

KINETICS OF THE CIS-TRANS ISOMERIZATION OF AZOBENZENE

by

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ABSTRACT

The catalytic effects of several acids and metal salts on the cis-trans isomerization of azobenzene in aqueous ethanol were examined kinetically. The effect of perchloric acid is apparently due to H^+ ions: a catalytic mechanism involving the formation of the conjugate acid of azobenzene has been postulated to interpret these results. To account for the much higher catalytic activity found for hydrochloric acid, an additional path, involving catalysis by undissociated HCl molecules has been proposed. Acetic acid was found to be inactive. Of the metal salts examined only those of Cu^{++} showed pronounced catalytic activity, which is interpreted in terms of a catalytic mechanism involving coordination of cupric ions with the azo group. Simultaneous coordination of Cu^{++} and H^+ has been proposed to account for the high catalytic activity of cupric salts in the presence of acids.

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INTRODUCTION

Cis-Trans Isomerization of Azobenzene

Cis-trans isomerism, due to restricted rotation about a double bond, was first observed for ethylenic compounds and while it had long been predicted also for molecules possessing $-N=N-$ bonds, this has been confirmed only relatively recently.

In 1937 Hartley (1,2) prepared cis-azobenzene by irradiation of a solution of the normal trans-form with ultraviolet light. The cis-isomer, although stable in crystalline form, undergoes spontaneous conversion into the trans-form in solution. This occurs by both thermal and photochemical mechanisms.

Hartley (2) studied the kinetics of the thermal conversion spectrophotometrically and found it to be of first order, with an activation energy of about 23 Kcal. per mole and a normal frequency factor ($\sim 10^{11}$ liter mole⁻¹ sec.⁻¹).

The kinetics of the cis-trans isomerization of ethylenic compounds have interpreted (3) in terms of two types of mechanisms. The first, characteristic of reactions having high activation energies (40 - 50 Kcal) and normal frequency factors (10^{10} - 10^{12} liter mole⁻¹ sec⁻¹) is adiabatic and involves rotation about the double bond without any change in the multiplicity of the electronic state of the molecule. The second, characterized by lower activation energies (15 - 25 Kcal) and abnormally low frequency factors (10^3 - 10^5 liter mole⁻¹ sec⁻¹) is apparently non-adiabatic and proceeds through the triplet state of the molecule in which the barrier to rotation about the double bond is removed. Although the activation energy of the isomerization of azobenzene is low compared to

that of most olefins, the normal frequency factor of the reaction suggests that its mechanism is of the former type.

SOLVENT EFFECTS

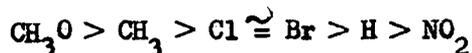
The effect of solvent variation on the kinetics of the cis-trans isomerization of azobenzene has been examined by Hartley (2) and more extensively by Halpern, Brady and Winkler (4). Rates were determined in a large number of solvents and were found to depend inversely on the solvent polarity. Thus at 60° C, k, the first order rate-constant, increased from 0.000489 to 0.001415 min⁻¹ in going from a polar solvent such as methanol to a non-polar one such as heptane. The activation energy correspondingly decreased from 24.8 to 22.8 Kcal/mole, but the effect of this was partially offset by a compensating decrease in the entropy of activation. These effects were correlated quantitatively with the internal pressure of the solvent in accordance with equations derived assuming regular solution theory behaviour.

The behaviour in mixed solvents was more complex and showed evidence of preferential solvation of azobenzene by the better solvent.

SUBSTITUENT EFFECTS

The cis-isomers of a number of substituted azobenzenes and related compounds have been prepared and the kinetics of their isomerization examined.

LeFèvre and Northcott (5) found the rate of substituted azobenzenes to follow the order:



but were unable to correlate this with any property of the substituents.

This order paralleled that found for the isomerization of substituted diazocyanides. The effect of solvent variation was qualitatively similar to that for azobenzene itself.

A more extensive study of the isomerization of substituted azobenzenes has recently been described by Talati (6). Para-substituents (both electron donating and withdrawing) were found to increase the rate of conversion but again the results failed to correlate in any simple way with substituent properties (e.g. σ values). Very high isomerization rates were observed for the para-cyano and nitro compounds and, in addition, it was found that for these compounds the rate was higher in more polar solvents. In explanation of this it was suggested that while other substituents operated only through an inductive effect, for these compounds contribution of resonance structures such as (I)



was possible, in which the π - electron density at the azo-linkage is decreased, resulting in reduced resistance to rotation. Furthermore, because of the charge separation involved, such structures should be favoured by increasing solvent polarity.

CATALYTIC EFFECTS

Acid catalysis of the cis-trans isomerization of azobenzene was first observed by Hartley (2) who did not however examine the effect in detail.

While this investigation was in progress, Schulte-Frohlinde (7) reported examining a large number of other substances for catalytic activity; Table (I), listing the inactive and active substances, is reproduced from his paper. The catalytically active substances are classified into two categories, electron donors and electron acceptors, acids being included among the latter.

Bases and weak acids ($K_a < 10^{-3}$) were found to be inactive. The catalytic effect of thiourea was found to be greatly enhanced by acids, the combined activity being greater than the sum of the separate activities. Benzene appears to have been used as the solvent in these studies and many of the inorganic substances tested were presumably insoluble. It is reasonable to suggest that in some instances failure to observe catalytic activity may have been due to this factor.

Schulte-Frohlinde has interpreted the pattern of catalytic effects in terms of the electron-transfer properties of the catalytic species and suggested that the catalytic path involves a transition state in which one or two electrons are transferred between the catalyst and azobenzene. The evidence for this concept does not appear to be convincing and there are notable exceptions to the suggested criterion for catalytic activity.

It should be emphasized that the studies referred to here are for the most part qualitative and this do not lend themselves to detailed interpretations.

GENERAL CONSIDERATION OF ACID CATALYSIS

In considering the acid catalysis of the cis-trans isomerization of azobenzene, it is of interest to review some concepts relating to acid catalysis in general.

TABLE (I)*

LIST OF INACTIVE AND ACTIVE SUBSTANCES

INACTIVE SUBSTANCES

- | | | | |
|---------------|-------------|----------------------|----------------------|
| 1. LiOH | 5. CaO | 9. Cu-powder | 13. MuO_2 |
| 2. NaOH | 6. BaO | 10. $Cu(OOC.CH_3)_2$ | 14. $KMnO_4$ |
| 3. NaCl | 7. $CaCl_2$ | 11. HgO | 15. PbO |
| 4. Na_2SO_4 | 8. SiO_2 | 12. $MuSO_4$ | 16. $(NH_4)_2S_2O_8$ |
-
17. Ethanol
 18. Phenol
 19. o-Dihydroxybenzene
 20. p-Dihydroxybenzene
 21. p-Hydroxyazobenzene
 22. Benzoic acid
 23. o-Chlorobenzoic acid
 24. p-Chlorobenzoic acid
 25. Trans-cinnamic acid
 26. o-Phthalic acid
 27. Isophthalic acid
 28. p-Amino-benzoic acid
 29. Pyridine
 30. Piperidine
 31. Diphenylamine
 32. Carbazole
 33. Urea
 34. Phthalimide

*Quoted from Von Dietrich Schulte-Frohlinde (7)

35. Diphenylbenzamidine
36. syn-and anti-pyridine 2-aldehyd-phenylhydrazone
37. 1,3 Dinitro-benzene
38. 2,4 Dinitro-phenol
39. m-Nitroaniline
40. p-Nitroaniline
41. 3 Methoxy - 5 - ethylbenzoquinone
42. 4 α, β - Tetramethylbutylbenzoquinone (1,2)
43. p-Quinone
44. Metoxy-p-quinone
45. Phenanthrene-quinone
46. 1,4- Dihydroxy-anthraquinone
47. N- Phenyl-N¹ - benzoyl-hydrazine

ACTIVE SUBSTANCES

a). Electron-donors

1. Sodium
2. Zinc dust
3. Solid μ -Sulphur in contrast to α -Sulphur
4. Colloidal sulphur
5. Hydrogen sulphide
6. Thiophenol
7. Hydrazobenzene
8. Phenylhydrazine
9. Benzaldehyde-phenyl-hydrazone

10. Hydroxylamine-hydrochloride

11. Semicarbozide-hydrochloride

12. Ferrous-sulphate

13. Arsenious-acid

b). ELECTRON ACCEPTORS

1. Bromine

2. Iodine

3. Tetrachloro-p-quinone

4. Tetrabromo-p-quinone

5. Tetrahydroxy-p-quinone

6. Potassium-nitroso - bisulphonate

7. Lead oxide

8. Ferric sulphate

9. Hydrochloric acid

10. Oxalic acid

11. Salicylic acid

12. Picric acid

13. 2,4,6, Trinitro-benzoic acid

These have been found to have validity in relation to a great variety of reactions (8) and it seems likely that they apply also to the present system.

While most acid-catalyzed reactions are believed to proceed through the conjugate acid of the reactant a distinction is made between several different types of mechanisms.

The first, called "unimolecular" postulates as rate determining step the decomposition of the protonated species found in a rapid pre-equilibrium, to give the products:



such a mechanism we will designate as (I).

Mechanism (II) known as the "bimolecular" mechanism, also involves a rapid protonation pre-equilibrium, but in this case the rate-determining step is the attack of a molecule of solvent (S) on the protonated species to give further intermediate AHS^+ which decomposes to yield the products.



The third type of mechanism involves the protonation itself as rate determining step



One of the most widely used criteria for distinguishing between these three types of mechanisms involves the Hammett acidity function, H_0 . This function was introduced by Hammett and Deyrup (8,9) and is defined in terms of the ionization equilibria of a class of indicators, namely those functioning as uncharged bases,



by the equation:

$$H_o = -\log \frac{C_{BH^+}}{C_B} + pK_{BH^+} \quad (8)$$

where $\frac{C_{BH^+}}{C_B}$ is the ratio of the concentration of the indicator in its acid and basic form, directly measurable for a given solution by means of a spectrophotometer or a colorimeter, and K_{BH^+} is the thermodynamic ionization constant of the conjugate acid BH^+ .

This definition is equivalent to

$$H_o = -\log \frac{a_{H^+} f_B}{f_{BH^+}} \quad (9)$$

where a_{H^+} is the hydrogen ion activity and f_B and f_{BH^+} are molar concentration activity coefficients.

It has also been found useful to define the function h_o which is related to H_o by the expression

$$H_o = -\log h_o \quad (10)$$

In the limiting case of ideal dilute solutions:

$$H_o = pH$$

and $h_o = [H^+]$

A characteristic feature of the H_o acidity scale for aqueous solutions of the strong acids is that with increasing acid concentration h_o increases more rapidly than $[H^+]$. Fig. 1 shows the deviation from linearity in the plot of h_o versus $[H^+]$ for $HClO_4$ and HCl in aqueous solution (8). Below 1M, the h_o values for $HClO_4$ and HCl are nearly identical but the divergence from linearity is already appreciable.

Zucker and Hammett (10,8) have suggested that if the acid catalyzed reaction proceed through a mechanism of type (I) a linear dependence of the rate on h_o is to be expected. On the other hand if the mechanism is of type (II) the rate should increase linearly with $[H^+]$.

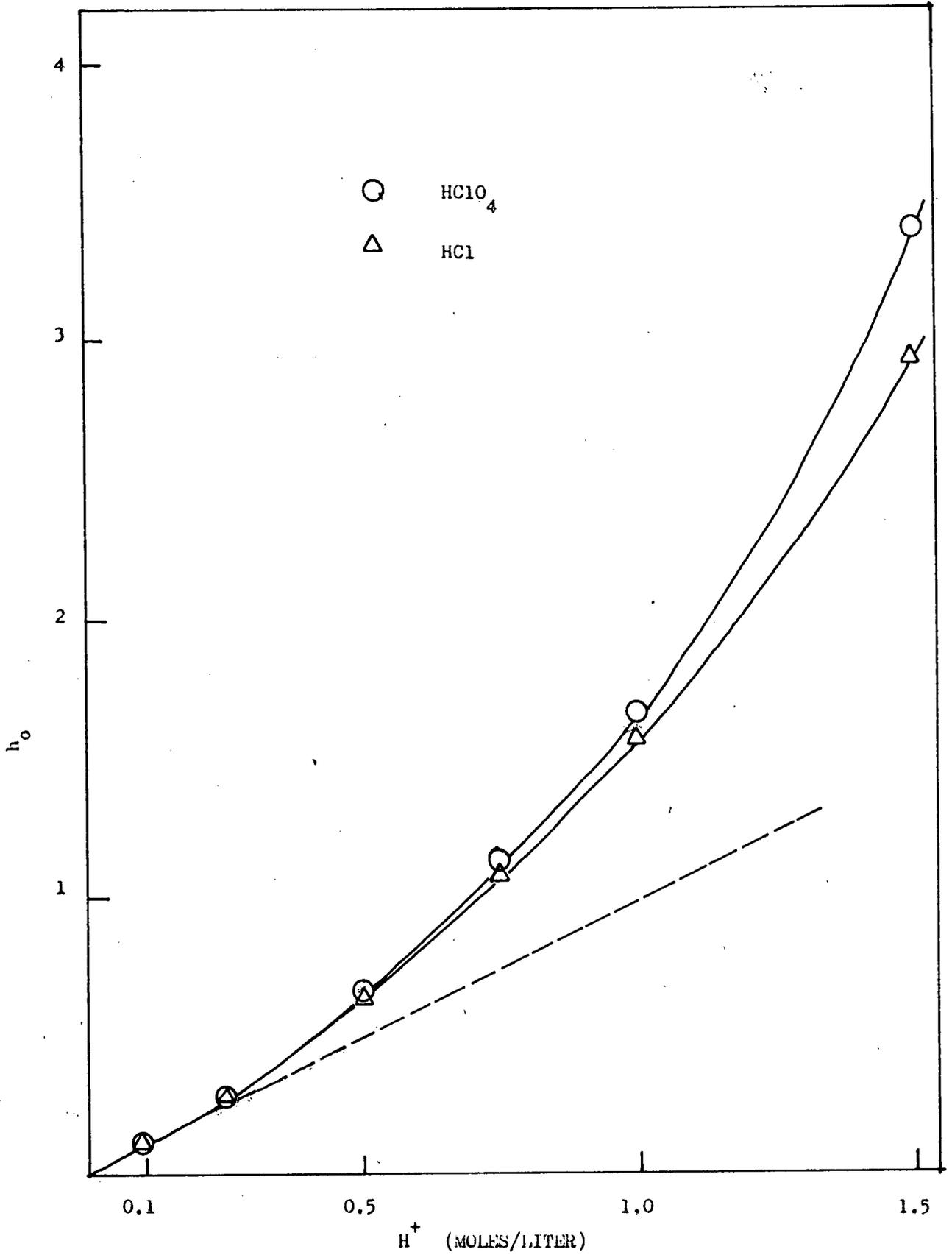


FIGURE 1. h_o for aqueous solutions of HCl and $HClO_4$ (8)

In the third case (slow protonation step) a linear dependence of the rate on h_0 is again suggested; this case should also be distinguishable from the other two by virtue of exhibiting general acid (rather than specifically hydrogen ion) catalysis.

It is necessary to point out that these criteria are by no means unambiguous, nor is the theoretical foundation on which they rest of unquestioned validity (8). Furthermore although empirical correlations of rates with H_0 may be observed in acid catalyzed reactions of charged molecules and in reactions of higher order, the significance of these (i.e. when applied to reactions other than those in which the initial step involves a single uncharged molecule and an H^+ ion) is very questionable. Furthermore since the variation of activity coefficients with change in medium is not well understood, caution must be observed in the interpretation of studies made in non-aqueous or mixed solvents.

Although the H_0 concept is applicable in principle to non-aqueous solutions, including mixed solvents, relatively little work has been done on such systems. Some measurements by Braude and Stern (11, 12, 13) on solution of HCl in aqueous ethanol, acetone and dioxane are reproduced in Fig. 2. A common feature of these systems is that for a given concentration of HCl, H_0 passes through a minimum as the solvent composition is varied from pure water to the pure organic liquid: in each case this minimum occurs in the vicinity of 50 mole % H_2O . Braude and Stern (12, 13) found a similar dependence on changes of solvent composition for the rates of reactions known to follow an H_0 - dependent mechanism. This is shown in Fig. 3 which depicts their results for the rearrangement of the ethynylpropenylcarbinol in solutions of 1M HCl in aqueous ethanol. This provides some indication of the validity of the H_0 concept in these media.

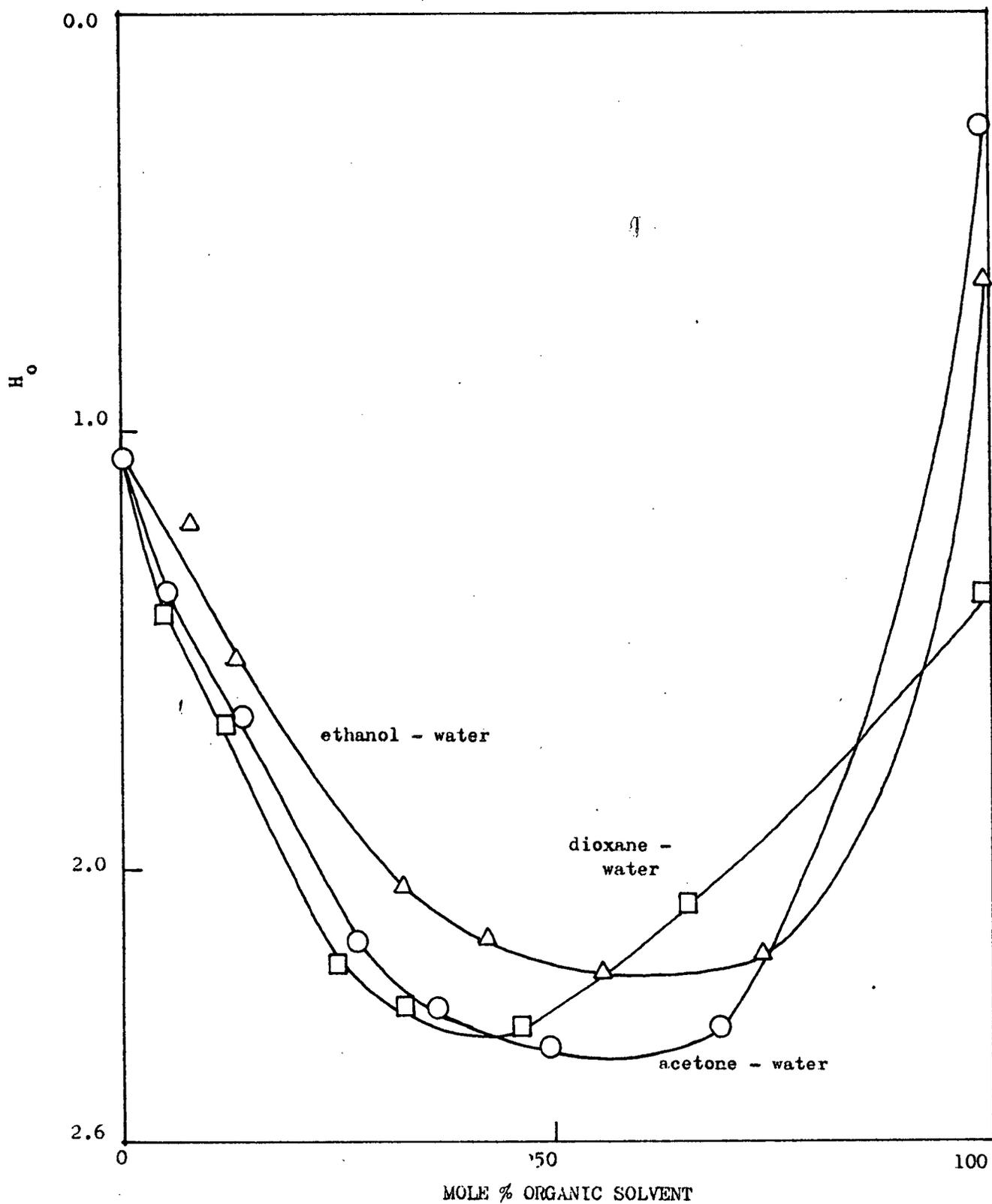


FIGURE 2. H_0 in mixed solvents containing 0.1 M HCl. (13)

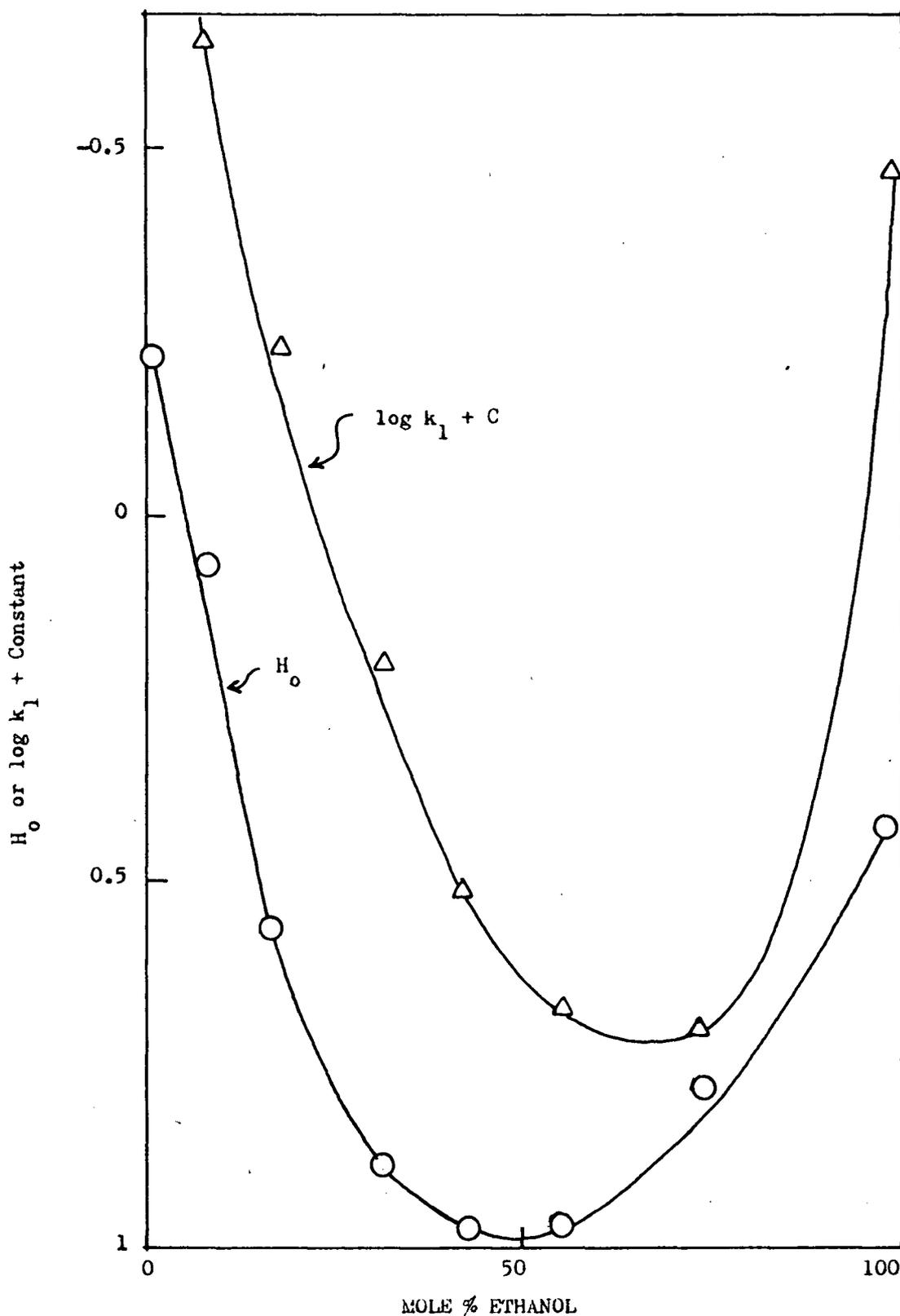


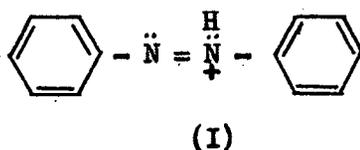
FIGURE 3. Dependence on solvent composition of rate of reactions following an H_o - dependent mechanism (12,13) (Rearrangement of Ethynylpropenyl-Carbinol in solution of 1 M HCl)

Structure of the Conjugate Acid of Azobenzene

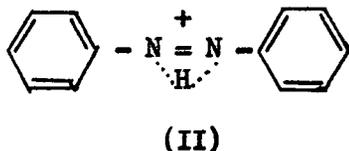
The results of recent studies of the conjugate acids of azobenzene and its derivatives (14, 15) are consistent with the suggestion that acid catalysis of the cis-trans isomerization involves the formation of a protonated species.

The protonation equilibrium of azobenzene has been studied spectrophotometrically in aqueous sulphuric acid solutions containing approximately 20% ethanol by volume, at the constant temperature of 25°C. Due to the rapid isomerization only the trans-form (probably in equilibrium with small amount of cis-form) could be studied. A pK_a of -1.6 for the conjugate acid of azobenzene was calculated taking Hammetts' H_0 scale as reference. Klotz (16) had previously reported -2.48 for the pK_a of azobenzene, calculated with reference to the acidity scale of Michaelis and Granick (17).

The structure of AH^+ has not been conclusively established. Klotz and co-workers (16) assume structure (I) with the proton localized on one of the nitrogens through a bond involving lone pair electrons.



Jaffe (14) on the other hand favors structure (II) in which the hydrogen ion is equally shared by the two nitrogen atoms through delocalized bonds.



This suggestion is based in part on measurements on unsymmetrically substituted azobenzenes which yielded a single Hammett plot in spite of the presence in the molecule of two non-equivalent N atoms. The proposed structure (II) in which the H atom is associated with both N atoms is more readily reconciled with this result, than is structure (I). Jaffe (14) had also concluded on theoretical grounds, that the cis-conformation of structure (II) is the more stable one.

SCOPE OF PRESENT INVESTIGATION

At the time this investigation was undertaken only the acid catalysis of the cis-trans isomerization of azobenzene had been reported and the initial objective of the investigation was to examine the kinetics and mechanism of the acid-catalyzed reaction.

Three acids were selected for study, HClO_4 , HCl , CH_3COOH , considered as examples of strong, intermediate and weak acids. Furthermore, since it appeared likely that the acid catalysis involved protonation of nitrogen atoms or of the $-\text{N}=\text{N}-$ bond, it was also considered of interest to examine the catalytic effects of metal ions such as Cu^{++} , Ag^+ and Co^{++} , whose tendency to coordinate with nitrogen-containing ligands is well known.

Most of the measurements were made using aqueous alcohol as solvent, since both azobenzene and the catalysts were conveniently soluble in this medium. A few measurements using organic acids and salts as catalysts were made in benzene solution.

EXPERIMENTAL

Materials

Cis-azobenzene was prepared by the method of Hartley (1). 100 grams of commercial azobenzene, consisting almost entirely of the trans-isomer (M.pt. 67°C) was dissolved in 1000 ml of Glacial Acetic Acid containing 20 ml of water, and the solution was irradiated with a GE (275 W) sunlamp for 24 hrs. An appreciable change in color, due to increasing concentration of the cis-isomer, which is darker, was observed. 900 ml of water was then added to precipitate the trans-isomer. The latter was separated by filtration and recycled (i.e. subjected to further exposure in acetic solution as described above.) The filtrate was further diluted with a liter of water and the cis-isomer extracted with chloroform. The chloroform extract was evaporated in a vacuum desiccator and the crude cis-isomer recrystallized from petroleum ether until a constant melting point of 70°C was achieved. The yield of pure cis after two exposures was about 8 grams. All operations involved in the separation and purification of cis-azobenzene were performed in the dark since the two isomers are photochemically interconverted.

Other Reagents

Distilled water and ethanol, redistilled from KOH, were used as solvents. Cupric perchlorate (G.F.Smith reagent) was recrystallized from perchloric acid. Acids and other reagents were of reagent grade.

Spectrophotometric and Kinetic Measurements

Trans-azobenzene shows a strong absorption band in the region 430-440 m ($\lambda_{\text{max}} = 435 \text{ m}$) which has been ascribed (18,19) to the $-N=N-$ linkage. The cis-isomer absorbs in the same region (the band is shifted slightly toward the lower wave lengths) but with an extinction coefficient at 430 m about twice that of trans. Thus the decrease in optical density

at 430 m μ can be used to follow the isomerization reaction and this procedure, used in most of the earlier studies of the cis-trans isomerization of azobenzene, was also adopted in this investigation. Measurements were made with a Beckmann DU Spectrophotometer.

In the kinetic experiments, solutions containing known concentrations of azobenzene (generally 0.08 gm/l. = 4.39×10^{-4} moles/liter) were immersed in a constant-temperature bath maintained at 60° C. Samples were removed at measured time intervals and transferred directly to the spectrophotometer cells, cooled rapidly by immersion in an ice-salt mixture (to quench the reaction) and the optical density determined. Since the absorption of both cis and trans isomers followed Beer's law, the concentration of the cis-isomer present at any time, could be computed by the formula

$$[\text{cis-A}] = \frac{(D - D_{\infty})}{(D_0 - D_{\infty})} [\text{cis-A}]_0 \quad (11)$$

where:

D , is optical density at time, t

D_{∞} , is optical density at infinite time (i.e. of trans-azobenzene.)

D_0 , is initial optical density (i.e. of cis-azobenzene) and $[\text{cis-A}]_0$ is the initial concentration of cis-azobenzene.

The validity of this procedure was unaffected by the catalysts. Thus HClO_4 , HCl and AgClO_4 in the concentrations used did not appreciably affect the optical densities of solutions of either cis or trans-azobenzene (Fig. 4, 5.) Cupric and cobaltic salts did absorb appreciably at the wave length used but their optical densities and that of azobenzene apparently were additive (Fig. 6) so that effect was cancelled out by the subtraction of the optical density terms in equation (11).

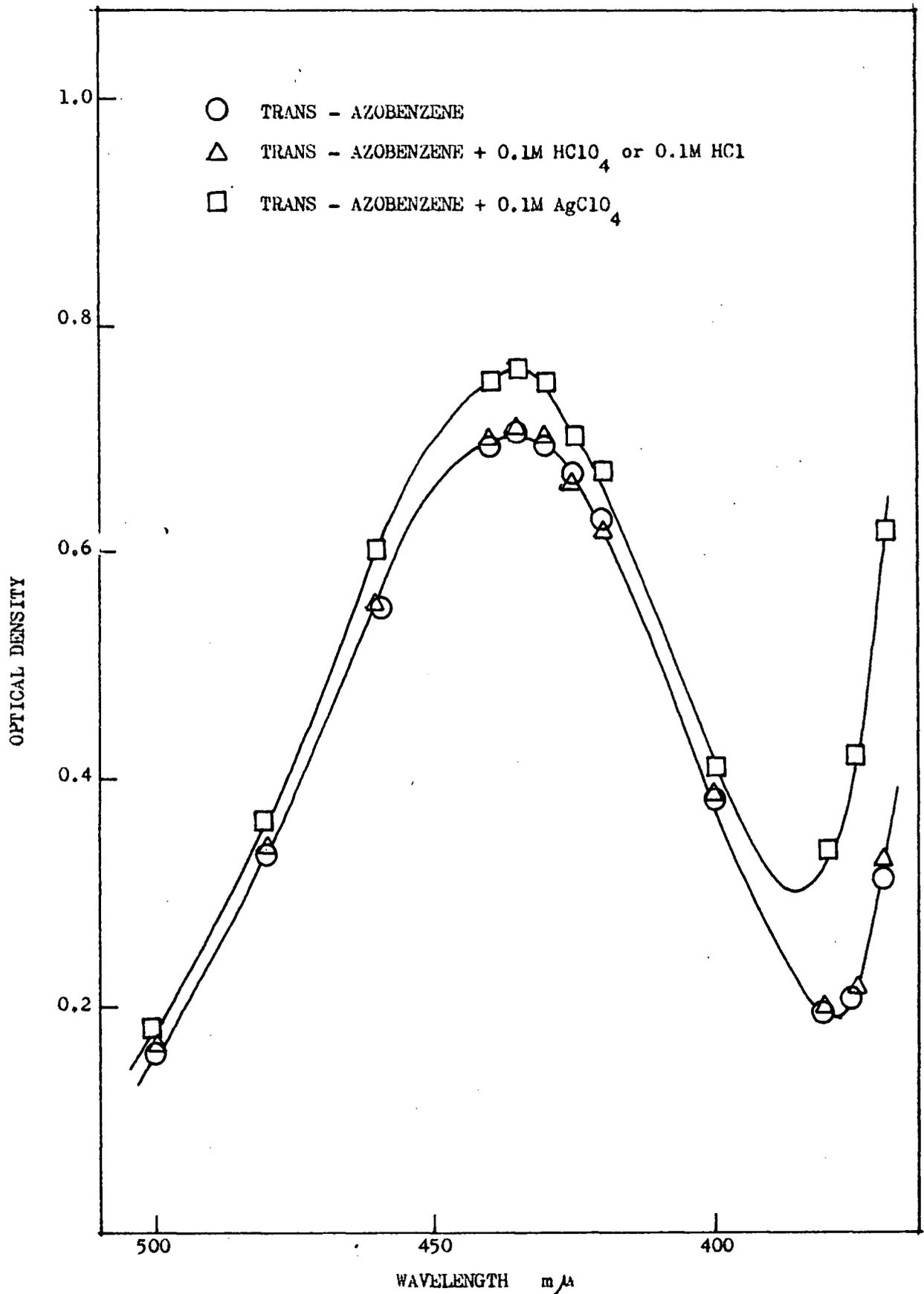


FIGURE 4. Spectrum of trans-azobenzene in 50 mole % ethanol in the presence of HClO₄, HCl and AgClO₄.

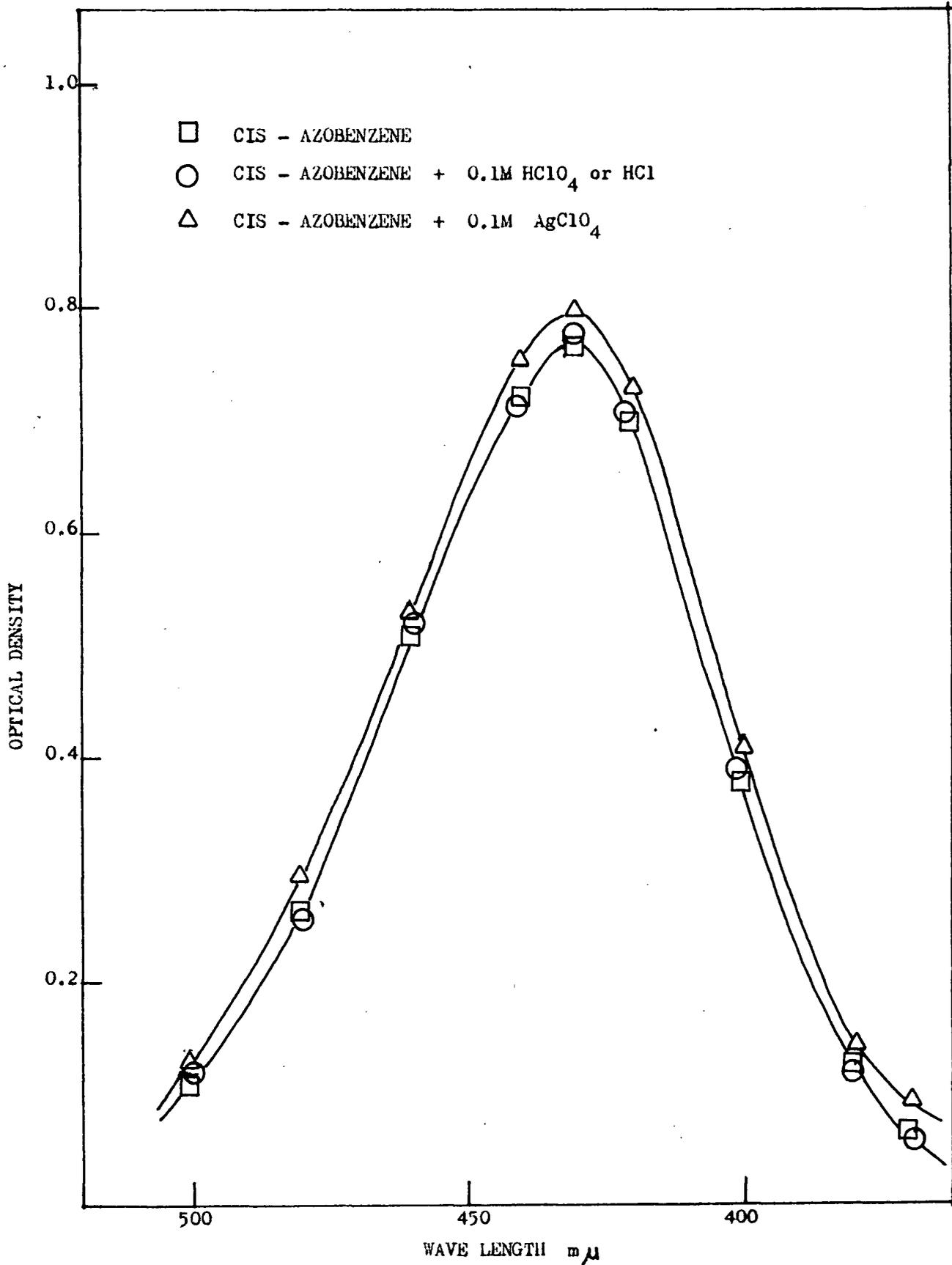


FIGURE 5. Spectrum of cis-azobenzene in 50 mole % ethanol in the presence of HClO₄, HCl and AgClO₄.

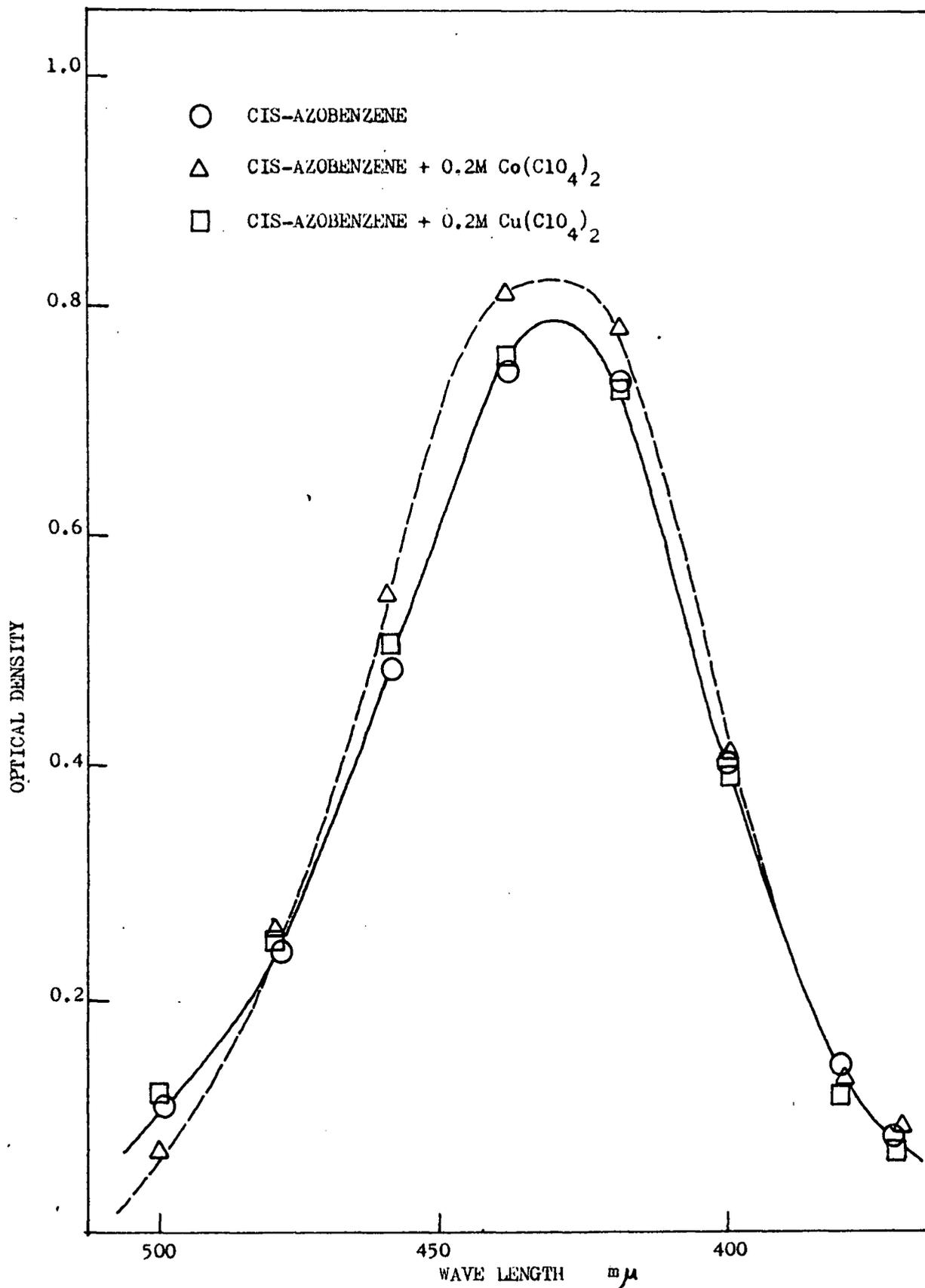


FIGURE 6. Spectrum of cis-azobenzene in 50 mole ethanol in the presence of $\text{Cu}(\text{ClO}_4)_2$ and $\text{Co}(\text{ClO}_4)_2$

RESULTS AND DISCUSSIONS

Of the three acids examined, HClO_4 and HCl , selected as typical strong and intermediate acids, showed pronounced catalytic activity while the weak acid CH_3COOH was inactive.

The effects of $\text{Cu}(\text{ClO}_4)_2$, $\text{Co}(\text{ClO}_4)_2$, AgClO_4 , CuCl_2 , $\text{Cu}(\text{CH}_3\text{COO})_2$ were also investigated; of these only the cupric salts showed pronounced catalytic activity, which was greatly enhanced in the presence of acids.

These effects are considered separately below.

In every case the kinetics were first order in *cis*-azobenzene, and conformed the rate law,

$$-d[\text{cis-A}]/dt = k[\text{cis-A}] \quad (12)$$

where the pseudo-first order rate constant k contained contributions from both the uncatalyzed (k_0) and catalyzed (k_{cat}) path, i.e.

$$k = k_0 + k_{\text{cat}}. \quad (13)$$

k_0 was measured separately and k_{cat} determined by difference

(a) EFFECT OF PERCHLORIC ACID

Three series of experiments, in each of which the HClO_4 concentration was varied, were performed using different solvent mixtures; 25, 50 and 75 mole percent ethanol. The temperature was kept at 60.1°C and the initial concentration of *cis*-azobenzene was 0.08 gr. per liter.

The maximum HClO_4 concentrations which could be studied were 1.1 M in the 50% solvent mixture, and 0.5 M in the other two solvents. Below these concentrations the kinetics were of first order in *cis*-azobenzene as shown by the kinetic plots in Fig. 7. At higher acid concentrations the first order rate plots deviated significantly from linearity, possibly due to side reactions of azobenzene with the acid.

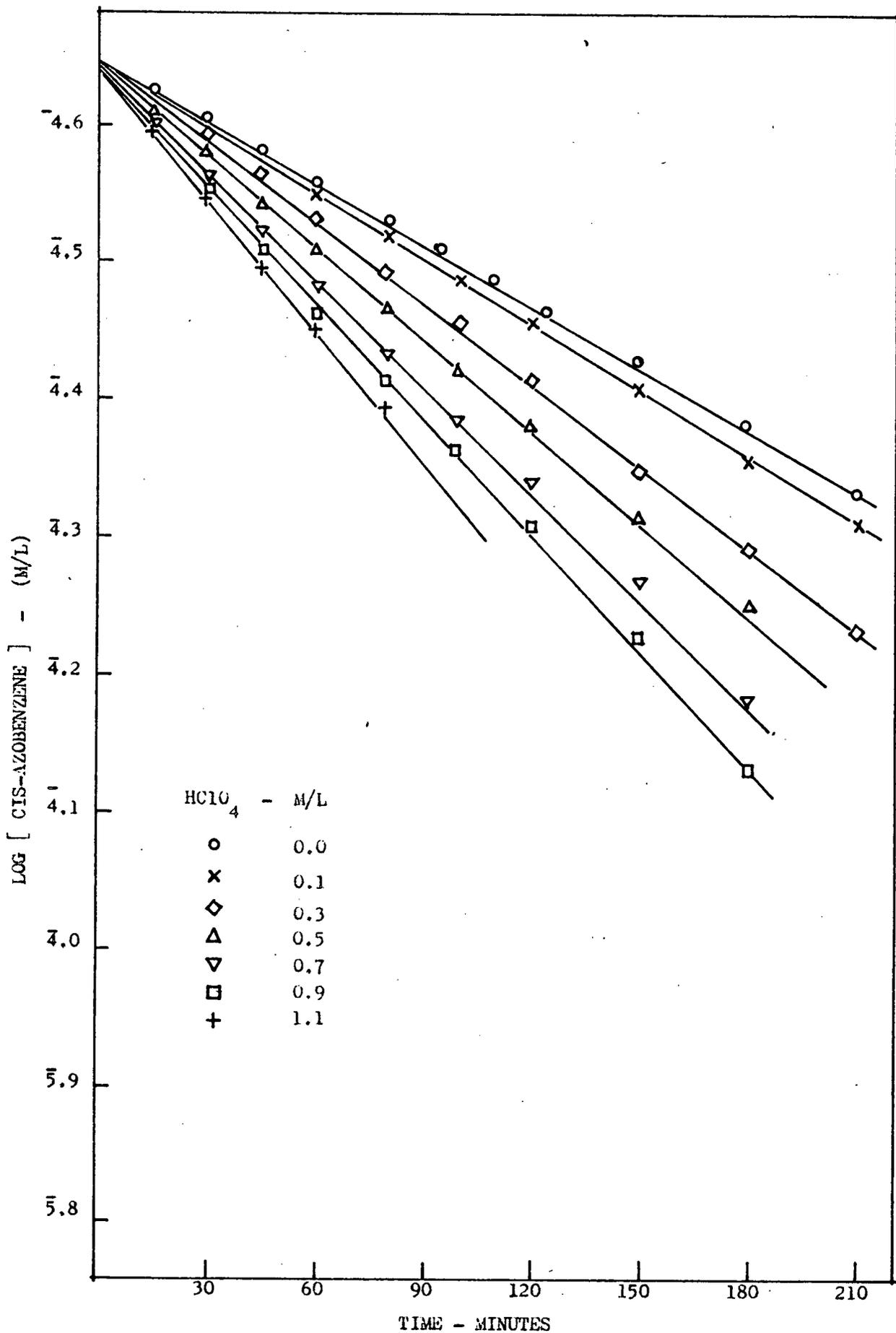


FIGURE 7. First order kinetic plots for uncatalyzed and HClO₄ catalyzed cis-trans isomerization of azobenzene in 50 mole % EtOH at 60° C.

The results for these series of experiments are summarized in Table (II) and Fig. 8. The catalytic rate appears to be first order in perchloric acid corresponding to the rate law.

$$k_{\text{cat}} = k_{\text{H}^+} [\text{HClO}_4] \quad (14)$$

Where k_{H^+} is 7.4, 5.5, 6.5 $\text{mole}^{-1} \text{sec}^{-1}$ in 25, 50 and 75 mole percent ethanol respectively. The solvent effect is not large but the catalytic rate in 50 mole % ethanol, is definitely smaller than at the other concentrations. (Fig. 9)

The perchlorate ion and ionic strength effects do not appear to be important as indicated by the observation that 0.5M NaClO_4 , either alone or in the presence of 0.5M HClO_4 , was without effect (Table VIII).

It seems likely that perchloric acid is completely dissociated in these solutions and hence that the observed catalytic effect is due to H^+ (i.e. H_3O^+ or EtOH_2^+) ions. The general considerations concerning the kinetics and mechanisms of acid catalyzed reactions, outlined in the introduction, would appear to be applicable to the present system which involves the reaction of a single uncharged molecule. Of the three general types of mechanisms considered, the third, involving the protonation of the reacting species as rate determining step, seems to be most unlikely in this case as the protonation of nitrogen atoms is usually quite fast. The other two mechanisms however, appear plausible. The first assumes that the catalyzed isomerization involves the formation of the conjugate acid of azobenzene followed by a slow unimolecular step. i.e.

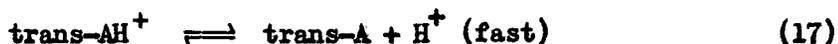


TABLE II
EFFECTS OF PERCHLORIC ACID AT 60° C.

Solvent	Acid moles/liter	$k \times 10^5$ sec ⁻¹	$k_{cat} \times 10^5$ sec ⁻¹
75 mole%			
EtOH	0	7.04	0
"	0.1	7.51	0.47
"	0.2	8.32	1.28
"	0.3	8.96	1.92
"	0.4	9.60	2.56
50 mole%			
EtOH	0	5.76	0
"	0.1	6.40	0.64
"	0.3	7.68	1.92
"	0.5	8.62	2.86
"	0.7	9.60	3.84
"	0.9	10.6	4.84
"	0.1	11.2	5.44
25 mole%			
EtOH	0	5.11	0
"	0.1	5.72	0.61
"	0.2	6.70	1.59
"	0.3	7.39	2.28
"	0.4	7.96	2.86
"	0.5	8.81	3.70

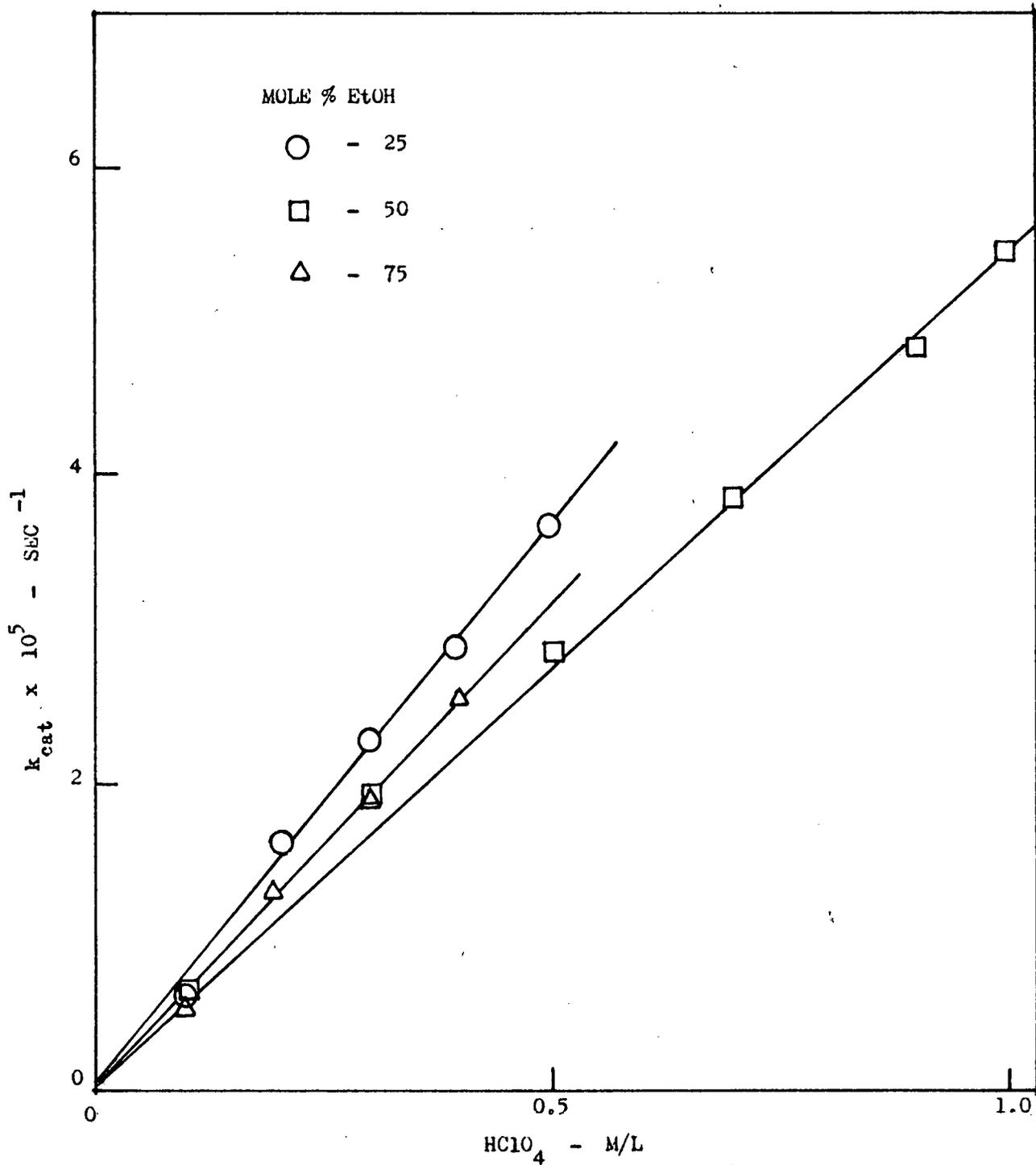
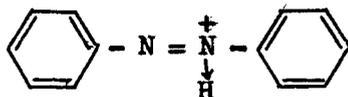


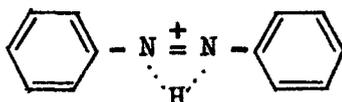
FIGURE 8. Catalytic effect of perchloric acid at 60° C.

As for the structure of the protonated complex, referring to the discussion reported in the introduction, model (I)



(I)

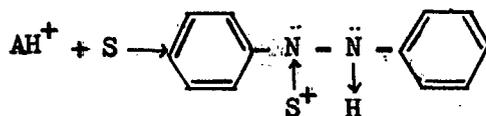
would be more consistent with the enhanced ease of isomerization, since the localization of the proton on one of the nitrogen atoms should result in polarization of π electrons and a decrease in degree of double bond character of the azo-linkage. Model (II)



(II)

on the contrary does not explain readily the enhanced isomerization, particularly if, as suggested by Jaffe (14), the cis-conformation of this structure is the more stable one.

An alternative description of the slow isomerization step, which we are inclined to favour, involves the formation of the intermediate (III)



(III)

in which free rotation about the double bond is possible. Such a mechanism is consistent with either structure (I) or (II) for the conjugate acid.

The simple criterion suggested by Zucker and Hammett (10,8) for distinguishing between these two types of mechanisms, i.e. the expectation of a linear dependence of k_{cat} on h_0 in the first case and on $[H^+]$ in the second, is not readily applicable here in view of the limited acidity range

accessible to kinetic measurement and of the absence of h_0 data in mixed solvent. In aqueous solutions a plot of h_0 versus $[H^+]$ diverges appreciably from linearity even at concentrations below 1 M $HClO_4$ (Fig 1) Such a divergence was not observed in our case. (Fig 8). On the other hand the dependence of k_{cat} on solvent composition (Fig. 9) appears to follow h_0 which, at least for HCl, has been shown to pass through a minimum in the vicinity of equimolar concentration of H_2O and EtOH. (Fig. 3).

Because of the conflicting nature of these indications, and the questionable theoretical validity of the Zucker-Hammett hypothesis, it is not possible to distinguish conclusively between the alternative mechanistic possibilities.

(b) EFFECT OF HYDROCHLORIC ACID

Essentially the same procedure was followed as for $HClO_4$, but since the kinetics remained constantly first order in cis-azobenzene the measurements were extended up to about 1.5M HCl, above which the rates became too high for convenient measurement. Typical rate plots are shown in Fig. 10.

Four series of experiments were performed using 25, 50, 75 and 95 mole percent ethanol as solvent. The results are recorded in Table III and attention is directed to the following features:

1. Except at very low concentrations, the catalytic activity of HCl is higher than that for corresponding concentrations of $HClO_4$ in each solvent.

2. The kinetic dependence of k_{cat} on the total HCl concentration is apparently greater than first order, (Fig. 11).

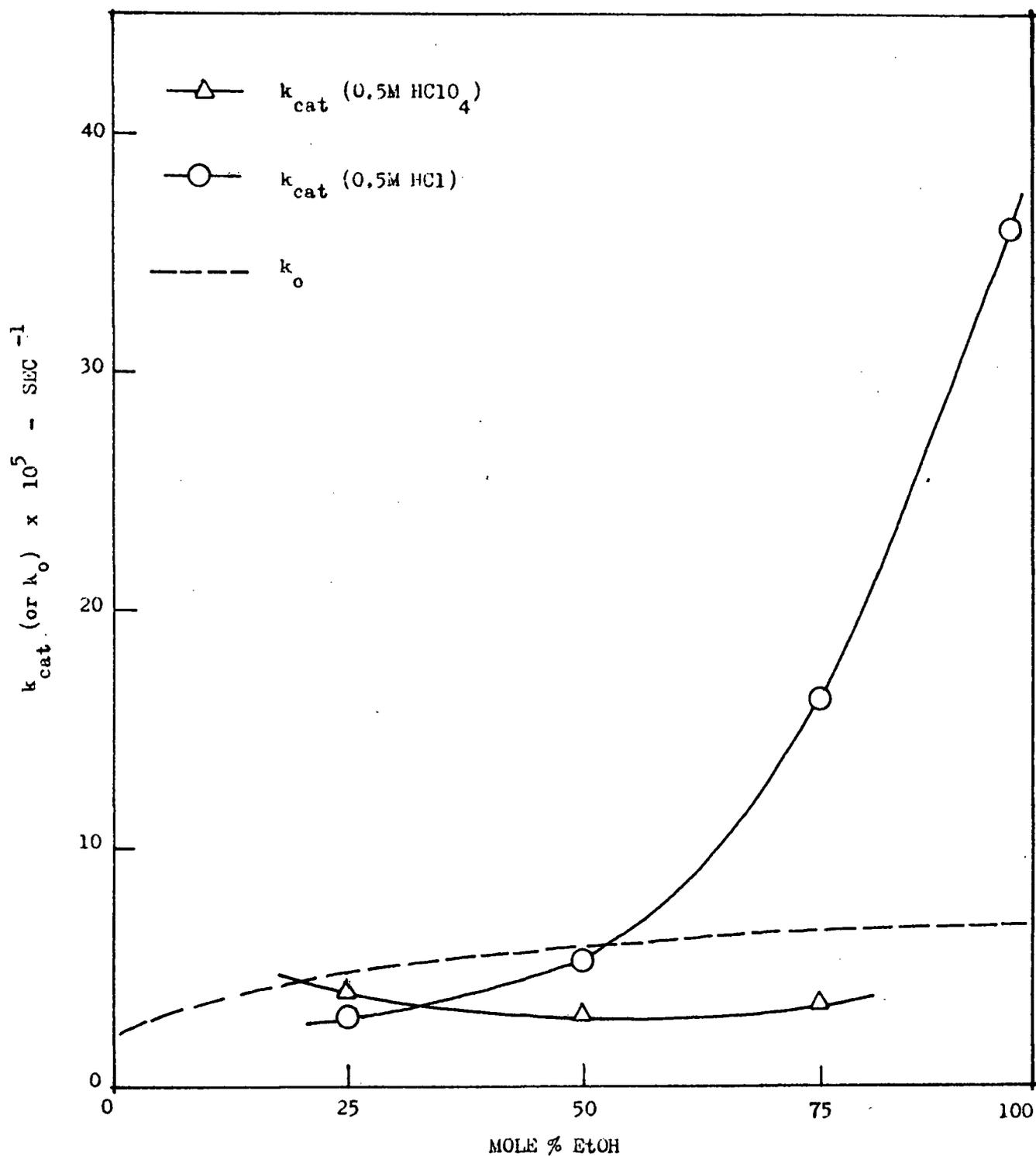


FIGURE 9. Solvent dependence of the catalytic effects of perchloric and hydrochloric acids at 60° C. The broken line depicts the solvent dependence of the uncatalyzed rate (k_o)

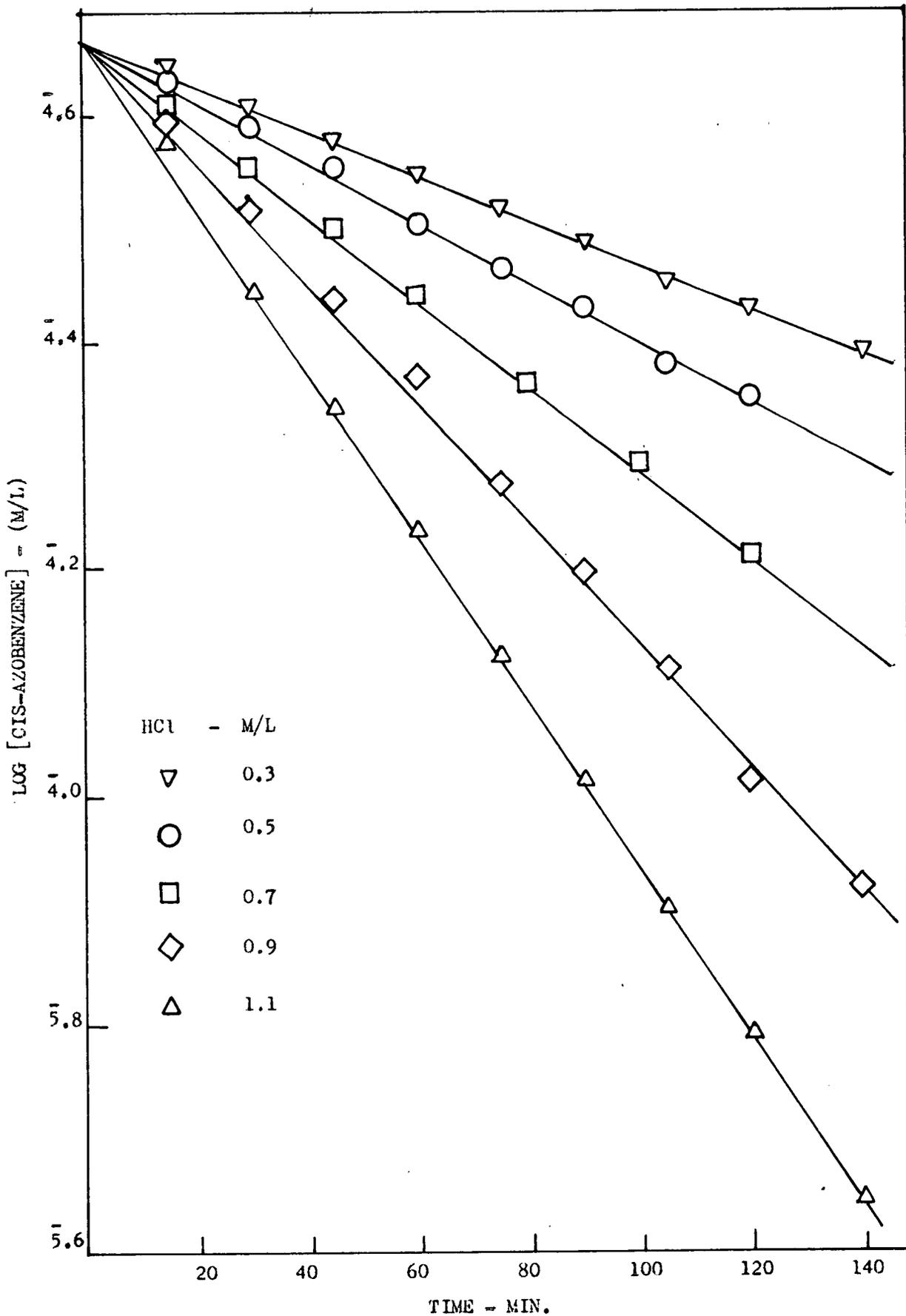


FIGURE 10 First order kinetic plots for HCl catalysed cis-trans isomerization of azobenzene in 50 mole % EtOH at 60°C.

TABLE III
EFFECT OF HYDROCHLORIC ACID AT 60° C.

Solvent	HCl. moles/liter	$k \times 10^5$ sec^{-1}	$k_{\text{cat}} \times 10^5$ sec^{-1}
95 mole %			
EtOH	0	6.70	0
"	0.1	10.0	3.30
"	0.3	22.6	15.9
"	0.5	42.9	36.2
"	0.7	76.1	69.4
"	0.85	104	97.3
"	1.0	139	132
75 mole %			
EtOH	0	6.75	0
"	0.1	8.05	1.30
"	0.3	13.1	6.35
"	0.5	23.1	16.3
"	0.7	35.77	28.9
"	0.8	44.7	38.0
"	0.9	56.9	50.1
"	1.0	67.2	60.4
"	1.1	88.4	81.6
"	1.2	105	98.3

TABLE III

(cont.)

50 mole % EtOH			
"	0	5.76	0
"	0.2	6.40	0.64
"	0.3	7.78	2.02
"	0.5	10.8	5.09
"	0.7	15.0	9.24
"	0.8	17.8	12.0
"	0.9	21.4	15.6
"	1.0	24.2	18.4
"	1.1	27.5	21.7
"	1.2	33.1	27.3
"	1.3	40.8	35.0
"	1.5	54.7	48.9
"	1.7	72.8	67.0

TABLE III (cont'd)

25 mole %

EtOH	0	4.78	0
"	0.1	5.56	.78
"	0.3	6.39	1.61
"	0.5	7.78	3.00
"	0.7	10.0	5.22
"	0.8	11.4	6.62
"	0.9	12.8	8.02
"	1.0	14.2	9.42
"	1.1	15.8	11.0
"	1.3	23.2	18.4

TABLE IV
EFFECT OF ACETIC ACID AT 60°C.

Solvent	HAc moles/liter	$k \times 10^5$ sec^{-1}	$k_{\text{cat}} \times 10^5$ sec^{-1}
50 mole% EtOH	0	5.76	0
"	0.1	5.50	0.26
"	0.5	5.50	0.26
"	0.7	5.50	0.26
"	0.9	5.50	0.26

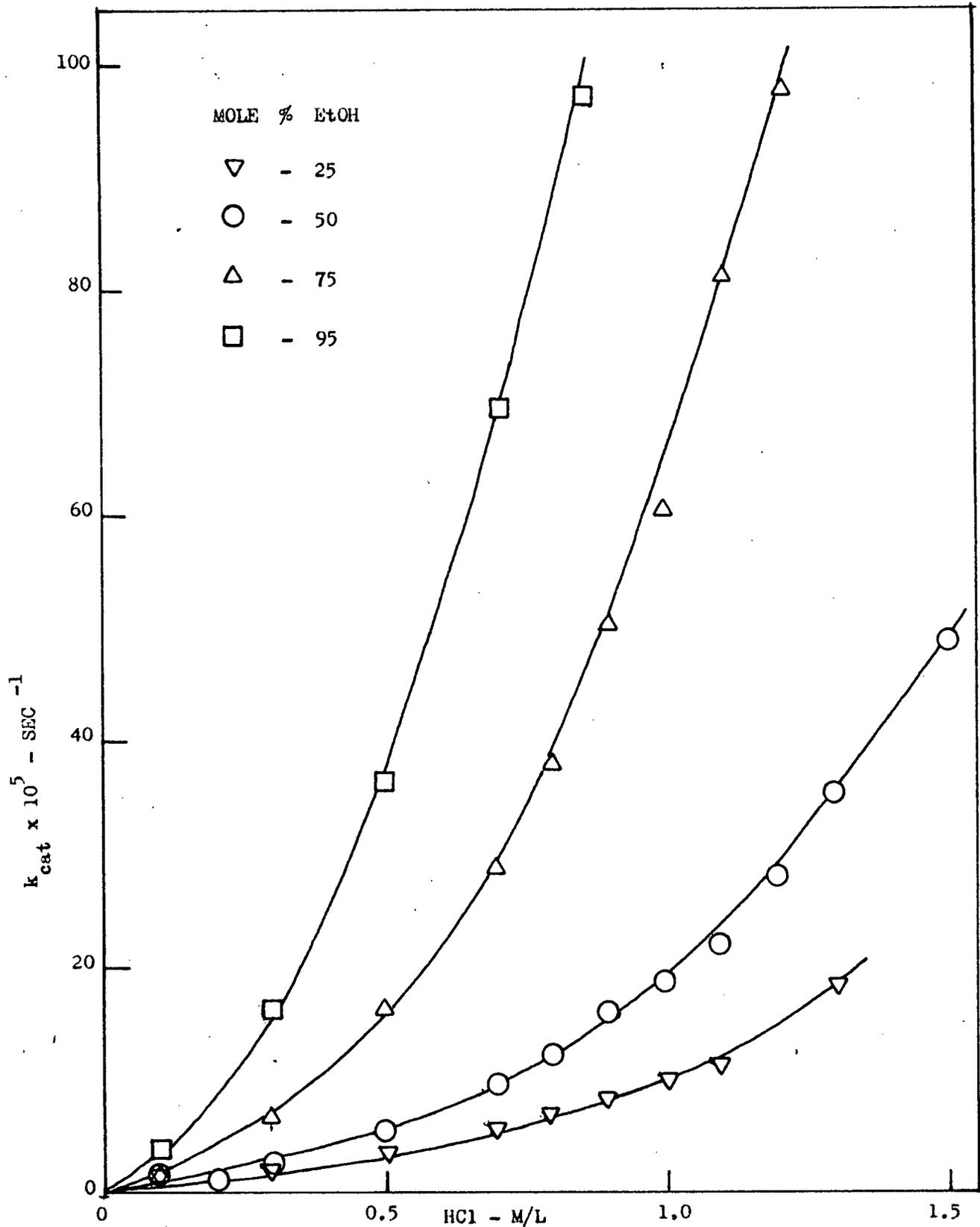


FIGURE 11. Catalytic effect of hydrochloric acid at 60° C

3. The rate shows an inverse dependence on the H_2O content of the solvent, that is on its polarity. (Fig. 11)

4. The rates approach (and in some cases actually fall below) those for $HClO_4$ (i) at low HCl concentration and (ii) in solvents of high water content (Fig. 9, 11).

These observations suggest that in addition to the H^+ ion catalysis observed with $HClO_4$, there is an additional catalytic effect which may be due to undissociated HCl molecules. As might be expected this becomes unimportant at low HCl concentrations and in solvents of high water content, since HCl tends to become completely dissociated under these conditions. The catalytic activity then approached that of the stronger acid $HClO_4$.

The results of an experiment involving addition of NaCl are also of interest in this connection. Due to the low solubility of the salt in aqueous alcohol the maximum concentration of NaCl that could be added was about 0.2 M. While this concentration of NaCl alone was without effect, in the presence of HCl it produced a slight enhancement of the catalytic activity which may be attributed to an increase in concentration of undissociated HCl (Table VIII). As mentioned previously corresponding addition of $NaClO_4$, either alone or in the presence of $HClO_4$, was without effect.

The rate law predicted on the basis of this interpretation is,

$$k = k_o + k_{H^+} [H^+] + k_{HCl} [HCl] \quad (18)$$

$$\text{whence } k_{cat} = k - k_o = k_{H^+} [H^+] + k_{HCl} [HCl] \quad (19)$$

$$= k_{H^+} [H^+] + (k_{HCl}/K) [H^+] [Cl^-] \quad (20)$$

where k is the dissociation constant of HCl. If the fraction of undissociated HCl is small, then $[H^+] \simeq [Cl^-] \simeq [HCl]_o$

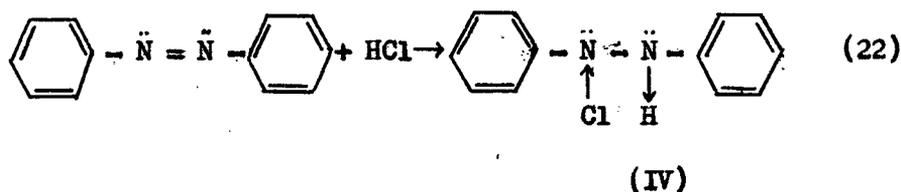
where $[HCl]_o$ is the total HCl concentration and equation (20) becomes

$$k_{\text{cat}} = k_{\text{H}^+} [\text{HCl}]_0 + (k_{\text{HCl}}/K) [\text{HCl}]_0^2$$

or
$$k_{\text{cat}} / [\text{HCl}]_0 = k_{\text{H}^+} + (k_{\text{HCl}}/K) [\text{HCl}]_0 \quad (21)$$

Plots of $k_{\text{cat}} / [\text{HCl}]_0$ vs. $[\text{HCl}]_0$ at the various solvent composition, are shown in Fig. 12. In accord with equation 21 these are fairly linear up to HCl concentration of about 1 M. Their intercepts yield values for k_{H^+} somewhat lower than those obtained with HClO_4 . One possible explanation for this is that the H^+ - catalyzed reaction follows an h_0 rather than H^+ - dependence and that h_0 for HCl, even at low concentrations, is appreciably lower than for HClO_4 . It is interesting to note, however, that the values of k_{H^+} obtained from the intercepts, like those for HClO_4 , pass through a minimum for the 50 mole percent EtOH solvent composition.

A mechanism which would account for the catalytic effect of undissociated HCl molecules, involves the simultaneous coordination of H^+ and Cl^- at the azo linkage to give an intermediate (IV), analogous to (III), in which the role of the solvent molecule (5) is effectively assumed by Cl^-



It is interesting to note that a similar mechanism may account for the combined catalytic effect of H^+ and thiourea reported by Schulte-Frohlinde (7). The kinetic dependence is of the form, $k_{\text{cat}} = [\text{H}^+] [\text{thiourea}]$, and can be accounted for by the formation of an intermediate analogous to (IV) through the reaction of azobenzene with the conjugate acid of thiourea.

Also in accord with these suggestions are the results of Nozaki and Ogg (20) for the acid-catalyzed cis-trans isomerization of maleic acid. Different acids were found to exhibit widely differing catalytic activities (HCl, for

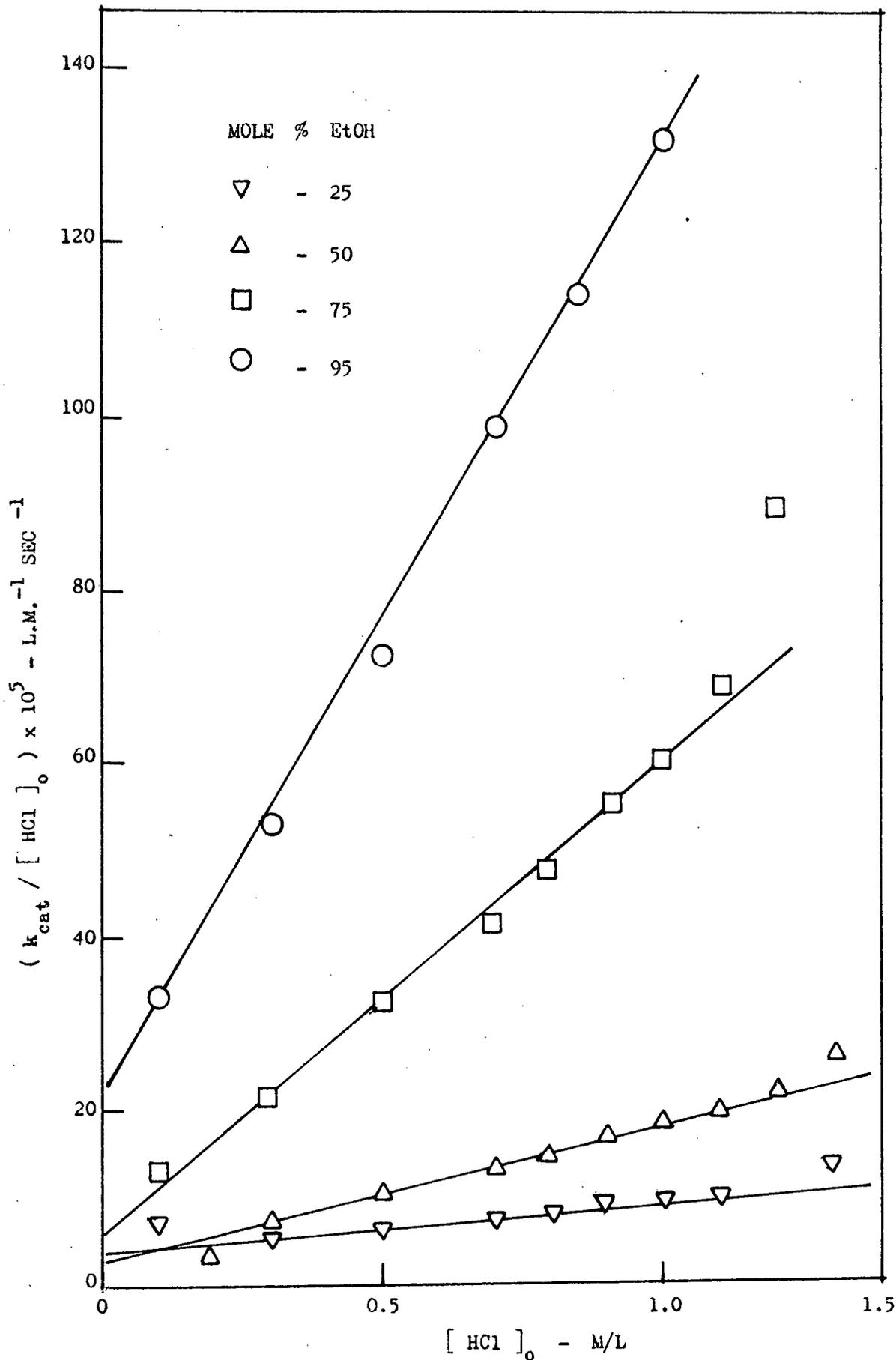
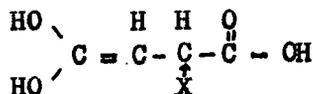


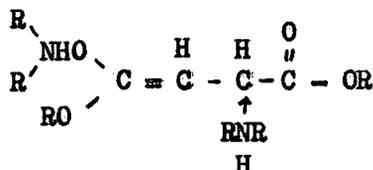
FIGURE 12. Concentration - dependence of HCl catalysis plotted according to equation (21)

example, being more than 50 times as effective as HClO_4) suggesting that the anion also plays an important role in the reaction.

A mechanism, involving the simultaneous coordination of the anion and H^+ (at the double bond and one of the carboxyl oxygen, respectively) was proposed, which is in some respects analogous to that described above. The structure of the proposed intermediate is



An analogous mechanism, assuming the formation of an intermediate which involves coordination of both an electron donor and an electron acceptor has also been proposed (21,22) for the catalysis by secondary amines of the cis-trans isomerization of diethyl and dimethylmaleate. Two molecules of amine are found to react in the rate determining step; one conjugates through N at the double bond the other through H at the carbonyl oxygen.



(c) EFFECT OF ACETIC ACID

As shown in Table (IV) no appreciable catalytic effect could be detected for concentrations of up to 1 M of acetic acid in 50 mole percent ethanol at 60° .

Referring to our previous discussion on the effect of HClO_4 and HCl it is clear that for every proposed mechanism the acid catalysis appears to involve the formation of a protonated species between the uncharged azobenzene molecule and the acid. It seems reasonable to suggest that the absence of any catalytic activity for acetic acid is due to the fact that this acid is too weak to give rise to any protonated species analogous to (I), (II), or (IV).

(d) EFFECT OF CUPRIC PERCHLORATE

The effect of cupric ions on the isomerization rate, was examined systematically at 60°C in 50 mole percent ethanol. The cupric perchlorate concentration was varied up to 1M, above which the rate became immeasurably fast. Zero time uncertainties, due to fast rates, may also account for the apparent "induction periods" (i.e. failure of the first order plots to extrapolate back through the initial concentrations) reflected in the first order rate plots in Fig. 13. Apart from this initial effect, however, the first order plots were convincingly linear. The kinetic results are summarized in Table (V) and Fig. 13 and show the following features:

1. The specific catalytic activity of $\text{Cu}(\text{ClO}_4)_2$ is much higher than that of the two acids previously studied.
2. The kinetic dependence of k_{cat} on the cupric perchlorate concentration is greater than first order (approximately 1.5) as shown by the plots of k_{cat} vs. $[\text{Cu}(\text{ClO}_4)_2]$ in Fig. 14 and of $\log k_{\text{cat}}$ vs. $\log [\text{Cu}(\text{ClO}_4)_2]$ in Fig. 15.

In the interpretation of these results it seems reasonable to attribute the catalytic effect of $\text{Cu}(\text{ClO}_4)_2$ to the coordination of Cu^{++} with the azo-nitrogen atoms to give an intermediate analogous to that suggested for acid catalysis.

The significance of the observed deviation from first order dependence is not clear, but two contributing factors can be suggested:

1. A medium (e.g. ionic strength) effect, superimposed upon the Cu^{++} concentration effect, when the concentration of cupric perchlorate is increased.
2. Contributions from a "second-order" path (i.e. in Cu^{++}) in addition to a first order one. This would imply a mechanism involving coordination of two Cu^{++} ions with azobenzene possibly through an intermediate:

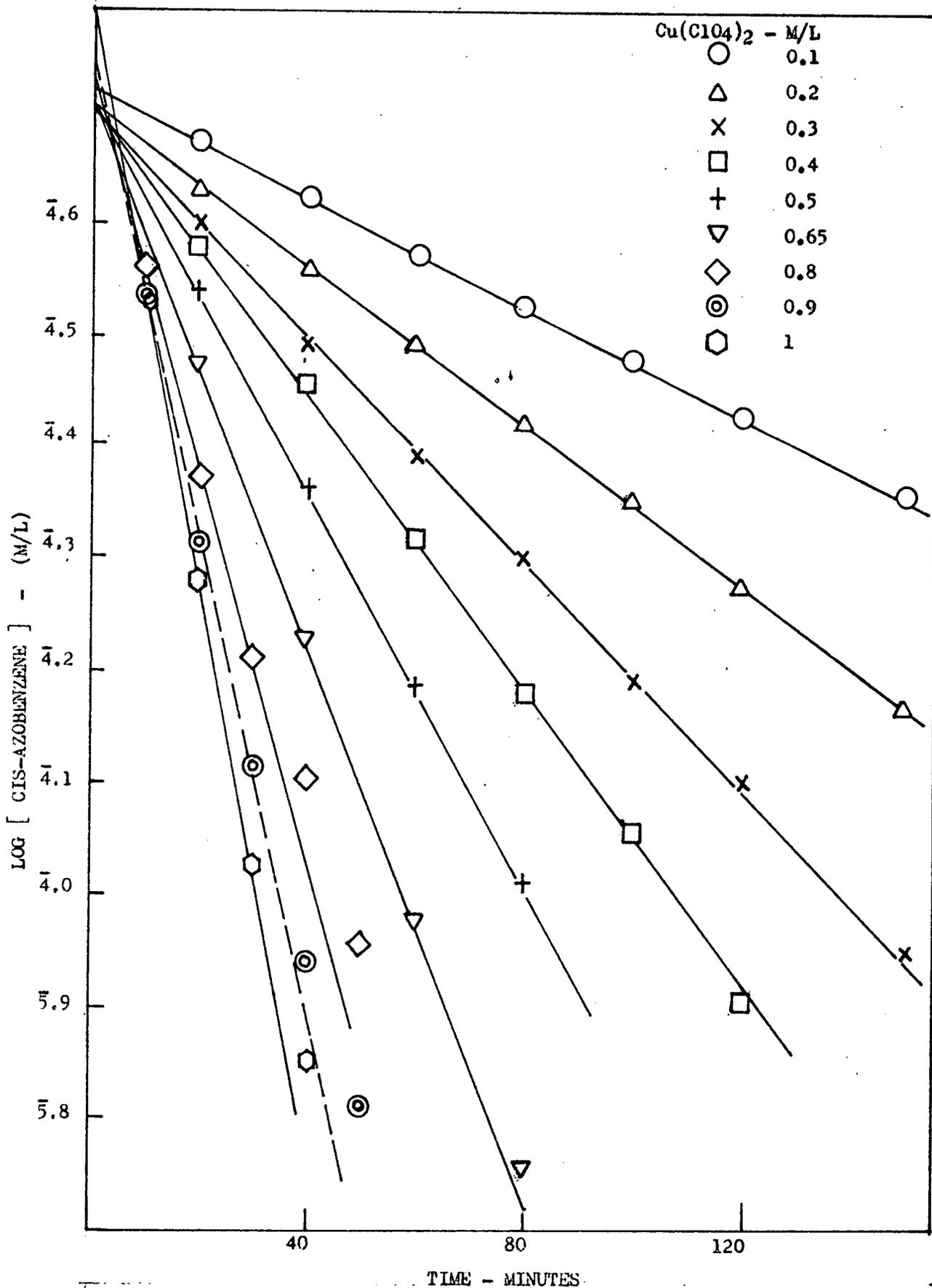


FIGURE 13. First order kinetic plots for $\text{Cu}(\text{ClO}_4)_2$ catalyzed cis-trans isomerization of azobenzene in 50 mole % ethanol at 60°C .

TABLE V

EFFECT OF CUPRIC PERCHLORATE AT 60° IN 50 mole % EtOH

HClO_4 moles/liter	$\text{Cu}(\text{ClO}_4)_2$ moles/liter	$k \times 10^5$ (sec^{-1})	$k_{\text{cat}} \times 10$ (sec^{-1})
0	.0	5.76	0
"	0.10	9.60	3.84
"	0.20	14.1	8.34
"	0.30	19.2	13.4
"	0.40	25.7	19.9
"	0.50	35.0	29.2
"	0.64	47.0	41.2
"	0.80	65.6	59.8
"	0.90	80.1	74.3
"	1.00	90.4	84.6
.050	0	6.07	0.31
"	0.02	19.5	13.7
"	0.04	27.8	22.0
"	0.06	33.9	28.1
"	0.08	39.5	33.7
.10	0	6.40	0.64
"	0.01	24.1	18.3
"	0.02	30.7	24.9
"	0.04	46.0	40.2
"	0.06	59.8	54.0

TABLE V (cont.)

HClO_4	$\text{Cu}(\text{ClO}_4)_2$ moles/liter	$k \times 10^5$ (sec^{-1})	$k_{\text{cat}} \times 10$ (sec^{-1})
.20	0	7.04	1.28
"	0.01	42.6	36.8
"	0.02	58.9	53.1
"	0.04	84.5	78.7
"	0.06	137	131
.32	0	7.67	1.91
"	.01	57.6	51.8
"	.02	85.8	80.0
"	.04	137	131
"	.06	184	178
"	.08	215	209
.42	0	8.12	2.36
"	.01	69.4	63.6
"	.02	113	107
"	.04	177	171
"	.06	240	234
.52	0	8.60	2.83
"	.01	81.2	75.4
"	.02	121	115
"	.03	162	156
"	.04	184	178
"	.06	254	248
"	.08	316	310

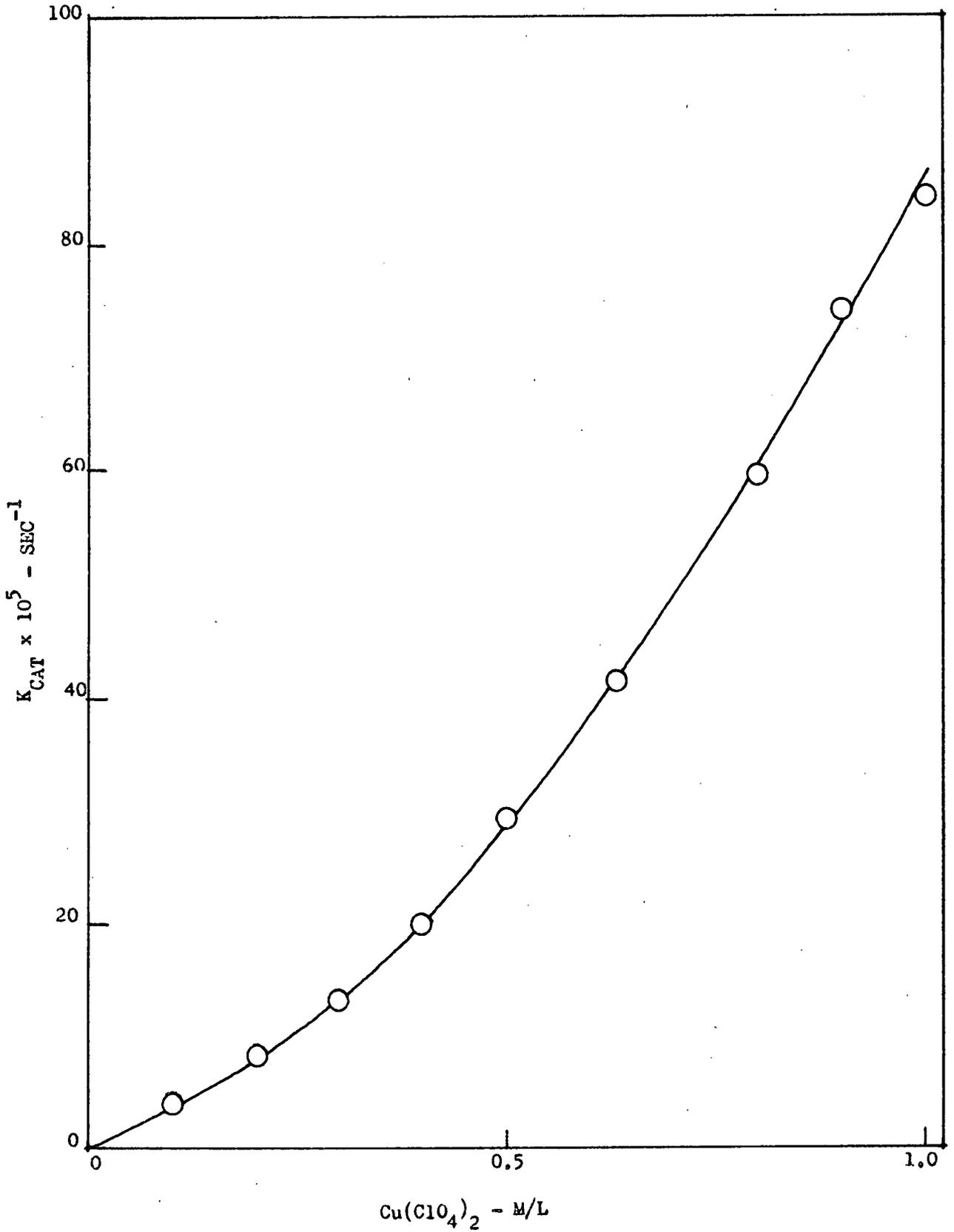


FIGURE 14. Catalytic effect of cupric perchlorate in 50 mole % Ethanol at 60°C.

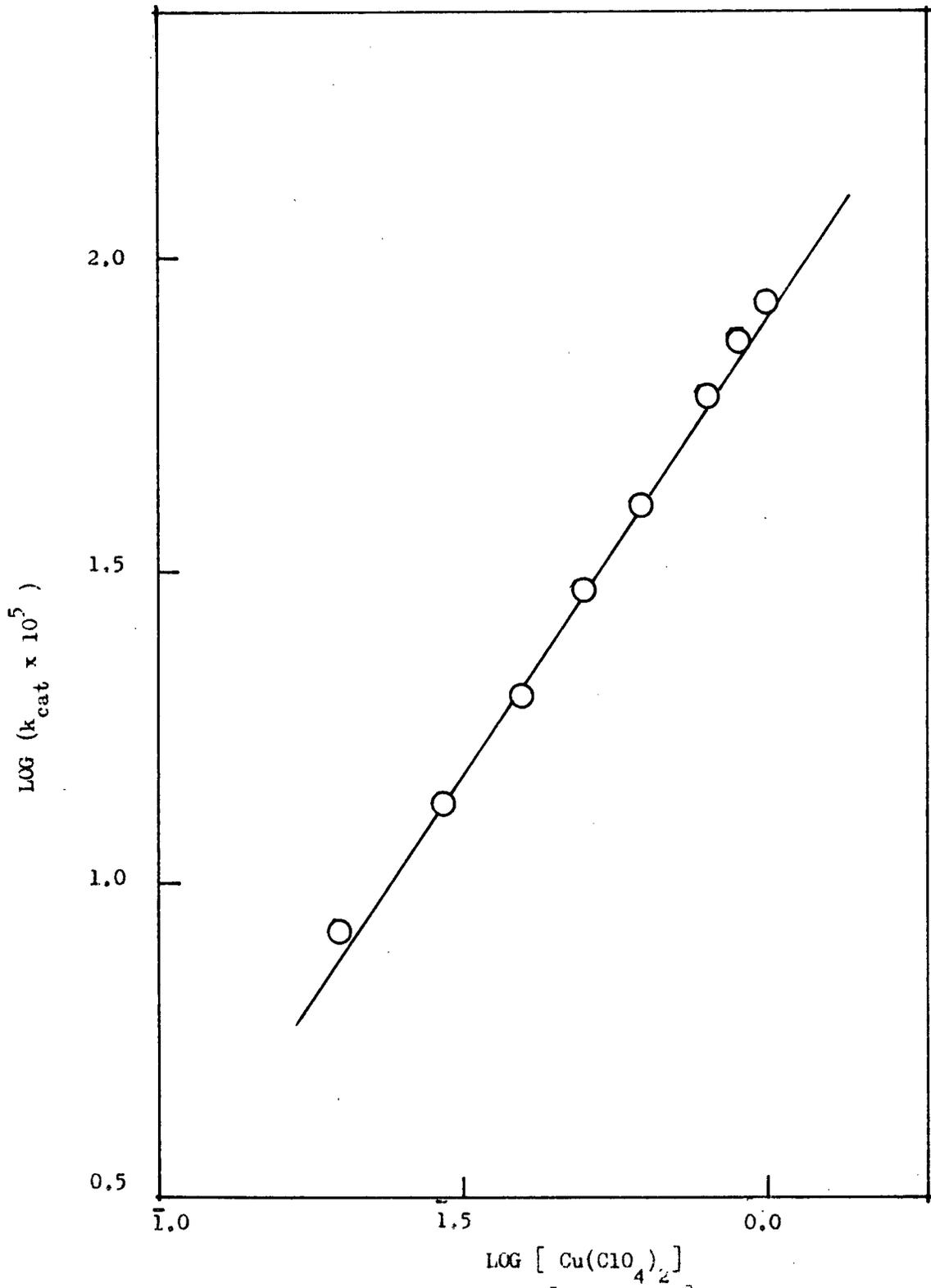
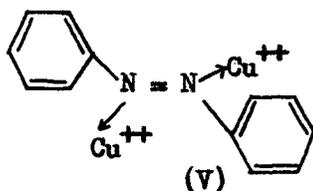
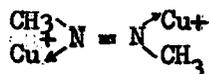


FIGURE 15. plot of $\log k_{\text{cat}}$ vs. $\log [\text{Cu}(\text{ClO}_4)_2]$



While there is no a priori reason to expect such a complex to form, it is of interest that the existence of an analogous stable cuprous chloride complex of azomethane i.e.



has been reported. (23)

The addition of small amounts of perchloric acid in the presence of cupric perchlorate proved to have an unexpectedly large effect, the combined catalytic effect being many times greater than the sum of the separate effects of the two catalysts. This effect was investigated systematically in a series of experiments in which the HClO_4 and $\text{Cu}(\text{ClO}_4)_2$ concentrations were simultaneously varied (from 0.1 to 0.5 M and from 0.005 to 0.06 M respectively). Again, because of high rates and the initial complications discussed earlier, measurements could not be made for Cu^{++} concentrations above 0.06 M.

Typical first order rate plots for these experiments are shown in Fig. 16 and 17. At constant acid concentration, plots of k_{cat} versus $[\text{Cu}(\text{ClO}_4)_2]$ show a good linear dependence with the exception of the region of very low $[\text{Cu}^{++}]$, where the curves bend sharply towards the origin (Fig. 18). Plots of k_{cat} versus $[\text{HClO}_4]$ at constant $[\text{Cu}^{++}]$ (Fig. 19) are linear except for high $[\text{H}^+]$ (about 0.5 M HClO_4) where they tend to level off. From these observations it appears that, over a considerable concentration range of Cu^{++} and H^+ , the predominant contribution to the catalytic rate is of the kinetic form:

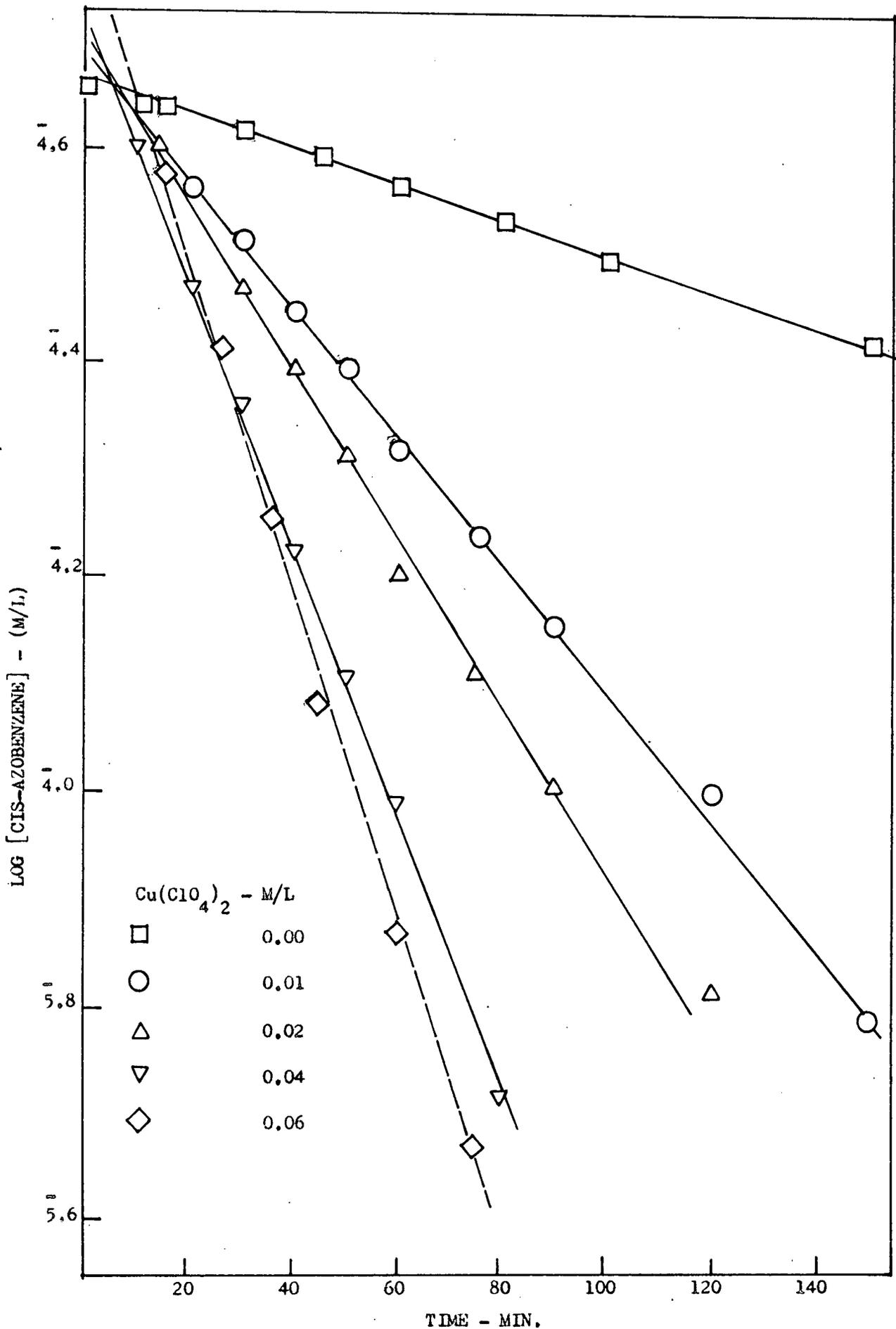


FIGURE 16. First order kinetic plots for the cis-trans isomerization of azobenzene catalyzed by $\text{Cu}(\text{ClO}_4)_2$ in the presence of 0.1 M HClO_4 in 50 mole % EtOH at 60° C.

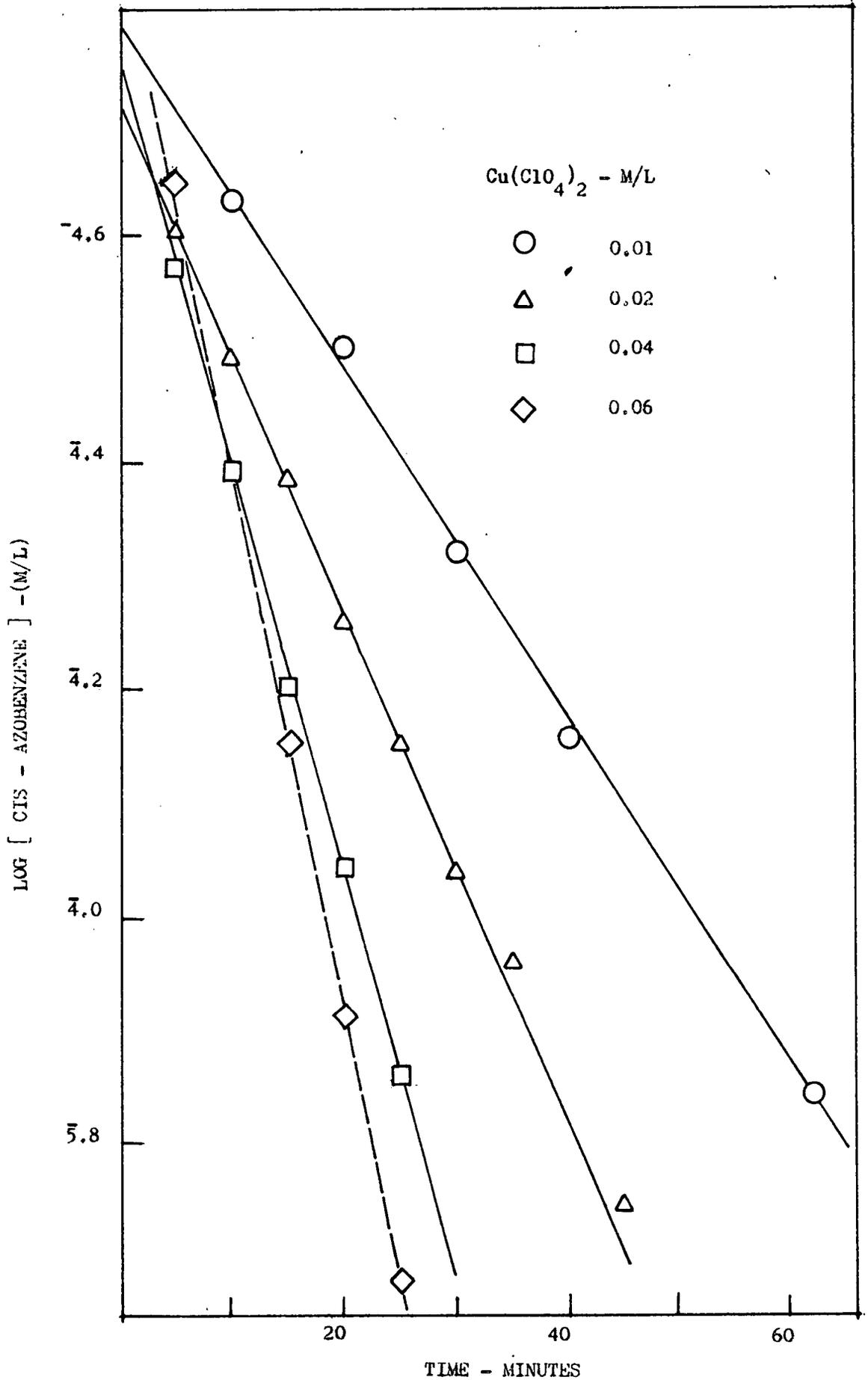


FIGURE 17. First order kinetic plots for the cis-trans isomerization of azobenzene catalyzed by $\text{Cu}(\text{ClO}_4)_2$ in the presence of 0.1 M HClO_4 in 50 mole % EtOH at 60°C .

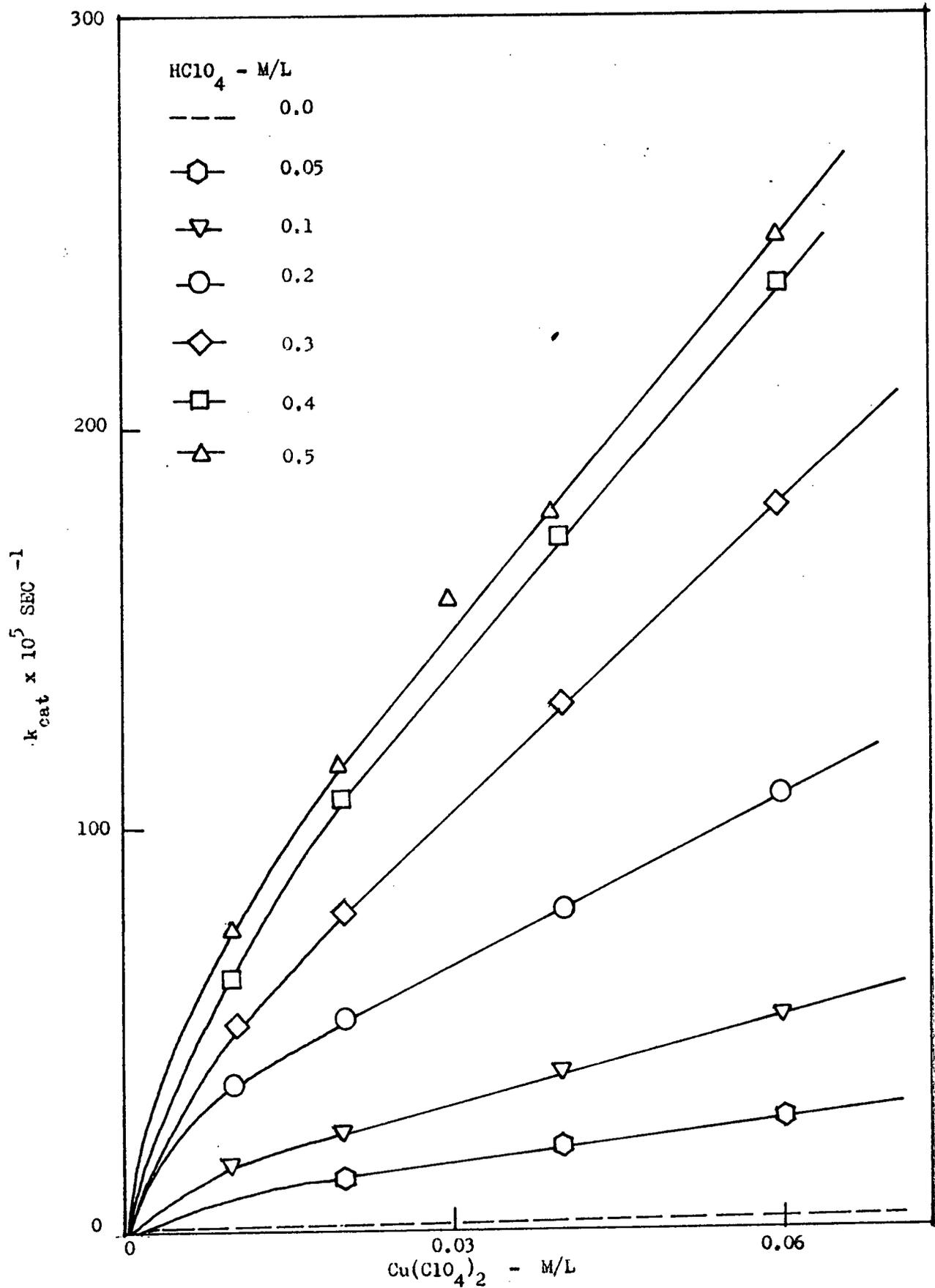


FIGURE 18. Combined catalytic effect of $\text{Cu}(\text{ClO}_4)_2$ and HClO_4 in 50 mole % EtOH

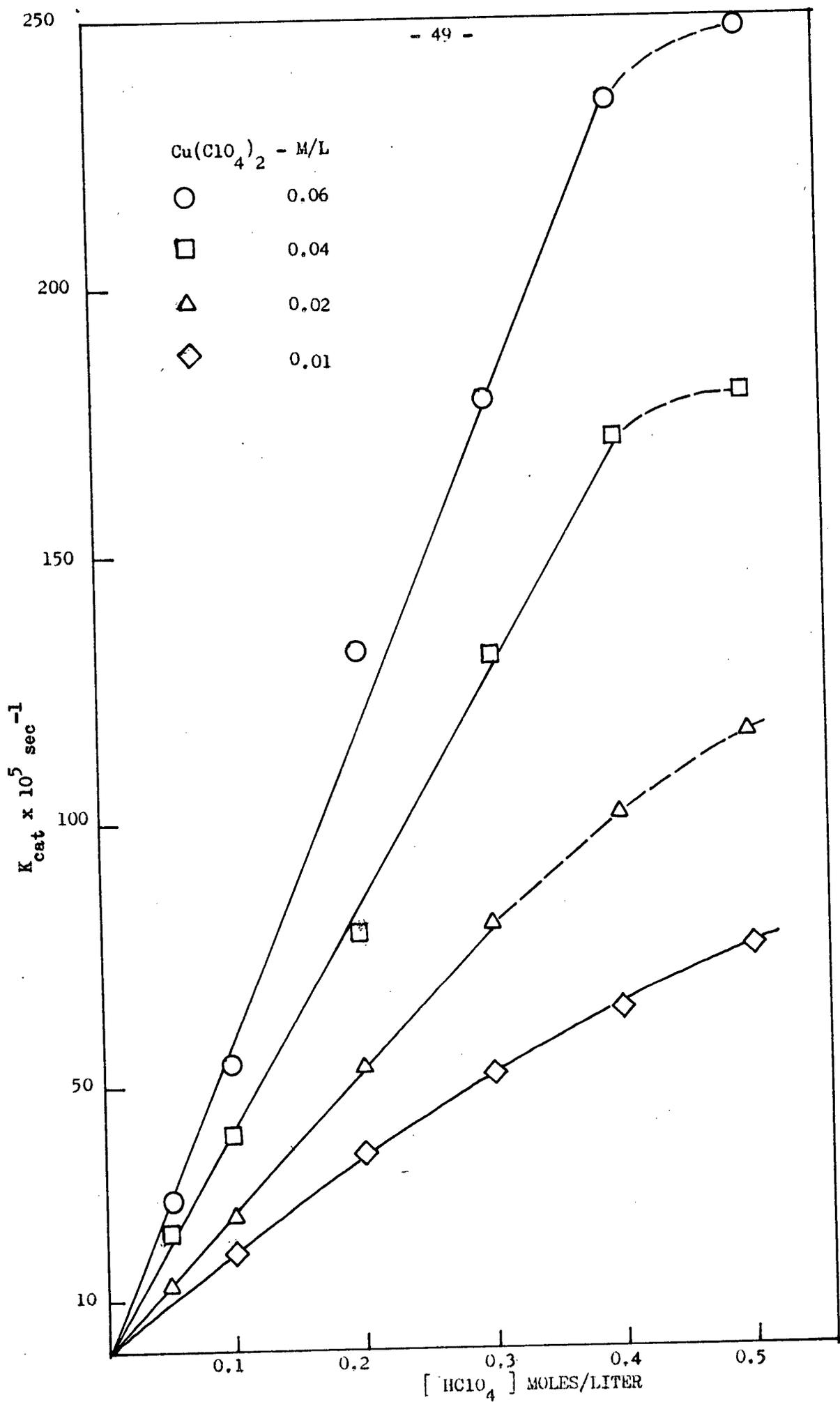


FIGURE 19. Combined catalytic effect of cupric perchlorate and

$$\text{Rate} = k [A][\text{Cu}^{++}][\text{H}^+]$$

or $k_{\text{cat}} = k[\text{H}^+][\text{Cu}^{++}]$

This implies a catalytic path involving the simultaneous interaction of H^+ and Cu^{++} with azobenzene. One possible interpretation is in terms of an intermediate complex analogous to (V) in which H^+ and Cu^{++} are coordinated to the two N atoms.

(f) EFFECT OF CUPRIC CHLORIDE

Because of complications due to solubility limitations the effect of cupric chloride could be examined only in the presence of hydrochloric acid. Three series of experiments were performed with 0.1, 0.2, 0.3 M HCl and various concentrations of up to 0.04 M CuCl_2 . The acid and the cupric salt concentration were restricted to this low range because of the extremely high catalytic rate. Typical first order rate plots are shown in Figs. 20 and 21 and the kinetic results are summarized in Table VI and Fig. 22.

It is seen that at constant acid concentration, plots of k_{cat} versus $[\text{CuCl}_2]$ are linear over the entire concentration range examined. The tendency for the catalytic activity to be enhanced by the acid is less marked than for cupric perchlorate, but this may be due to the much lower concentration range to which these measurements were confined. At low HCl concentrations k_{cat} is first order in CuCl_2 and is much greater than for $\text{Cu}(\text{ClO}_4)_2$ at comparable HClO_4 concentrations.

(g) EFFECT OF CUPRIC ACETATE

Again solubility limitations precluded addition of cupric acetate alone. One experiment was made with approximately 0.2 M cupric acetate in the presence of 0.5 M acetic acid. A measureable catalytic effect was noted (Table VIII) which was, however, much smaller than for corresponding perchlorate or chloride solutions. No further quantitative studies were attempted.

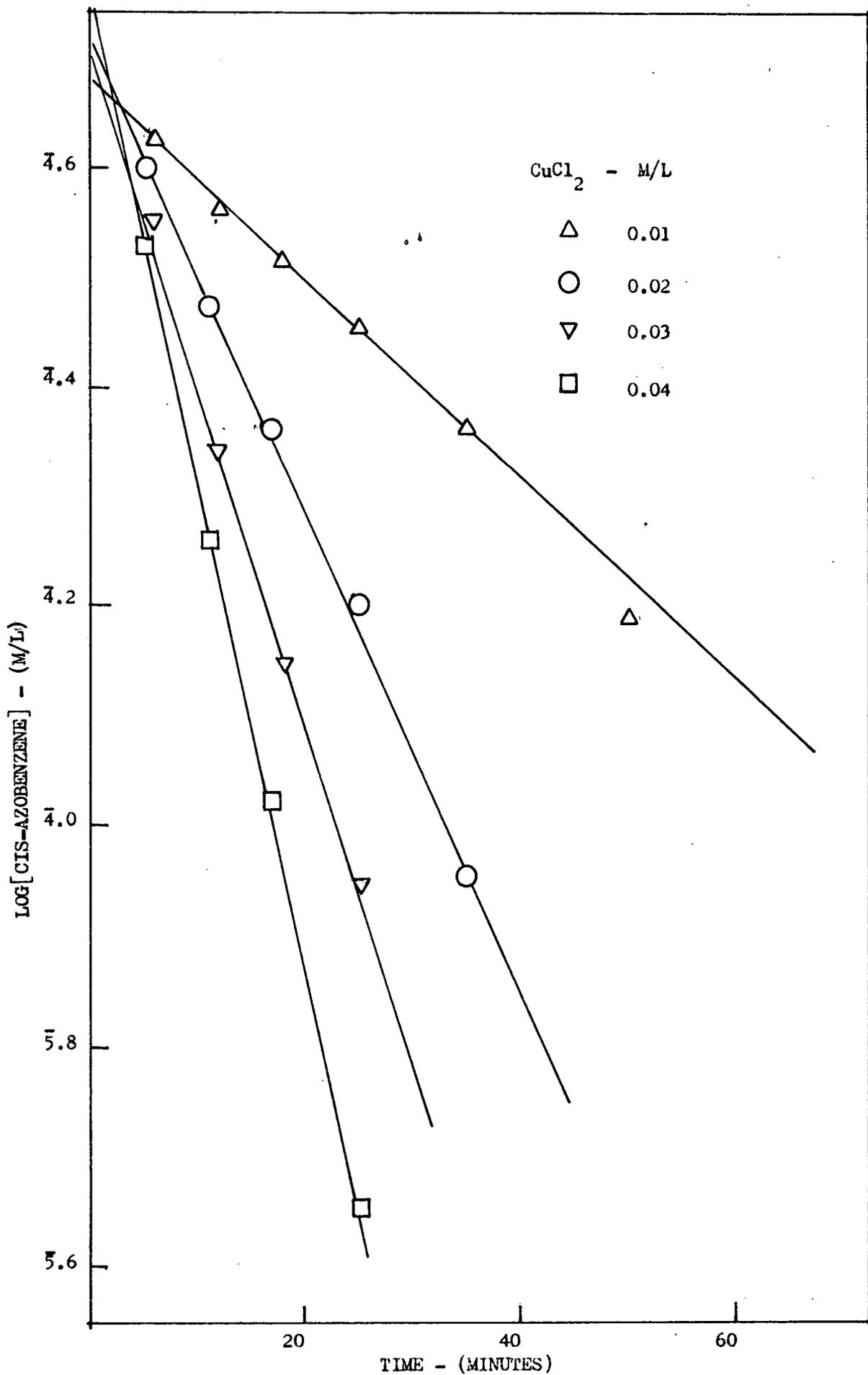


FIGURE 20. First order kinetic plots for the cis-trans isomerization of azobenzene catalyzed by CuCl_2 in the presence of 0.01 M HCl in 50 mole % EtOH

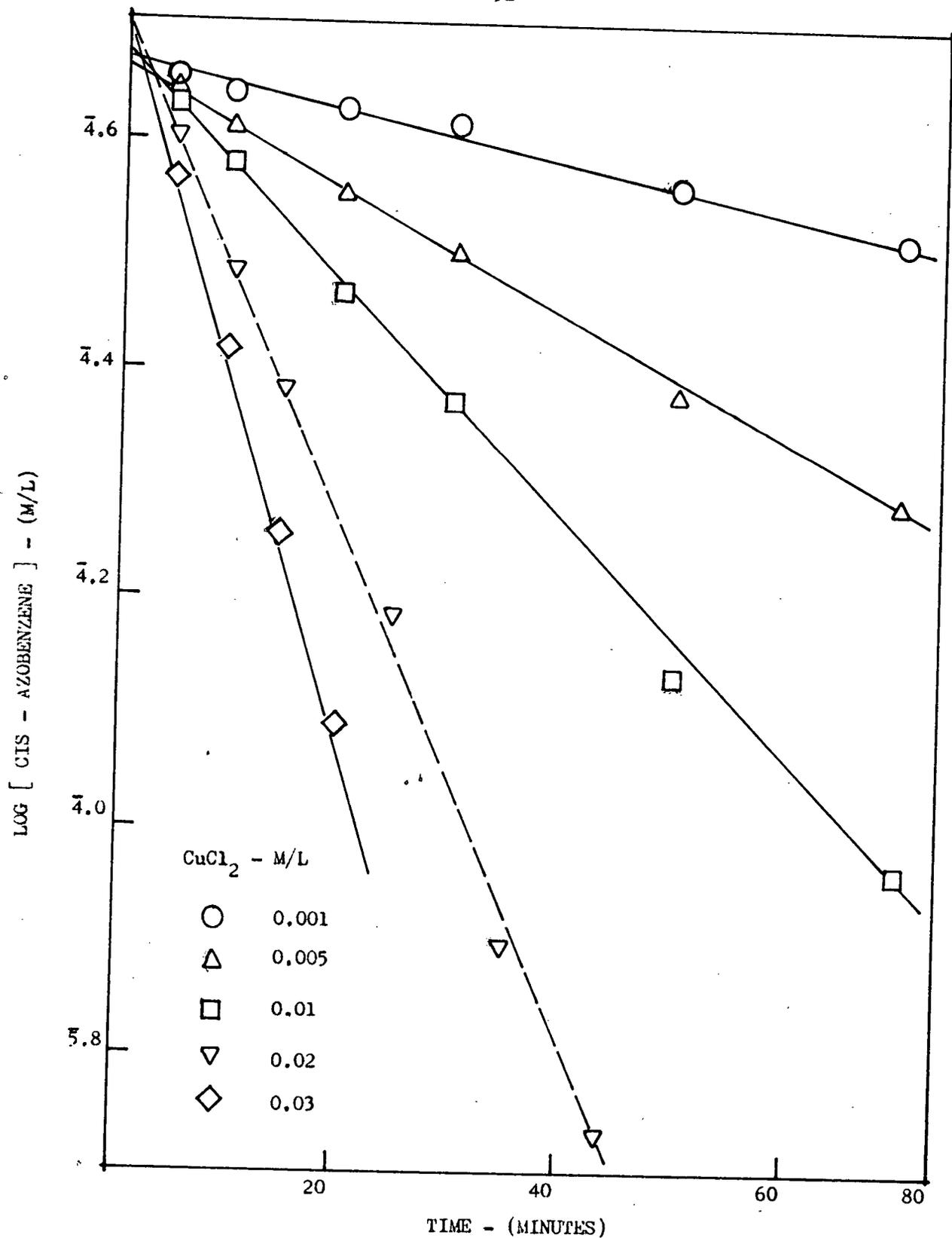


FIGURE 21. First order kinetic plots for the cis-trans isomerization of azobenzene catalyzed by CuCl_2 in the presence of 0.02 M HCl in 50 mole % EtOH at 60°C .

TABLE VI

EFFECT OF CUPRIC CHLORIDE

VI Solvent: 50 mole % EtOH - Temp. 60° C.

HCl moles/liter	CuCl ₂ moles/liter	k x 10 ⁵ (sec ⁻¹)	k _{cat} x 10 ⁵ (sec ⁻¹)
0.01 M	0	5.76	0
"	0.01	35.8	30.0
"	0.02	69.0	63.2
"	0.03	101	95.2
"	0.04	169	163
"	0.06	316	310
"	.2M NaClO ₄	105	99
"	.2M NaCl	155	149
.02	0	5.76	0
"	0.001	8.96	3.20
"	0.005	21.0	15.2
"	0.01	39.8	34.0
"	0.02	78.2	72.4
"	0.03	110	104
"	0.04		
.03	0	5.76	0
"	0.005	25.6	19.8
"	0.01	49.8	44.0
"	0.02	94.0	88.2
"	0.03	146	140
"	0.04	191	185

TABLE VII

EFFECT OF CUPRIC ACETATE

Solvent 50 mole % EtOH - Temp. 60° C.

CH_3COOH mole/liter	$\text{Cu}(\text{CH}_3\text{COOH})_2$ moles/liter	$k \times 10^5$ (sec^{-1})	$k_{\text{cat}} \times 10^5$ (sec^{-1})
.5M	0	5.51	0
.5M	0.2	15.3	9.50

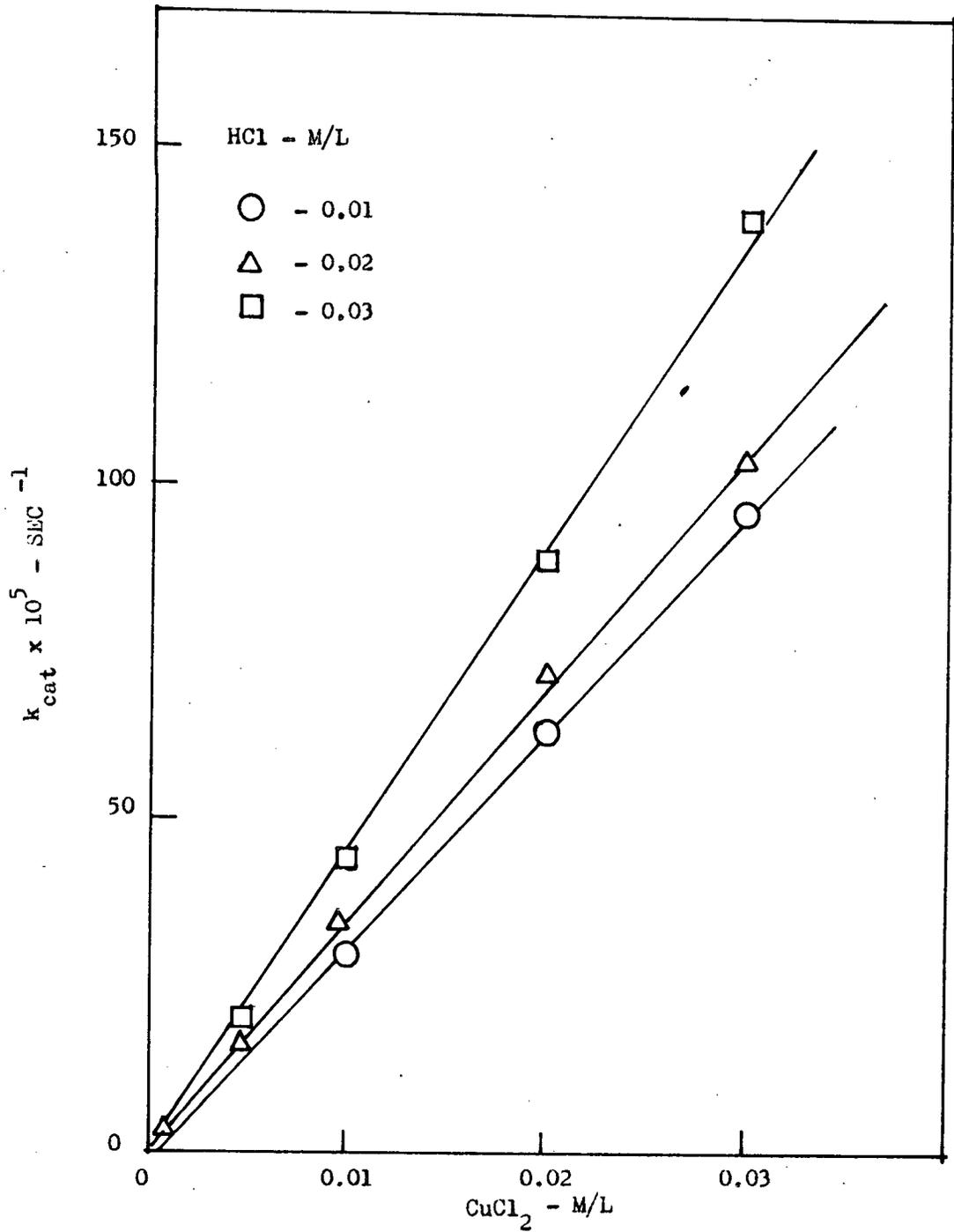


FIGURE 22. Combined catalytic effect of cupric chloride and hydrochloric acid in 50 mole % EtOH at 60° C.

(h) RESULTS IN BENZENE

A few catalytic measurements were also made in benzene solutions, using heptanoic acid and cupric heptanoate. Measurements were confined to low concentration (≈ 2 M) of the latter, both because of its low solubility and its intense colour which interfered with the spectrophotometric method used to follow the reaction.

Under these conditions no catalytic effect was noted and this may be attributed to the low concentrations of H^+ and Cu^{++} and their corresponding low coordinating tendencies in these solutions.

(i) MISCELLANEOUS EFFECTS

Among the other salts examined were $Co(ClO_4)_2$ and $AgClO_4$ and some results for these are listed in Table VIII. 0.5 M $Co(ClO_4)_2$ (in the presence of 0.1 M $HClO_4$) did not appear to have any effect, while 0.5 M $AgClO_4$ gave a catalytic rate only slightly higher than that due to the acid alone. Since the coordination of the catalyst to the azo-nitrogen atoms appears to be a common feature of all the catalytic effects noted, this behaviour may be related to the very much smaller tendencies of Co^{++} and Ag^+ (relative to Cu^{++}) to form complexes with nitrogen ligands in general.

TABLE VIII

MISCELLANEOUS RESULTS

a. Salt effect

Solvent 50 mole % EtOH - Temp. 60° C.

Acid HClO ₄ mole/liter	Salt NaClO ₄ mole/liter	k x 10 ⁵ (sec ⁻¹)	k _{cat} x 10 ⁵ (sec ⁻¹)
0	0	5.76	0
0	.5	5.76	0
.5	0	8.62	2.86
.5	.5	8.62	2.86

HCl mole/liter	NaCl mole/liter	k x 10 ⁵ (sec ⁻¹)	k _{cat} x 10 ⁵ (sec ⁻¹)
0	0	5.76	0
0	.2	5.50	
.2	0	6.51	.75
.2	.2	6.71	.95

b. Results in benzene- Temp. 60° C.

Heptanoic acid moles/liter	Cupric Heptanoate moles/liter	k x 10 ⁵ (sec ⁻¹)	k _{cat} x 10 ⁵ (sec ⁻¹)
0	0	12.7	0
.2	0	11.2	0
.2	.2	14.3	1.6

c. Results with Co(ClO₄)₂ and AgClO₄ in the presence of HClO₄

Solvent 50 mole % EtOH - Temp. 60° C.

Co(ClO ₄) ₂ moles/liter	HClO ₄ moles/liter	k x 10 ⁵ (sec ⁻¹)	k _{cat} x 10 ⁵ (sec ⁻¹)
0.5	0.1	6.4	0.6

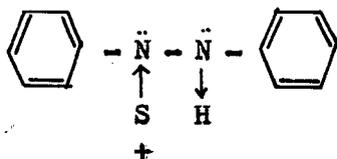
TABLE VIII (con't)

AgClO_4 moles/liter	HCl moles/liter	$k \times 10^5$ (sec^{-1})	$k_{\text{cat}} \times 10^5$ (sec^{-1})
0.5	0.1	8.3	2.5

SUMMARY AND CONCLUSIONS

Although a number of common features have been recognized for the different catalysts examined, it has not been possible to suggest a single mechanism to account for all of them.

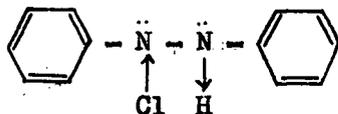
In the case of the H^+ - catalyzed reaction ($HClO_4$) it has been postulated as most probable the formation of a protonated species by action of H^+ on azobenzene. The suggested mechanism involves the subsequent reaction of the protonated complex with a molecule of solvent to give the intermediate (III) in which H^+ and the molecule of solvent S are coordinated with the nitrogen atoms at the azo linkage. The proposed structure for (III) is:



(III)

in which free rotation about the N-N bond is possible.

The greater catalytic activity shown by HCl is interpreted in terms of an additional effect of undissociated HCl molecules. The proposed mechanism involves simultaneous conjugation of Cl^- and H^+ at the azo-linkage to give an intermediate (IV) analogous to (III)



(IV)

This suggestion is supported by the fact that analogous mechanisms, assuming the formation of an intermediate which involves both an electron donor and an electron acceptor, have been proposed in other cases of cis-trans isomerization.

The predicted rate law is then

$$k_{\text{cat}} = k_{\text{H}^+} [\text{H}^+] + k_{\text{HCl}} [\text{HCl}]$$

and the results were found to be in accord with this.

Acetic acid was found to be inactive.

The kinetic dependence of k_{cat} on cupric perchlorate was found to be of order greater than first. Coordination of Cu^{++} with the azo-nitrogen atoms, to give an intermediate analogous to (III), appears to be probable; to explain higher order path, contribution of two cupric ions to give a complex, Azobenzene. $\cdot 2 \text{Cu}^{++}$ has been postulated.

The greatly enhanced catalytic activity of $\text{Cu}(\text{ClO}_4)_2$ in the presence of HClO_4 is attributed to the formation of a similar complex by simultaneous coordination of H^+ and Cu^{++} at the azo-nitrogen atoms.

Similar results have been obtained for CuCl_2 although the enhancement by HCl is less marked in this case.

The much lower catalytic activities of Ag^+ and Co^{++} ions are attributed to their lesser tendency to coordinate with nitrogen ligands.

SUGGESTION FOR FURTHER WORK

It would be of interest to extend this work and to examine further several problems which developed during the course of this investigation, in connection with acid catalysis and with the mechanism of cis-trans isomerization. Among these are:

1. Determination of h_0 for the solutions and temperatures used in this study with a view to establishing more conclusively whether the acid catalyzed reaction follows an h_0 or H^+ dependence, and hence applying the Zucker-Hammett criterion to differentiate between the various alternative mechanisms. Alternatively it might be possible to achieve this by extending the measurements to higher acid concentrations (this may be possible at lower temperatures) or to aqueous solutions for which h_0 is already known. The latter involves some experimental difficulties because of the solubility of azobenzene in water, but it might be possible to overcome these.

2. To test the suggestion of an additional catalytic path due to undissociated HCl by varying the H^+ and Cl^- concentrations independently using a suitable chloride salt. Some measurements of this type were attempted with NaCl which, however, proved too insoluble in aqueous alcohol.

3. To examine other acids (particularly those of intermediate strength) with a view to ascertaining whether the behaviour observed for HCl is general and to correlating catalytic activity quantitatively with acid strength.

4. In the same connection other substances, known to have both nucleophilic and electrophilic properties, such as amines, should be investigated. These are known (21,22) to catalyze cis-trans conversion of olefinic compounds and it would be of interest to ascertain whether they are effective also for azobenzene.

5. The effect of temperature, should also be investigated in order to determine the activation energy for the catalysed conversion.

6. Finally, it would be very interesting to extend the quantitative catalytic studies to substituted azobenzenes.

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