CATALYSIS OF THE CIS-TRANS ISOMERIZATION OF AZOBENZENE BY ACIDS AND CUPRIC SALTS¹

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ABSTRACT

The catalytic effects of various 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 and is interpreted in terms of a catalytic mechanism involving the conjugate acid of azobenzene. The much greater catalytic effect found for hydrochloric acid is attributed to an additional path involving catalysis by the undissociated acid. Acetic acid was found to be inactive. Of the metal salts examined only those of Cu⁺⁺ showed pronounced activity which was attributed to co-ordination with the azo group. Kinetic evidence was obtained for a catalytic path involving Cu⁺⁺ and H⁺ simultaneously.

INTRODUCTION

It has been reported (1, 2) that the *cis-trans* isomerization of azobenzene, which proceeds spontaneously in solution, is susceptible to catalysis by acids, certain metal salts, and a variety of other inorganic and organic substances. However, while the kinetics of the uncatalyzed isomerization have been examined extensively (1, 3), few quantitative measurements have been made on the catalyzed reactions whose mechanisms are thus for the most part unresolved. This paper describes a kinetic study of the catalysis of the isomerization of azobenzene in aqueous alcohol solution by acids and cupric salts and an attempt is made to elucidate the mechanisms of the catalytic effects in these systems.

EXPERIMENTAL

Cis-azobenzene was prepared by the method of Hartley (1) and recrystallized from petroleum ether to a constant melting point of 70°. Distilled water and ethanol, redistilled from KOH, were used as solvents. Cupric perchlorate (G. F. Smith Reagent) was recrystallized from perchloric acid. The acids and other reagents were of reagent grade.

The kinetics of the isomerization reaction were measured using the procedure described earlier (3). The absorption spectra of *cis*- and *trans*-azobenzene were determined in each of the media used and were found to be substantially unaffected by the added acids and metal salts. Solutions of azobenzene were prepared, and all experiments performed, in the dark to prevent photochemical isomerization.

RESULTS AND DISCUSSION

All the kinetic experiments were made at 60° . The solvent was generally aqueous alcohol in which both azobenzene and the catalysts were conveniently soluble. A few experiments were also made in benzene solution.

Typical rate plots for the uncatalyzed and catalyzed reactions are shown in Fig. 1. The kinetics were generally first order in *cis*-azobenzene yielding a pseudo first order rate constant, k, which contained contributions from both the uncatalyzed (k_0) and catalyzed

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 (k_{cat}) paths, i.e.

[1] -d [cis-A]/dt = k [cis-A]where

[2]

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 $k = k_0 + k_{\rm cat},$

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

Deviations from first order kinetics were sometimes observed at high catalyst concentrations (particularly with perchloric acid), possibly due to side reactions of azobenzene with the catalyst. In such cases only the region of first order behavior was investigated and the range of results reported below reflects this limitation.

Table I summarizes some of the observed catalytic effects. Of the three acids examined in aqueous alcohol, namely HClO₄, HCl, and CH₃COOH (selected as typical strong, intermediate, and weak acids), the first two showed pronounced catalytic activity while the last was inactive. The unimportance of ionic strength effects is indicated by the observation that 0.5 M NaClO₄ or 0.2 M NaCl, either alone or in the presence of equivalent concentrations of the corresponding acid, were substantially without effect.

Since it seemed likely that the acid catalysis was associated with protonation of the azo group, salts of a number of metal ions (Cu⁺⁺, Co⁺⁺, Ag⁺) with known tendency to coordinate with nitrogen were also examined for catalytic effects. Of these only the cupric salts showed pronounced activity, which was further enhanced in the presence of acids. These effects are discussed further below.

Perchloric Acid

[3]

The results for this acid, in solvents of various compositions, are summarized in Fig. 2. The range of catalyst concentrations in each case is that for which the kinetics remained first order in *cis*-azobenzene. In this region the catalytic effect conforms to the rate law,

$$k_{\text{cat}} = k_{\text{H}^+} [\text{HClO}_4]$$

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	TABL	ΕI		
Some	catalytic	effects	at	60°

Solvent	Catalyst	(sec^{-1})	$10^{3}R_{cat}$ (sec^{-1})
50 mole% EtOH	None	5.8	0.0
50 mole% EtOH	$0.1 M \text{HClO}_4$	6.4	0.6
50 mole% EtOH	$0.5 M \text{HClO}_4$	8.6	2.8
50 mole% EtOH	$1.0 M HClO_4$	11.2	5.4
50 mole% EtOH	$0.5 M \text{ NaClO}_4$	5.8	0.0
50 mole% EtOH	$0.5 M \text{HClO}_4 + 0.5 M \text{NaClO}_4$	8.6	2.8
50 mole% EtOH	0.2 M HCl	6.4	0.6
50 mole% EtOH	1.0 <i>M</i> HCl	24.2	18.4
50 mole% EtOH	0.2 M NaCl	5.5	-0.3
50 mole% EtOH	0.2 M HCl + 0.2 M NaCl	6.7	0.9
50 mole% EtOH	0.5 <i>M</i> HOAc	5.5	-0.3
50 mole% EtOH	$0.5 M \mathrm{KI}$	5.8	0.0
50 mole% EtOH	$0.5 M \operatorname{Cu}(\operatorname{ClO}_4)_2$	35.0	29 , 2
50 mole% EtOH	$0.04 \ M \ Cu(ClO_4)_2 + 0.1 \ M \ HClO_4$	46.0	40.2
50 mole% EtOH	$0.03 \ M \ CuCl_2 + 0.01 \ M \ HCl$	101	95
50 mole% EtOH	$0.2 M \operatorname{Cu}(\operatorname{OAc})_2 + 0.5 M \operatorname{HOAc}$	15.3	9.5
50 mole% EtOH	$0.5 \ M \ Co(ClO_4)_2 + 0.1 \ M \ HClO_4$	6.4	0.6
50 mole% EtOH	$0.5 M \operatorname{AgClO}_4 + 0.1 M \operatorname{HClO}_4$	8.3	2.5
Benzene	None	12.7	0.0
Benzene	0.2 M heptanoic acid	11.2	-1.5
Benzene	$0 \ 2 \ M$ heptanoic acid $+ \ 0.2 \ M$		
	cupric heptanoate	14.3	1.6



FIG. 2. Catalytic effect of perchloric acid at 60°.

where the values of $10^{5}k_{\rm H}$ are 7.4, 5.1, and 6.5 l. mole⁻¹ sec⁻¹ in 25, 50, and 75 mole per cent EtOH, respectively.

It seems likely that $HClO_4$ 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. A plausible mechanism, depicted below, assumes that the catalyzed isomerization proceeds through the conjugate acid of azobenzene (AH⁺), formed in a rapid pre-equilibrium step, i.e.

$$cis-A + H^+ \rightleftharpoons cis-AH^+ (fast)$$
 [4]

$$cis-AH^+ \rightarrow trans-AH^+ (slow)$$
 [5]

$$trans-AH^+ \rightleftharpoons trans-A + H^+$$
 (fast). [6]

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The protonation equilibrium of azobenzene in acidic solutions is well known (4, 5) although, because of the rapid isomerization, it can be studied only for the *trans* isomer. Spectrophotometric measurements have yielded values of -2.5 (4) and -1.6 (5) for pK_a of AH⁺ at 25°. The equilibrium concentration of AH⁺ in our solutions is thus very small ($\sim 1\%$ at 1 M H⁺) and is not detected spectrophotometrically.

The structure of AH^+ has not been conclusively established. Klotz (4) has proposed structure (I) in which the proton is localized on one of the N atoms through a bond involving lone pair electrons. On the other hand Jaffé (5, 6), on the basis of convincing evidence, favors the non-classical structure (II) in which H is attached to both N atoms through



delocalized bonds. Enhanced ease of isomerization is more readily explained in terms of the first model where some reduction in the degree of double bond character of the azo bond might be expected through polarization. It is less obvious why structure (II) should lead to enhanced isomerization particularly if, as suggested by Jaffé (5, 6), the *cis*-conformation of this structure is the more stable one.

An alternative description of the slow isomerization step, which we are inclined to favor, involves the attack of a solvent molecule (S) on AH^+ to give an intermediate (III) in which free rotation about the N—N bond is possible, i.e.

This mechanism is readily consistent with either structure (I) or (II) for AH⁺.

Zucker and Hammett (7, 8) have suggested a criterion for distinguishing between a mechanism of the type represented by equations [4], [5], and [6] and one in which the rate-determining step [5] is replaced by step [7] involving attack on the conjugate acid by a solvent molecule. This is based on the expectation of a linear dependence of k_{eat} on h_0 (related to the Hammett acidity function H_0 (9, 10) by $H_0 = -\log h_0$ in the first case and on [H⁺] in the second. Unfortunately this criterion is not readily applicable here in view of the limited acidity range accessible to kinetic measurement and of the absence of h_0 data for mixed solvents. In aqueous solution the dependence of h_0 on [H⁺] does diverge appreciably from linearity even below 1 M HClO₄ and this divergence is not reflected in plots in Fig. 2. On the other hand the dependence of k_{ext} on solvent composition appears to follow h_0 which, at least for HCl, has been shown to pass through a minimum in the vicinity of equimolar concentrations of H₂O and EtOH (11). Because of their conflicting nature, and because of the questionable theoretical validity of the Zucker-Hammett hypothesis (8), these indications are considered as inconclusive. An alternative kinetic interpretation, namely that the protonation step [4] is rate determining, also leads to an expected h_0 , rather than [H⁺], dependence but is considered unlikely in view of the low rates.

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FIG. 3. Catalytic effect of hydrochloric acid at 60°.

FIG. 4. Solvent dependence of the catalytic effects of perchloric and hydrochloric acids at 60° . The broken line depicts the solvent dependence of the uncatalyzed rate (k_0) .

Hydrochloric Acid

The results for this acid are depicted in Figs. 3 and 4. Attention is directed to the following features.

(1) Except at very low concentrations, the catalytic activity of HCl is greater than that of $HClO_4$.

(2) the kinetic dependence of k_{cat} on the total HCl concentration, [HCl]₀, is apparently greater than first order.

(3) The catalytic effect increases markedly with the EtOH content of the medium. At low EtOH content it approaches that of $HClO_4$.

This behavior can be interpreted in terms of a catalytic contribution due to undissociated HCl in addition to that due to H^+ . The predicted rate law is then

[8]
$$k_{\text{cat}} = k_{\text{H}^+} [\text{H}^+] + k_{\text{HCl}} [\text{HCl}]$$

[9]
$$= k_{\rm H^+} [{\rm H^+}] + (k_{\rm HCl}/K) [{\rm H^+}] [{\rm Cl^-}],$$

where K is the dissociation constant of HCl. If the fraction of undissociated HCl is small, $[H^+] \sim [Cl^-] \sim [HCl]_0$, and equation [9] becomes

[10]
$$k_{cat} = k_{H^+} [HCl]_0 + (k_{HCl}/K) [HCl]_0^2$$

or

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11]
$$k_{\text{cat}}/[\text{HCl}]_0 = k_{\text{H}} + (k_{\text{HCl}}/K) [\text{HCl}]_0$$

The linear plots of $k_{\text{cat}}/[\text{HCl}]_0$ vs. $[\text{HCl}]_0$ in Fig. 5 are, on the whole, in accord with this, although their intercepts yield values of k_{H^+} which are somewhat lower than those obtained with HClO_4 (like the latter, however, these pass through a minimum at 50 mole per cent EtOH). Again this may be due to the fact that the H⁺-catalyzed reaction follows h_0 rather than [H⁺] and that in these media the former is appreciably lower for HCl than for HClO_4 even at low concentrations.

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FIG. 5. Concentration-dependence of HCl catalysis plotted according to equation [11].

A plausible mechanism for the catalysis by undissociated HCl involves protonation, coupled with simultaneous co-ordination of Cl⁻, to give an intermediate (IV), analogous to (III), in which the role of the solvent molecule is effectively assumed by Cl⁻.

$$\underbrace{N = N}_{i} + HCl \rightarrow \underbrace{N - N}_{f} + \underbrace{N}_{Cl} H$$

$$(IV)$$

$$\begin{bmatrix} 12 \end{bmatrix}^{i}$$

A similar mechanism may account for the combined catalytic effect of H⁺ and thiourea on the *cis-trans* isomerization of azobenzene, observed by Schulte-Frohlinde (2). This has the kinetic form, $k_{cat} = [H^+]$ [thiourea] and may involve a reaction analogous to equation [12] between azobenzene and the conjugate acid of thiourea.

It is also of interest that the above pattern of catalytic effects for $HClO_4$ and HCl resembles that found by Nozaki and Ogg (12) for the *cis-trans* isomerization of maleic acid. In the latter case also a mechanism involving simultaneous co-ordination of H⁺ and Cl⁻ (although not at adjacent positions) was proposed to account for the higher activity of HCl. Analogous mechanisms have also been proposed (13, 14) for the catalysis by secondary amines of the *cis-trans* isomerization of diethyl and dimethyl maleate.

Cupric Salts

Figure 6 depicts the catalytic effect due to cupric perchlorate. The kinetic dependence of k_{cat} on the cupric perchlorate concentration is greater than first order (approximately 1.5) implying some contribution from a path involving more than one Cu⁺⁺ ion. As for H⁺, it seems plausible to interpret the catalytic effect of Cu⁺⁺ in terms of a mechanism involving co-ordination of Cu⁺⁺ with the azo nitrogen atoms to give intermediates analogous to (III). The significance of the higher order path is not clear but a plausible interpretation is in terms of a complex, azobenzene.2Cu⁺⁺, in which Cu⁺⁺ ions are

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co-ordinated to both N atoms of the azobenzene molecule. The existence of an analogous cuprous complex of azomethane (azomethane.2Cu⁺) has been reported (15).

A similar complex, involving simultaneous co-ordination of H⁺ and Cu⁺⁺ with the two N atoms of azobenzene, may account for the unexpected and very marked enhancement of the catalytic activity of cupric perchlorate by perchloric acid shown in Fig. 7. Over a considerable range of concentrations the combined effect of the two catalysts is much greater than the sum of their separate effects and the predominant contribution to k_{cat} is of the kinetic form, k [H⁺] [Cu⁺⁺], implying a catalytic path involving H⁺ and Cu⁺⁺ simultaneously.



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Because of solubility limitations the effect of $CuCl_2$ in aqueous ethanol could be examined only in the presence of HCl. The results are shown in Fig. 8 and again reveal a



Catalytic effect of cupric chloride in 50 mole% EtOH at 60°.

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tendency, although less marked than for cupric perchlorate, for the catalytic activity to be enhanced by the acid. At low HCl concentrations k_{eat} is first order in CuCl₂ and is much greater than for $Cu(ClO_4)_2$ at comparable $HClO_4$ concentrations.

Cupric acetate in aqueous ethanol and cupric heptanoate in benzene (in each case in the presence of the corresponding acid which by itself was without effect) were also found to catalyze the isomerization reaction (Table I), but their effects were not examined quantitatively.

Co-ordination of the catalyst to the azo nitrogen atoms appears to be a common feature of all the catalytic effects described and the low catalytic activities of Co⁺⁺ and Ag⁺, relative to Cu⁺⁺ (Table I), may be related to their much smaller tendencies to form complexes with nitrogen ligands in general.

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