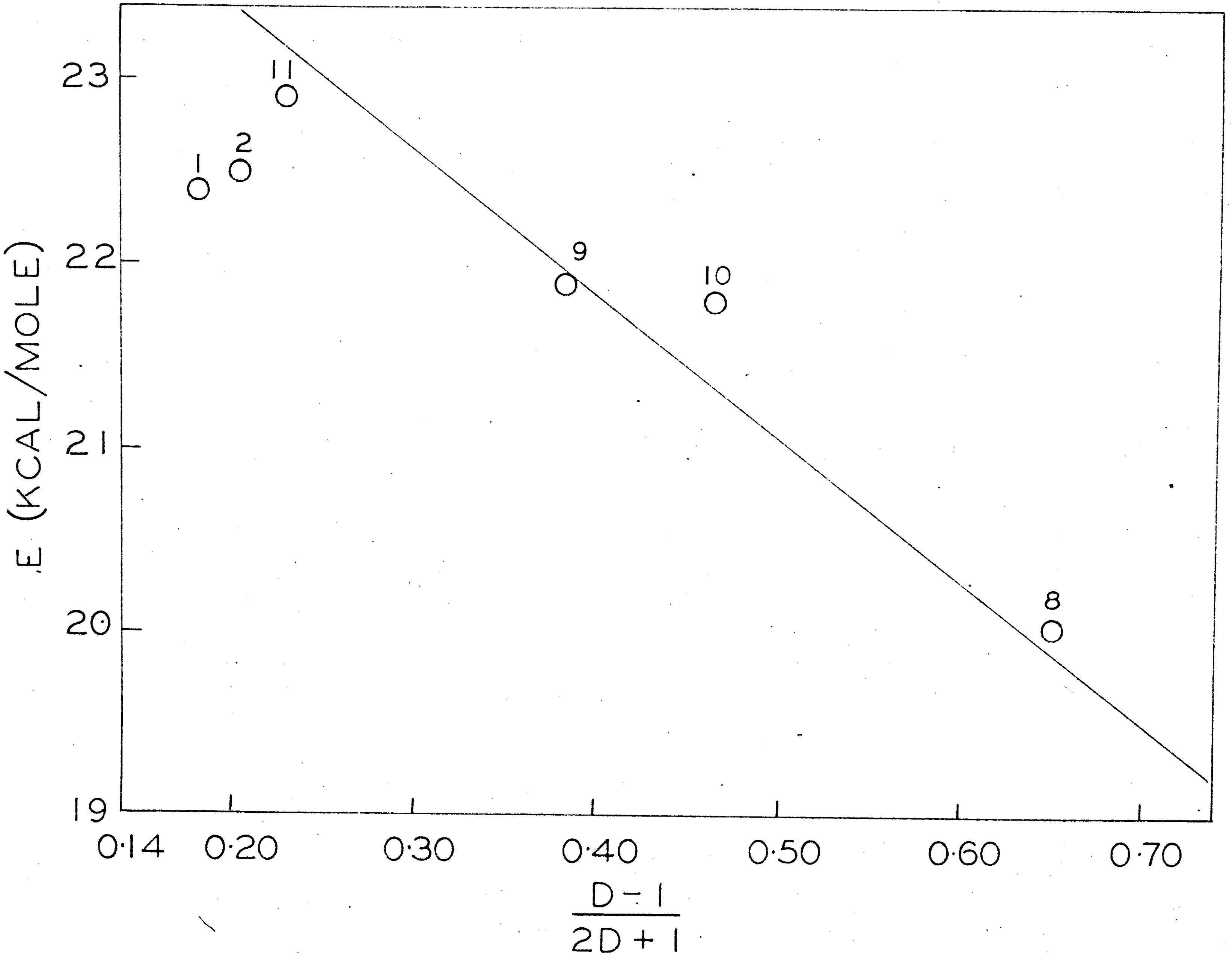


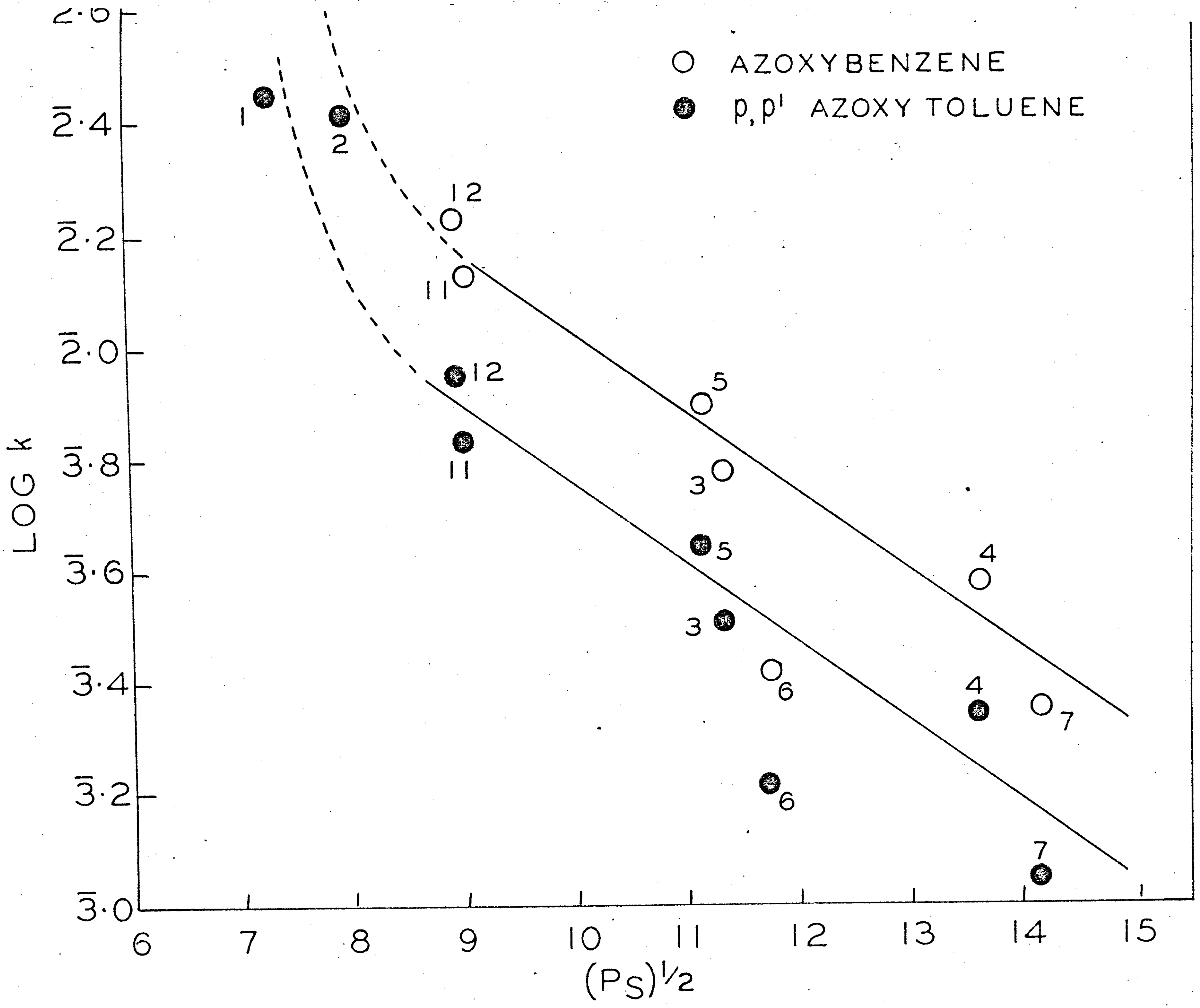
Fig. 27. Relation between E and $\frac{D-1}{2D+1}$ for the Isomerization of p-Chlorobenzene-

than between solvent and reactant. This interaction may result in a lowering of the potential energy of the activated complex with a consequent decrease in the activation energy that becomes greater as the dielectric constant of the solvent increases.

## ISOMERIZATION OF AZOXYBENZENE AND p,p'-AZOXYTOLUENE

The kinetic data for the cis-trans isomerization of azoxybenzene and p,p'-azoxytoluene in nine solvents have been summarized in Tables XIII and XVII. A twenty-five fold increase in the rate is observed for azoxybenzene in methanol as compared with heptane at 35°C. while a twenty fold change in rate is observed for the isomerization of p,p'-azoxytoluene in the same series of solvents at the same temperature. The activation energies for the two reactions range from 22.4 to 24.1 K.cal./mole.

Figure 28 shows that the rates of isomerization of azoxybenzene and p,p'-azoxytoluene follow closely the linear relation of log k against $(P_S)^{1/2}$ at 35°C. as predicted by the treatment of Halpern, Brady and Winkler (33). At an internal pressure, $(P_S)^{1/2}$ for the solvent of nine, both reactions show a sharp increase in rate corresponding to a small decrease in internal pressure. The curvature in the lines at the $(P_S)^{1/2}$ value for toluene seems to represent a transition from polar to non-polar solvents in the group of solvents used. This would further seem to indicate that in



log k and $(Ps)^{1/2}$ at 75°C for the Isomerization of non-polar solvents the increase in rate of reaction is greater than in polar solvents over a corresponding interval pressure. The deviation from the log k vs. $(P_S)^{1/2}$ relations observed for both reactions in acetonitrile are probably to be expected owing to the large dipole moment of acetonitrile. Halpern, Brady and Winkler found a similar discrepancy with acetonitrile in the isomerization of azobenzene (33).

The slope of the lines in Figure 28 are negative. Reference to Equation 25 indicates that the internal pressure of the activated complex of azoxybenzene and p,p'-azoxytoluene is less than that of the reactant. This conclusion might be anticipated from a consideration of the dipole moments of the cis and trans isomers (1.71, 1.74 and 4.68, 5.06 Debye unit respectively). It is noteworthy that in the isomerization reactions of azobenzene, azoxybenzene, p,p'-azoxytoluene and p-chlorobenzenediazocyanide, all involving isomerization at the N = N double bond, the tendency for the rate of the reaction to increase or decrease with the internal pressure of the solvent, as inferred from the dipole moments of the isomers, is experimentally confirmed.

A plot of E or log A as a function of $(P_S)^{1/2}$ , and of log A as a function of E, for azoxybenzene and p,p'-azoxytoluene does not reveal the correlation expected from the dependence of the rate upon the internal pressure and the similarity of these isomers to azobenzene. Since the total variation in both E and log A is small, the relative error in E, which is large and variable, is sufficient to mask a possible linear relation of log A or with $(P_S)^{1/2}$. In contrast, the large variation in the rate constants, together with the small relative error make a correlation between log k and $(P_S)^{1/2}$ readily discernible (Figure 28).

The extent to which the rate is influenced by entropy and activation energy changes can be seen qualitatively by plotting E as a function of log k. If changes in the rate of isomerization are due solely to the changes in the activation energy, the rate constants for the different solvents should lie on a line of slope 2.303 RT. If the frequency factor does not vary as a function of E or log k, there will be little correlation between log k and E. Figures 29 and 30 show such plots at 35°C., where the broken line represents the theoretical relation with slope 2.303 RT and the solid line represents an approximate graphical average obtained from the data in this investigation. A comparison of the slopes in Figure 29 with those in Figure 30 indicate that the isomerization of azoxybenzene is more influenced by entropy changes than the isomerization of p,p'-azoxytoluene.

## EFFECT OF SUBSTITUENTS

The specific rate of any reaction can be expressed by means of the equation,

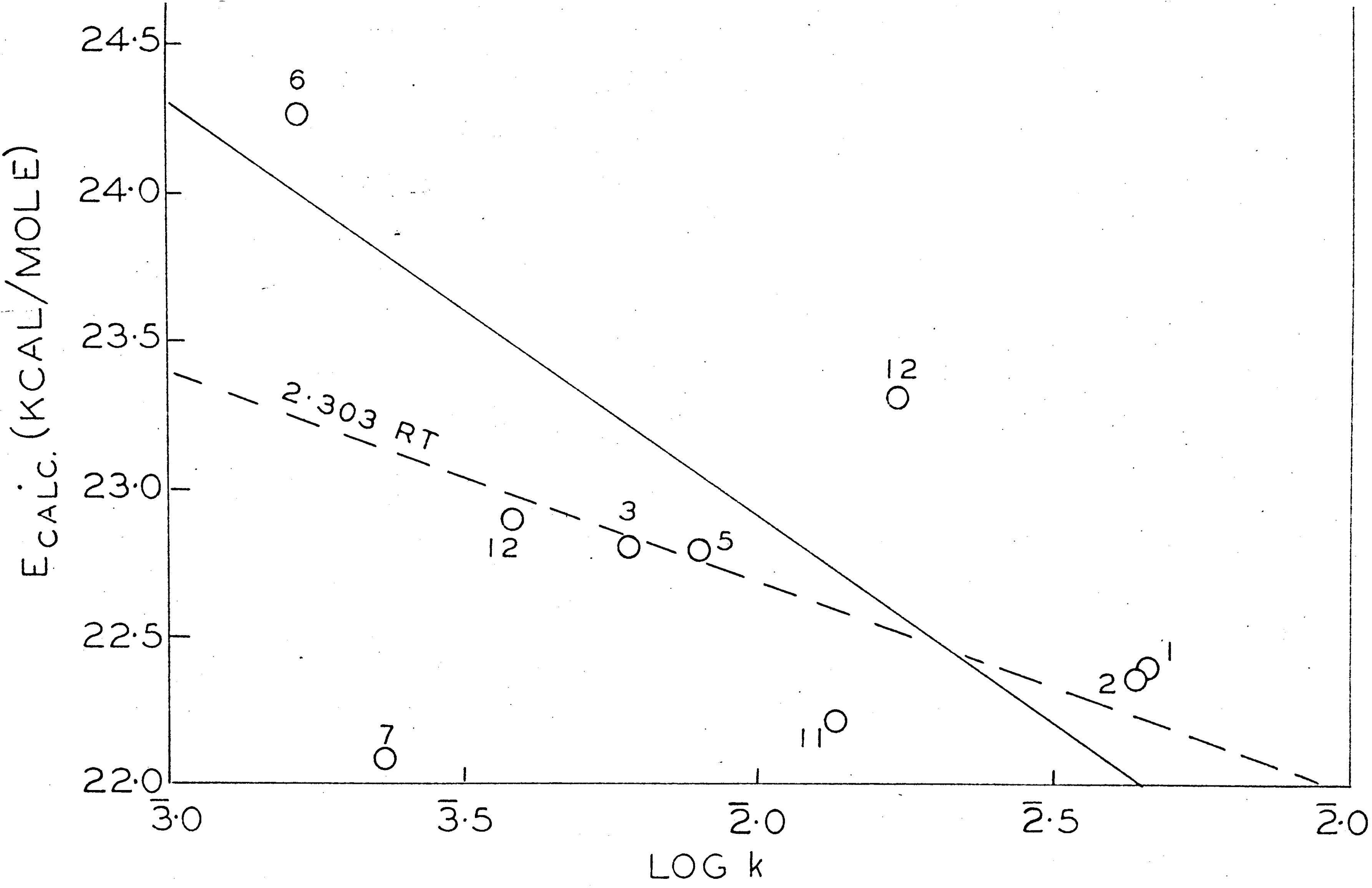


Fig. 29. Relation between $E_{calc.}$ and log k at 35°C. for the Isomerization of Azoxybenzene in Different Solvents

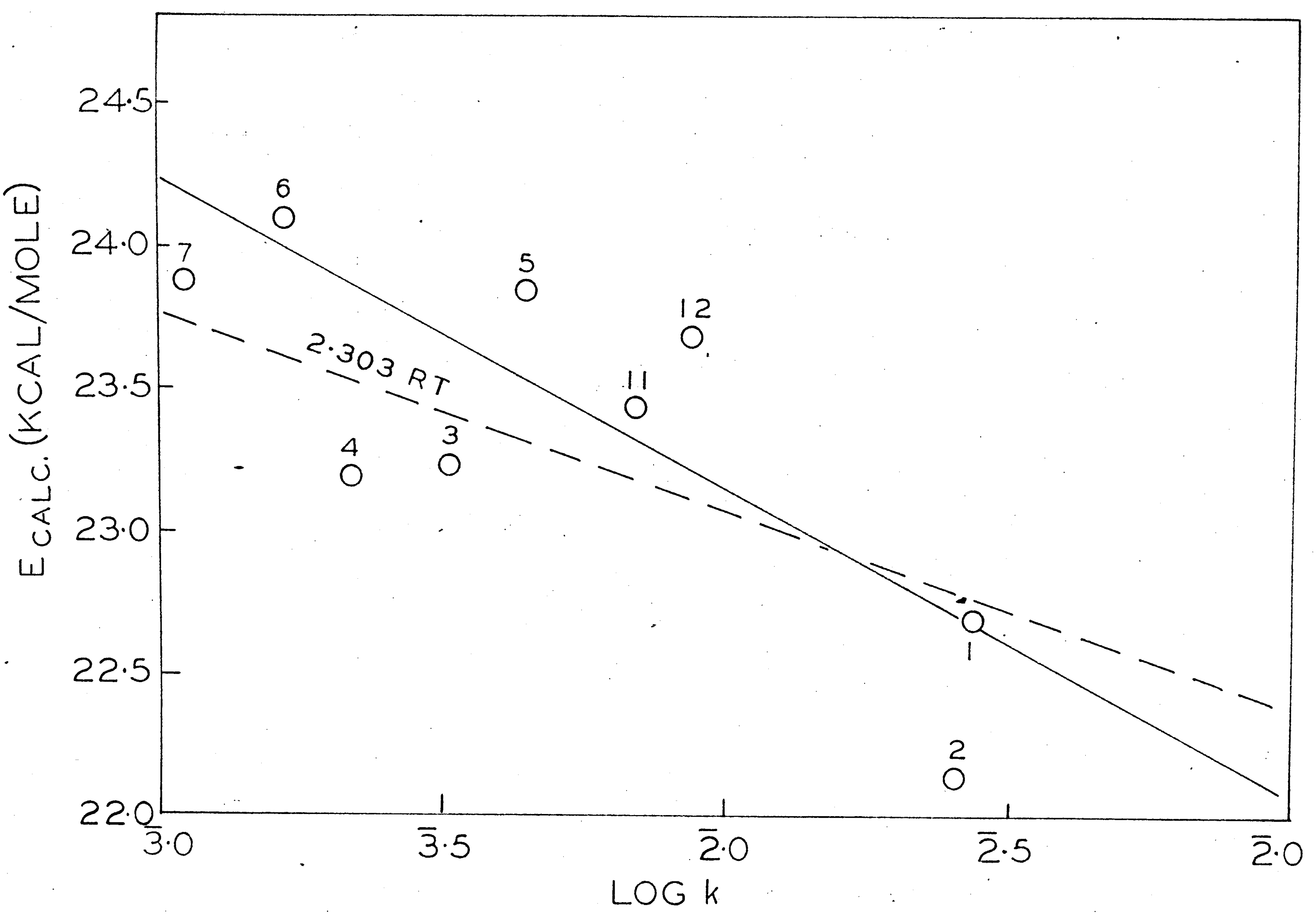


Fig. 30. Relation between $E_{calc.}$ and log k at 35°C. for the Isomerization of p,p'-Azoxytoluene in Different Solvents

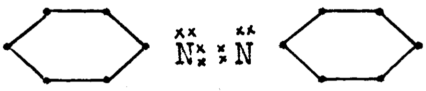
$$k = \frac{k'T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

where $\Delta S^{\ddagger}$ is the entropy of activation, and $\Delta H^{\ddagger}$ is the heat of activation. The effect of substitution can be reflected in changes in the heat or the entropy of activation. In many cases it has been found that the entropy of activation remains constant while the energy of activation varies (75). In other reactions both the activation energy and the entropy of activation vary in a parallel manner. The effect of substitution in a unimolecular reaction in solution has received little attention and from the data available no definite conclusion can be reached regarding variation of the frequency factor A and the activation energy with substitution.

A substituent may change the reactivity of a parent compound by altering the availability of electrons at the site of reaction. Certain types of reactions are favoured by an increase of electron density in a certain region and substituents which effect such an increase cause the rate to increase. The change in the rate of a reaction due to the alteration of the electron density has been interpreted in terms of several electrical effects. These are the inductive and mesomeric effects which are permanent, and the inductomeric and electromeric effects which are only temporary. The first two effects are associated with a simple shift of electron density. The other effects are more complicated and occur only in conjugated structures in which a certain type of resonance is possible (Ref. 67, Chap. V).

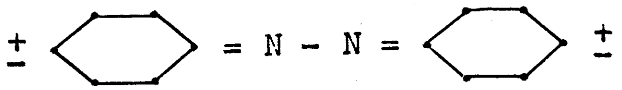
The relative rates of isomerization of azobenzene, azoxybenzene and p,p'-azoxybenzene can be interpreted in terms of these electrical effects.

Azobenzene can be represented electronically as



each nitrogen in the molecule having two free electrons. For cis-trans isomerization to occur it is necessary for the N = N double bond to become a N - N single bond, and this will occur if sufficient thermal energy is given to the molecule.

Contribution of N - N single bonds, arising from the different resonating forms of the molecule, may materially facilitate isomerization. Thus, a possible contributing resonance structure, arising from the displacement of the two free electrons on each nitrogen is, for azobenzene,

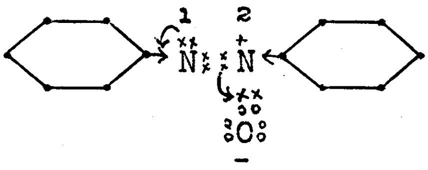


.

This implies that if different groups or substituents are present in the azobenzene molecule, there will be an increase or decrease in the contribution of the N - N single bond due to resonance or other electrical effects, which will be reflected in the rates of isomerization of the compounds.

In a given solvent the rate of isomerization of azoxybenzene is approximately 50 times that of azobenzene. This means that the oxygen atom in azoxybenzene enhances considerably its rate of isomerization. The reason for this can be seen from the following considerations.

Azoxybenzene has been represented (35) as



The oxygen atom, being attached to a nitrogen atom by a coordinate bond, has a formal negative charge, while the nitrogen atom concerned has a formal positive charge. As in azobenzene, there are the relatively weak inductive effects of the phenyl groups which shift electrons into the N = N double bonds and tend to reënforce that bond, and also the tendency for $\overset{1}{N}$ to give up electrons to the ring to form the quinoid structure and a N - N single bond. In addition to these two effects there is the added great tendency for the oxygen atom to take up electrons from the N = N double bond and form a coordinate covalent bond (↳ ). This strong tendency for the oxygen atom to act as an "electron sink" reduces greatly the double bond character of the N = N double bond and facilitates the rate of isomerization of the azoxy compounds.

Figure 28 showed that the rate of isomerization of p,p'-azoxytoluene is slower than that of azoxybenzene in a series of the same solvents. The decrease in the rate of isomerization due to the two methyl groups can be accounted for in the following manner.

In addition to the same effects operating in azoxybenzene, there will be an added inductive effect of the methyl groups operating to decrease the rate. However, the contribution of the inductive effects of the two methyl groups will be different. The displacement of electrons due to a methyl group on the benzene ring on the right, would not reach the N = N double bond since the two free electrons on $\overset{2}{N}$ are shared and cannot be displaced, while the electrons on $\overset{1}{N}$ can be displaced. The slower rate of isomerization of p,p'-azoxytoluene is thus due mainly to the methyl group on the benzene nucleus attached to the nitrogen not containing the oxygen.

It is apparent from the preceding argument that the faster rate of isomerization of azoxybenzene, as compared with azobenzene, can be adequately explained without invoking interaction of the oxygen atom with the benzene ring adjacent to it, which, if it were present, would tend to strain the double bond and facilitate isomerization.

The effect of solvent on the rate of isomerization of azobenzene, azoxybenzene, and p,p'-azoxytoluene can be expressed by a series of equations of the type

$$\log k = J - L\,(P_S)^{1/2}$$

where J and L are dependent on the temperature only. It follows then that at a given temperature the ratio of the rates for any two reactions in a series of solvents should be constant. Figure 31 shows log k of azoxybenzene at 35°C. plotted as function of log k of p,p'-azoxytoluene at the same temperature. A good linear relation is observed between the two, indicating that the ratio of the two rates is constant. This can be interpreted as meaning that although the substituent decreases the rate of isomerization, the decrease in rate relative to azoxybenzene is constant from solvent to solvent. In Figure 32 log k at 43°C. for azobenzene is plotted as a function of log k for p,p'-azoxytoluene at the same temperature. Again, a linear relation between the two is observed, similar to that in Figure 31. The constant ratios of the rate constants in Figures 31 and 32 thus relate the influence of a series of solvents on the rate of isomerization of one reaction to the rate of isomerization of another in a linear manner. This implies that the forces governing the rate of isomerization of azobenzene, azoxybenzene and p,p'-azoxytoluene are identical.

Analogous relations have been observed relating the influence of a series of substituents on the rate of

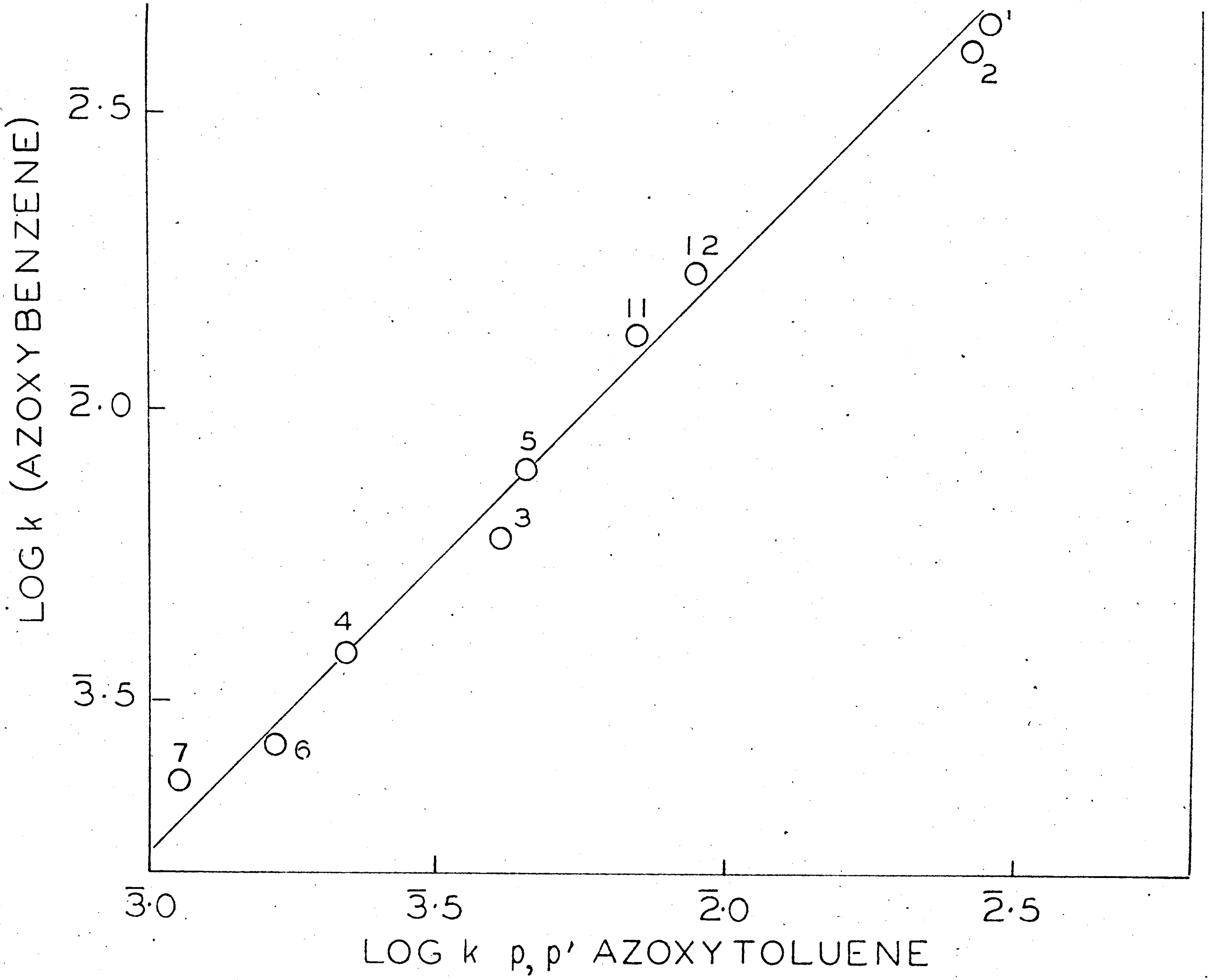


Fig. 31. Relation between log k Azoxybenzene and log k p,p'-Azoxytoluene at 35.35°C. in Different Solvents

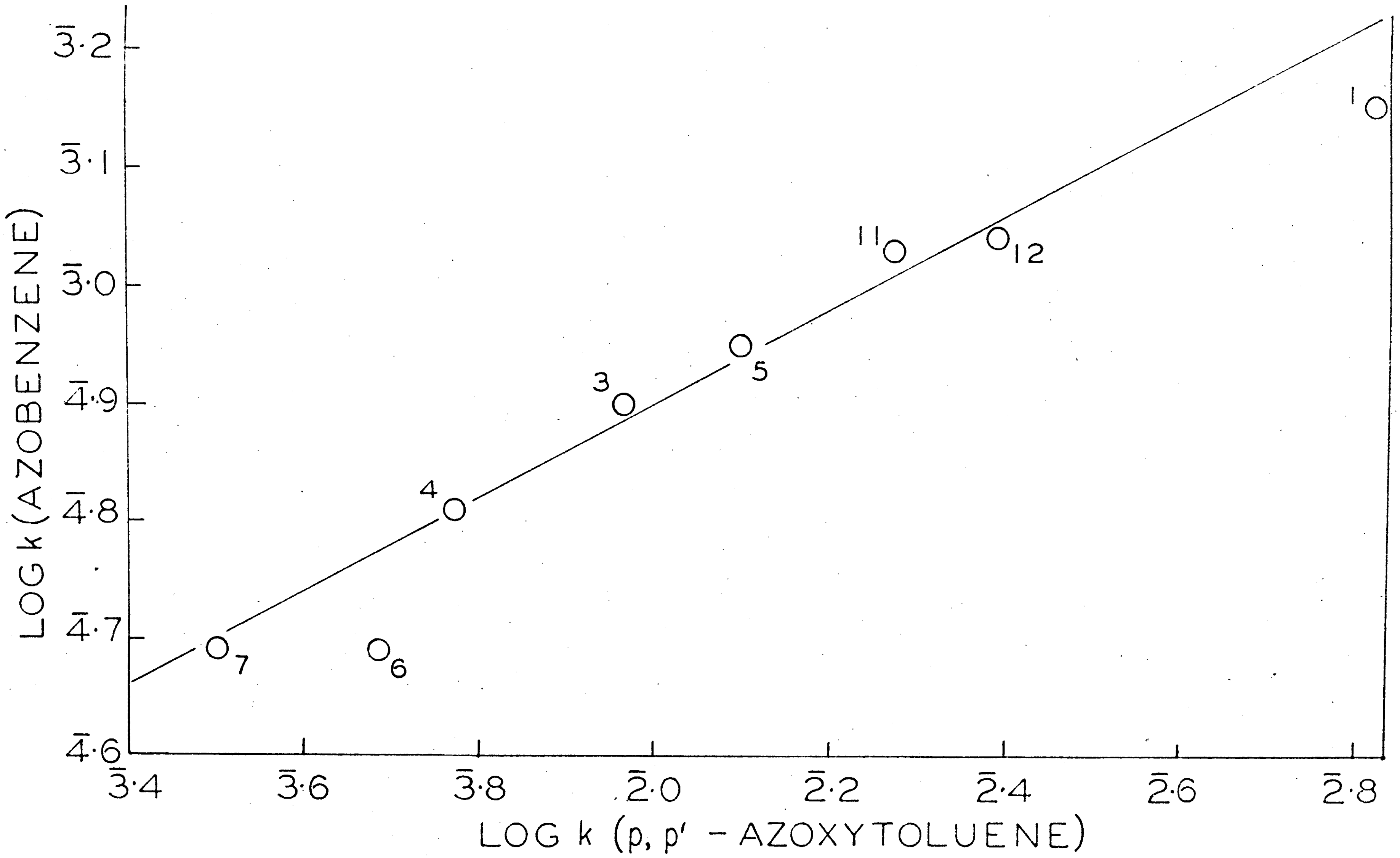


Fig. 32. Relation between log k Azobenzene and log k p,p'-Azoxytoluene at 43 85°C. in Different Solvents

a given type of reaction, to that of the same substituents on the rate of a related process (68). These relations have been interpreted by Evans and Polanyi (69), by considering the influence of external parameters on the free energy of activation in the equation,

$$\log k = \text{constant} - \frac{\Delta F^{\ddagger}}{2.303\ RT} \quad .$$

The linear relation results from the fact that the ratios of the free energy of activation of the reactions of one typeto those of the related process are constant.

The linear relations between the rate constants of the isomerization reactions in Figures 31 and 32 would seem to indicate the same constant ratios of the free energies of activation in the isomerization reactions of azobenzene, azoxybenzene and p,p'-azoxytoluene. It would be interesting to study a series of substituted azobenzenes and azoxybenzenes in a variety of solvents to see whether these logarithmic relation would apply both with respect to solvent and substituents.

## ISOMERIZATION AT N = N AND C = C DOUBLE BONDS

Kistiakowsky and co-workers (74) have studied the cis-trans isomerization reactions of ethylenic derivatives which involve a rotation of 180° about the C = C double bond. Their results show that these isomerization reactions can be divided into two groups, in one of which the specific reaction rates are given by the expression

$$k = 10^4 e^{-25,000/RT} \text{ sec.}^{-1} ,$$

while in the other

$$k = 10^{11} e^{-45,000/RT} \text{ sec.}^{-1} .$$

From the results it appears that compounds containing benzene rings have the higher activation energy. Within the temperature range of the investigations, all the reactions proceeded at approximately the same rate, which makes the differences between the two groups surprising. The reactions in both groups are kinetically of the first order and for such reactions the frequency factor, $\frac{k'T}{h}$, is normally about $10^{13}$sec.$^{-1}$. To account for the reactions with the low frequency factors, it has been postulated that ethylenic derivatives can have a triplet excited state, with this state lying 20 to 25 Kcal. above the normal singlet state.

The variation in potential energy on rotation about the double bond can be represented by curves 1 and 1' in Figure 33, where $\theta$ represents the angle of rotation. The potential energy of the triplet state is represented by the horizontal line III since in this state the energy depends very little on rotation. The normal type reaction moves from 1 to 1' through A without change in multiplicity, the point A being the activated state, while the reactions

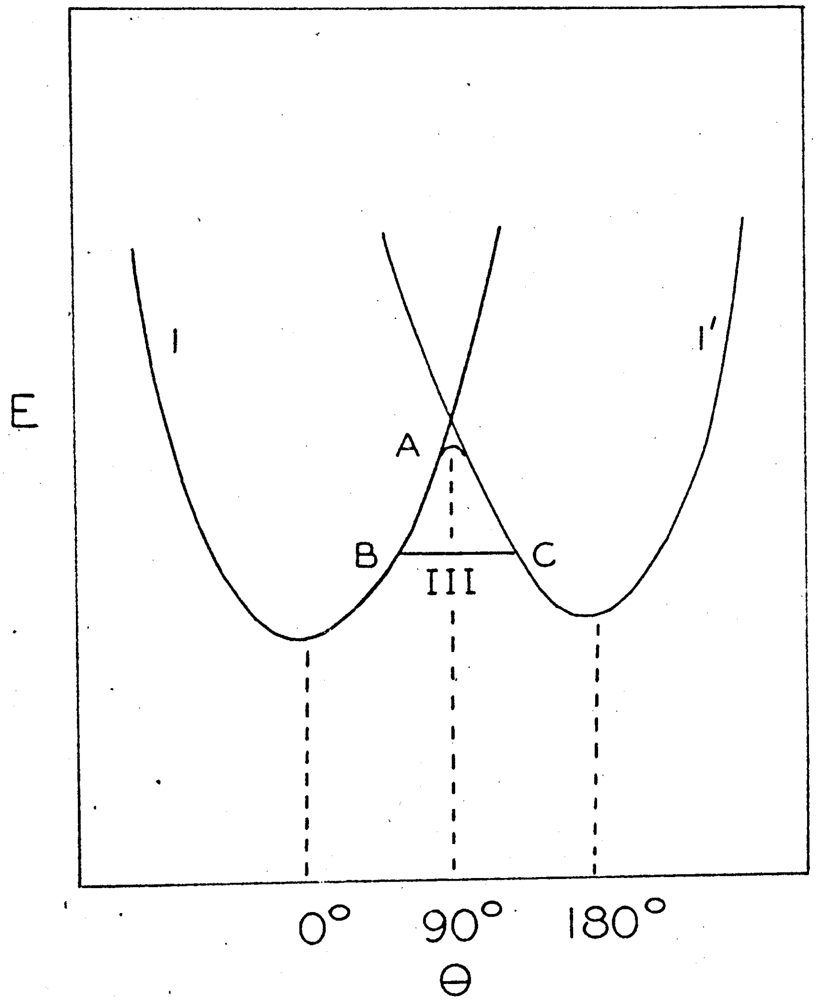


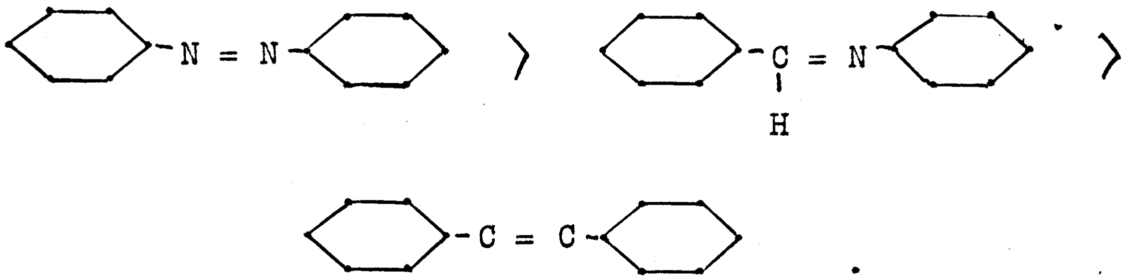
Fig. 33. Potential-energy curves for rotation of ethylene about the double bond

with the low frequency factors undergo an electronic transition from the singlet to the triplet state at B and back to the singlet state at C. For the latter type of reaction the probability of transfer is small which gives rise to a low frequency factor. The explanation that has been offered for the path of higher activation energy associated with compounds containing benzene rings is that when the double bond becomes a single bond i.e. at the activated state, the energy of the molecule in the singlet level depends on the ability of the two electrons thus made available to form other bonds. In molecules with phenyl groups attached to the ethylenic carbon atoms there is ample opportunity for resonance, and the singlet activated state has a lower potential energy than for molecules, such as butene-2 and maleic ester, where similar resonance cannot take place. The resulting decrease in the activation energy for the upper path makes this route the more favourable of the two alternatives for the benzene derivatives.

The three N = N double bond isomerization reactions in this investigation can now be compared with these C = C double bond isomerizations. The frequency factors and the activation energies for the cis-trans isomerizations of the N = N double bond ranged between $10^{12}$-$10^{14}$ min.$^{-1}$ and 20-24 K.cal./mole respectively. These frequency factors in no way suggest a change in multiplicity in the isomerization reaction although, from an energy consideration, they do seem to resemble the C = C bond isomerization where a change in multiplicity occurs.

The differences in activation energy between the isomerization of the C = C double bond where the frequency factor is approximately $10^{12}$ and the N = N double bond isomerization can be accounted for in terms of their different bond energies. The bond energy of the C = C bond is approximately 150 K.cal. (70), while the energy of the N = N bond is about 70 K.cal. (71). To cause rotation in the cis-trans isomerization it is necessary for the C = C or N = N double bonds to become a single bond in the activated state, and because a greater energy is required to break the C = C double bond than the N = N double bond, it follows that the activation energy for isomerization about the C = C double bond should be higher than that for isomerization involving the N = N double bond. The low activation energies and the normal frequency factors for isomerization about the N = N double bond would seem to suggest that the intersection points of the singlet state in the activated complex as sketched in Figure 33, is near or below the intersection points of the triplet state so that isomerization via the triplet state never predominates over isomerization via the singlet state.

LeFevre (73) suggests that the high resonance energy of the N = N double bond in the activated state may lower the intersection point of the potential energy curves of the cis and trans isomers, so that paths via the triplet state never have an advantage. Although there is no conclusive evidence that the resonance energy of the N = N double bond is higher than that of the C = C double bond in the activated state, Coates and Sutton, (72) have suggested, from a consideration of the excess energy of the normal (i.e., central double bonds) as compared with possible activated (i.e., with central single bonds) structures of stilbene, azobenzene, and benzylideneanil, that the order of resonance in these structures is,



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## SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

1. The kinetics of the cis-trans isomerization of p-chlorobenzenediazocyanide was investigated spectrophotometrically in six non-ionizing solvents. The reaction was found to be first order with a rate constant which increased six-fold in passing from cyclohexane to chloroform as solvent, the activation energy for the reaction varying from 22.5 to 20.05 K.cal./mole in the same series of solvents.
2. Attempts to determine the rate of isomerization of p-chlorobenzenediazocyanide in ionizing solvents revealed that the cis isomer decomposed in these solvents.
3. A linear relation between $\log k$ and $D-1/2D + 1$, where $D$ = dielectric constant of the solvent, was found to hold for the isomerization reaction in four solvents, but considerable deviation from the line was found for the reaction in heptane and cyclohexane. This was attributed to a lower degree of solvation of the reactant in these solvents.
4. The activation energy associated with the isomerization of p-chlorobenzenediazocyanide in the different solvents decreased linearly with $D-1/2D + 1$. This was interpreted as due to the larger electrostatic interaction between the activated complex and solvent than between reactant and solvent.
5. The kinetics of the cis-trans isomerization of azoxybenzene and p,p'-azoxytoluene were investigated spectrophotometrically in nine pure solvents of widely different types. The

reactions gave good first order rate constants.

6. The rate of isomerization of azoxybenzene increased twenty-five fold in passing from methanol to heptane, while the rate of isomerization of p,p'-azoxytoluene increased twenty-fold in the same series of solvents. The activation energies for the two reactions were approximately 23 K.cal./mole.

7. Linear relations were observed between log k and $(P_S)^{1/2}$, where $P_S$ is the internal pressure of the solvent, for the isomerization of azoxybenzene and its substituted derivative. Since the rates of the two reactions decreased with an increase in the internal pressure of the solvents, it was inferred that the internal pressure of the reactant is greater than that of the activated complex.

8. Satisfactory straight lines were obtained when log k for azoxybenzene was plotted as a function of log k for p,p'-azoxytoluene in the same series of solvents at 35°C. and when log k for azobenzene was plotted as a function of log k for p,p'-azoxybenzene at 43°C. in the same series of solvents. These linear relations indicate that the rates of isomerization of these reactions are determined by the internal pressure of the solvents, and that the ratios of the free energy of activation for the three reactions are constant.

9. The relative rates of isomerization of azobenzene, azoxybenzene and p,p'-azoxytoluene are accounted for in terms

of their electronic structure.

10. An activation energy of 25 K.cal./mole and a frequency factor of $10^{13}$min.$^{-1}$ for isomerization at the N = N double bond is consistent with the bond energies of the N = N double bond and a unimolecular reaction where a change in multiplicity does not occur.