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KINETICS AND MECHANISM OF THE DIAZO COUPLING REACTION OF ARENEDIAZO METHYL ETHERS WITH β-NAPHTHOL

Nabil K. Masoud
Administration of Chemistry, Research Department
Ministry of Industry, 12 Ramses Street, Cairo, Egypt

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ABSTRACT. The diazo coupling reaction of benzene and 4-nitrobenzene diazo methyl ethers with β-naphthol resulting in the formation of the corresponsing azo dyes, benzeneazo- and (1-[4'-nitrobenzeneazo]-2-naphthol), respectively (3_a and 3_f), was studied in hydrochloric acid solutions. The rates of this acid catalyzed reaction in dioxane - water, ethanol - water, and propan-2-ol - water mixtures have been determined over the appropriate range of medium composition, at hydrochloric acid concentrations of 0.1 and 1 M.

It was found that in these media (organic solvent - water -hydrochloric acid media), k_{obs} varies non linearly with the solvent composition, passing through a minimum in the region of equimolar portions of the two components. This is in contradiction to the behaviour in ethanol - dioxane and ethanol - propan-2-ol mixtures, where k_{obs} varies gradually with the solvent composition. The non linear variations of k_{obs} in the relatively aqueous media are paralleled by the corresponding changes in the Hammett's acidity function, H_o, and cannot be merely accounted for as dielectric constant effects. This relationship confirms with a reaction mechanism that involves a fast reversible proton transfer followed by a slow decomposition of the protonated substrate, DEH^+, to the diazonium ion, D^+. Variations in the rate constants, k_{obs}, with the medium composition are mainly attributable to variations in the reversible proton transfer equilibrium,

$$DE + SH^+ \rightleftharpoons DEH^+ + S$$

where SH^+ represents the solvated proton.

INTRODUCTION

Recently we proposed a mechanism for the diazo coupling reaction of arenediazo methyl ethers with β-naphthol, as a result of an investigation of the kinetics of the reaction in non-aqueous media (1).

It was thus important to extend the investigation to solvent water mixtures, for two interesting reasons, namely, the dependence of the reaction rate on medium composition and the additional information it would provide when studying the reaction mechanism. The variation of rate constants of benzenediazo methyl ether (2a the most reactive compound), and 4-nitrobenzenediazo methyl ether (2f the least reactive (1)) in dioxane - water, ethanol - water and propan-2-ol - water mixtures, was determined over appropriate ranges of medium composition at hydrochloric acid concentrations of 0.1 and 1 M.

RESULTS AND DISCUSSION

The effect of the medium exerted upon rate constants. The relevant data are enlisted in Table 1, and plotted in Fig. 1 and 2. In dioxane - water, ethanol - water, and propan -2-ol - water mixtures, and in the presence of HCl, the observed first-order rate constants, (k_{obs}), decrease markedly on gradual addition of water to the organic solvent, passing through a minimum in the region of nearly equimolar portions of the two components, followed by an increase at higher concentrations of water added (H_2O > 20% by volume). The probability that further higher values of k_{obs} could be attained upon increasing the water content to more than 40% by volume, exists. Some β-naphthol, as well as the reaction products (3a and 3f) are precipitated during the course of the reaction when water is present in higher amounts. The plots of log k_{obs} versus % mole fraction (m) of water are to be found in Fig. 1 and 2 (see Experimental). The curves for the two compounds 2a and 2f investigated are similar in form at the two acid concentrations of 0.1 and 1 M, with the only exception that the minima of which existed at positions of higher water content, in the case of the acid concentration of 1 M. It is evident from Table 1 that the amount of variations in k_{obs} with the solvent compositions in binary mixtures of these three solvents are found to decrease in the order of propan-2-ol > ethanol > dioxane.

Table 1. Rate constants for the diazo coupling reaction of benzenediazo methyl ether (2a) and 4-nitrobenzenediazo methyl ether (2f) with β-naphthol in aqueous solvent mixture at 25°C[a].

vol % of water	Dioxane [H_2O] m[b]	$10^6 k_{obs}$ (s^{-1})	$\log k_{obs}+6$	Ethanol [H_2O] m[b]	$10^6 k_{obs}$ (s^{-1})	$\log k_{obs}+6$	Propan-2-ol [H_2O] m[b]	$10^6 k_{obs}$ (s^{-1})	$\log k_{obs}+6$
2a : [HCl] = 0.1 M									
00.0	00.0	524.80	2.72	00.0	2692.00	3.43	00.0	5888.00	3.77
10.0	34.5	550.16	1.70	26.2	75.84	1.88	31.6	55.00	1.74
20.0	54.3	31.62	1.50	44.4	36.33	1.56	51.0	33.20	1.52
30.0	67.0	36.30	1.56	57.8	49.95	1.70	64.1	47.91	1.68
40.0	76.0	47.90	1.68	68.0	104.70	2.02	73.5	91.20	1.96
2a : [HCl] = 1 M									
00.0	00.0	4571.00	3.66	0.00	28180.00	4.45	00.0	190500.00	5.28
10.0	34.5	3467.00	3.54	26.2	2890.00	3.46	31.6	3631.00	3.56
20.0	54.3	2399.00	3.38	44.4	1514.00	3.18	51.0	1514.00	3.18
30.0	67.0	1820.00	3.26	57.8	1381.00	3.14	64.1	1150.00	3.06
40.0	76.0	1096.00	3.04	68.0	1778.00	3.25	73.5	1047.00	3.02
2f : [HCl] = 0.1 M									
00.0	00.0	18.20	1.26	00.0	63.10	1.80	00.0	158.00	2.20
10.0	34.5	2.63	0.42	26.2	1.91	0.28	31.6	2.76	0.44
20.0	54.3	1.45	0.16	44.4	1.32	0.12	51.0	1.51	0.18
30.0	67.0	1.55	0.19	57.8	1.74	0.24	64.1	1.82	0.26
40.0	76.0	2.09	0.32	68.0	2.63	0.42	73.5	2.76	0.44
2f : [HCl] = 1 M									
00.0	00.0	131.80	2.12	00.0	758.60	2.88	00.0	5248.00	3.72
10.0	34.5	75.86	1.88	26.2	56.23	1.75	31.6	104.70	2.02
20.0	54.3	45.71	1.66	44.4	29.08	1.46	51.0	43.65	1.64
30.0	67.0	30.22	1.48	57.8	31.63	1.50	64.1	41.80	1.62
40.0	76.0	19.52	1.29	68.0	43.65	1.64	73.5	50.12	1.70

[a] Concentration of 2a 5.5×10^{-5} M, concentration of 2f 3.5×10^{-5} M, that of β-naphthol both cases 4.5×10^{-3} M.

[b] Concentration of water expressed in % mole fraction (m) calculated as $m = 100\, M x / [M x + (100 - x)\, 18\, d]$ where x = mls of water, M & d are the M.W. and density of the organic solvent.

The available results emphasise the highly basic character of water when compared to dioxane, ethanol, or propan-2-ol. This fact is realised when we consider an acid HA at molality 'm' in mixtures of an organic solvent S, with water. The following acid - base equilibria are then established:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \tag{1}$$

$$H_3O^+ + S \rightleftharpoons SH^+ + H_2O \tag{2}$$

$$HA + S \rightleftharpoons SH^+ + A^- \tag{3}$$

Assuming that the molality of S and water remain constant, then the proton activity H_3O^+ (as a measure of acidity) can be expressed in terms of K_{HA} and K_{SH^+}, the acidity constants of HA and SH^+, respectively, the 'm' values represent molalities, and the 'f' ones refer to activity coefficients in the following equation

$$a_{H_3O^+} = K_{HA} \frac{m_{HA}\, f_{HA}\, f_{H_2O}}{m_{A^-}\, f_{A^-}} = K_{SH^+}\, m_{SH^+} \frac{f_{SH^+}\, f_{H_2O}}{f_S} \tag{4}$$

Since the concentration of free protons is negligibly small (2), hence the stoichiometric molality of HA (m_s) in the acid - solvent mixtures, is given by

$$m_s = m_{HA} + m_{A^-} = m_{HA} + m_{SH^+} \tag{5}$$

From (4), we get equation (6)

$$\frac{m_{HA}}{m_{A^-}} = \frac{K_{SH^+}\, f_{SH^+}\, f_{A^-}}{K_{HA} f_{HA} f_S}\, m_{SH^+} = K_1\, m_{SH^+} \tag{6}$$

Since $m_{SH^+} = m_{A^-}$ (according to eq. (5))

$$\frac{m_{HA}}{m_{A^-}} = K_1\, m_{A^-} \tag{7}$$

where

$$K_1 = \frac{K_{SH^+}\, f_{SH^+}\, f_{A^-}}{K_{HA}\, f_{HA}\, f_S}$$

Combining equations (5) & (7) gives eq. (8)

$$K_1\, m_{A^-}^2 + m_{A^-} - m_s = 0 \tag{8}$$

Solving eq. (8) for m_A and substituting its value in eq. (4), eq. (9) is achieved

$$a_{H_3O^+} = 1/2\, K_{HA} \frac{f_{HA}\, f_{H_2O}}{f_{A^-}} \left[-1 + \left(1 + 4m_S \frac{K_{SH^+}\, f_{SH^+}\, f_{A^-}}{K_{HA}\, f_{HA}\, f_S}\right)^{1/2} \right] \qquad (9)$$

According to eq. (9), increased basicity of the solvent results in decreasing the acidity of the medium.

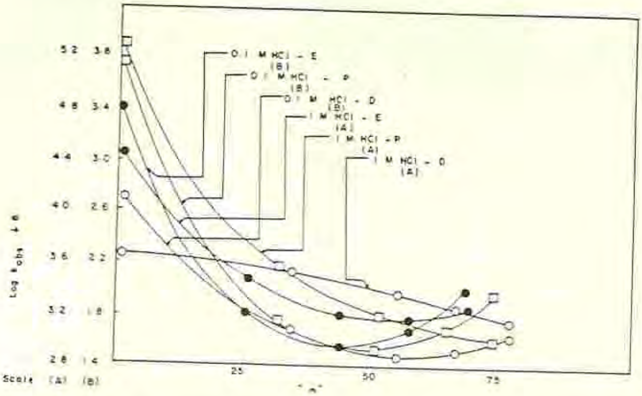

Fig. 1. Variation of reaction rate with solvent composition for the dizao coupling of benzenediazo methyl ether with β-naphthol in organic solvent - water mixtures at 25°C; D = dioxane, E = ethanol, P = propan-2-ol, scale (A), 1 M HCl, scale (B), 0.1 M HCl.

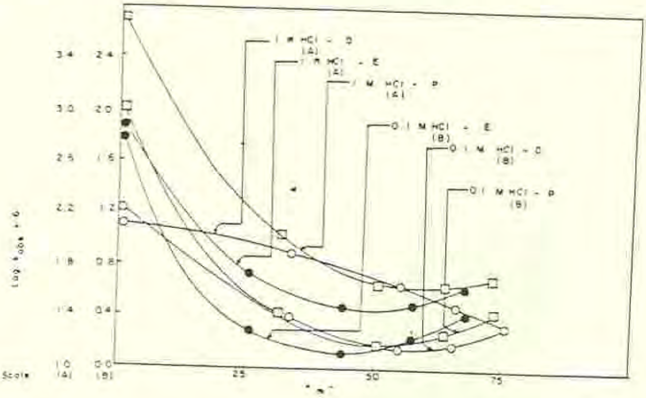

Fig. 2. Variation of reaction rate with solvent composition for the diazo coupling of 4-nitrobenzenediazo methyl ether with β-naphthol in organic solvent - water mixtures at 25°C; D = dioxane, E = ethanol, P = propan-2-ol, scale (A), 1 M HCl, scale (B), 0.1 M HCl.

Two special cases are of interest. First, in the decreasing (left - hand) parts of the curves relating k_{obs} and c_{H_2O} (Fig. 1 and 2), the reaction between HA and the solvent is incomplete since reaction (2) becomes predominant upon increasing the water content beyond ca. 20% (by volume). This results in shifting the point of equilibrium (3) to the left, favouring the basic form of the solvent. The last term of eq. (9) becomes much greater than unity, resulting in

$$a_{H_3O^+} = \sqrt{m_s \, K_{HA} \, K_{SH^+} \, \frac{f_{SH^+} \, f_{HA} \, f^2_{H_2O}}{f_S \, f_{A^-}}} \qquad (10)$$

Under this condition, the acidity of the medium depends on both K_{HA} and K_{SH^+}. Second, when the proportion of water becomes sufficiently large, that is in media containing more than 20% by volume of water, reaction (3) is substantially complete (HA is almost entirely converted to SH^+). In this case eq. (9) reduces to

$$a_{H_3O^+} = K_{SH^+} \, m \, \frac{f_{SH^+} \, f_{H_2O}}{f_S} \qquad (11)$$

The acidity of the solution is that of an m molal solution of the acid SH^+, which is weaker than HA. The extent of this acidity depends only on the magnitude of K_{SH^+}.

The increase of the rate constant (k_{obs}) with the water content, existing on the right - hand part of the curves (Fig. 1 and 2), can be mainly accounted for by dielectric constant effects. The increase in the dielectric constant of the medium results in an increase in the effective acid strength (3). The plot relating k_{obs} with the water composition in each of both Fig. 1 and 2, can be considered as a combination of two sections, a left hand part denoting a decline in the relation between k_{obs} and water composition, and a right hand section showing a gradual increase in the mentioned relation. The declination in the left hand side of the curve is attributable to the decrease in the ratio $m_{H_3O^+}/m_{SH^+}$. The electrostatic effect caused by the change in the dielectric constant of the solvent - water mixtures is superimposed by the basicity effect of water. Whereas, the gradual increase occurring in the right hand part can be accounted for by the increase in the acidity and the dielectric canstant of the medium.

This conclusion is in agreement with the discovery of Hall, Conant and their coworkers (4) that solutions of common acids in glacial acetic acid, a solvent of very low basicity, are much more acidic than those in water, where the strongest acid existing is the hydroxonium ion, H_3O^+. Likewise, Hardman and Lapworth (5) found that the acidity potentials in alcoholic solutions of hydrochloric acid are lessened by the addition of small amounts of water. A similar conclusion is achieved from determinations of the activity of hydrochloric acid (6) and from the Hammett's acidity functions (7) in these solutions, as well as from rate studies (8).

Further independent evidence from acidity function measurements is depicted as well. It was found that for a particular HCl concentration over the full range of aqueous ethanol mixtures, a minimum acidity value (maximum in H_o) occurs at a particular solvent composition (9). The value maximum in H_o occurred around 60 mole % ethanol. Similar results have been obtained by Salomaa (10) and by Bates and his coworkers (11).

Braude and Stern, (12) Eaborn, (13) and Sadek et. al. (14) have measured an H_o scale for solutions of HCl in aqueous dioxane. Braude and Stern's results showed also that for a fixed concentration of HCl over the complete range of aqueous dioxane composition there existed a minimum acidity (maximum in H_o) at a particular solvent composition. A comparative study of acidity functions in propan-2-ol - water mixtures has not been reported (15).

It appears from these findings that the variations in k_{obs} run parallel to those of the Hammett's acidity function H_o, since the minima in the observed rate constants (k_{obs}) are very similar to the maxima in H_o for hydrochloric acid in ethanol - water, (10, 11, 13) and dioxane - water solvents (12).

The kinetic behaviour of the reaction in the partly aqueous solutions is in sharp contrast to that in ethanol - dioxane, and ethanol - propan-2-ol mixtures, where the plots of log k_{obs} versus mole % of dioxane and propan-2-ol exhibit no minima and k_{obs} varies gradually with the solvent composition (Fig. 3). The kinetic data and the percentage mole fraction (m) of organic solvents are tabulated in Table 2 (see Experimental).

The striking contrast in the variation of the observed rate constants (k_{obs}) with solvent composition in the partly aqueous media as compared with that of the completely non aqueous ones, shows that the peculiar features of the former must be associated with water being a component.

Table 2. The dependence of reaction rate upon solvent composition for the diazo coupling of compounds 2a and 2f, with β-naphthol in ethanol - dioxane and ethanol - propan-2-ol mixtures at 25°C[a].

vol % of organic solvent	Ethanol - dioxane		log k_{obs} +6	Ethanol - propan-2-ol		log k_{obs}+6
	m^b	$10^6 k_{obs}$ (s^{-1})		m^b	$10^6 k_{obs}$ (s^{-1})	
			2a ; [HCl] = 0.1 M			
0	0.0	2692.0	3.43	0.0	2692.0	3.43
10	7.0	2814.0	3.45	7.9	2798.0	3.45
20	14.4	1886.0	3.46	16.1	2937.0	3.47
30	22.4	3014.0	3.48	24.7	3020.0	3.48
40	31.0	3030.0	3.48	33.8	3083.0	3.49
50	40.2	3088.0	3.49	43.4	3024.0	3.48
60	50.2	2958.0	3.47	53.5	2948.0	3.47
70	61.1	2842.0	3.45	64.1	3024.0	3.48
80	72.9	2401.0	3.38	75.4	3388.0	3.53
90	85.8	1827.0	3.26	87.3	4266.0	3.63
100	100.0	524.8	2.72	100.0	5888.0	3.77
			2f ; [HCl] = M			
0	0.0	760.7	2.88	0.0	760.7	2.88
10	7.0	829.8	2.92	7.9	832.4	2.92
20	14.4	871.3	2.94	16.1	869.9	2.94
30	22.4	911.9	2.96	24.7	891.3	2.95
40	31.0	933.4	2.97	33.8	955.3	2.98
50	40.2	928.9	2.97	43.4	912.2	2.96
60	50.2	891.2	2.95	53.5	871.8	2.94
70	61.1	791.3	2.90	64.1	831.8	2.92
80	72.9	631.1	2.80	75.4	1047.0	3.02
90	85.8	416.9	2.62	87.3	2398.0	3.38
100	100.0	132.3	2.12	100.0	5260.0	3.72

[a] Concentrations used similar to those mentioned in Table 1.

[b] 'm' is expressed in % mole fractions (see Experimental).

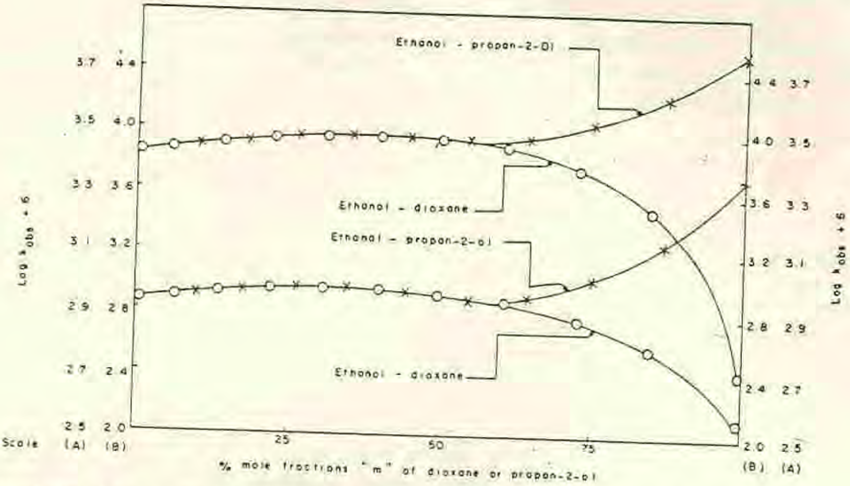

Fig. 3. Effect of changing solvent composition on $\log_{obs}$ for the diazo coupling reaction of benzene (2a) - and 4-nitrobenzene (2f) - diazo methyl ehters with β-naphthol in ethanol - dioxane and ethanol - propan-2-ol mixtures at 25°C. scale (A) for 2a, 0.1 M HCl, scale (B) for 2f, 1 M HCl.

These observations indicate that the dielectric constant or similar effects cannot be regarded as being the only factor affecting the diazo coupling reaction of arenediazo methyl ethers (DE) with β-naphthol. If this had been the case, such effects would have been noticed distinctly in ethanol - dioxane mixtures, the dielectric constants of which cover a wide range ($D = 24.3$ to $D = 2.2$).

The conclusion that the basicity and the dielectric constant of the solvent are the principal factors in the acid catalyzed reaction between arenediazo methyl ethers and β-naphthol is reasonable.

Mechanism of reaction. On the basis of the various experimental facts, it seems that the reaction is governed by the following set of equilibria

$$\text{(a)}\quad HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$\text{(b)}\quad HA + S \rightleftharpoons SH^+ + A^-$$

$$\text{(c)}\quad HA + DE \rightleftharpoons DEH^+ + A^-$$

$$\text{(f)}\quad DEH^+ \xrightarrow{k_f} D^+ + CH_3OH$$

$$\text{(g)}\quad D^+ + HOC_{10}H_7\text{-}\beta + A^- \xrightarrow[\text{fast}]{} ArN_2C_{10}H_6(OH)\text{-}\beta + HA$$

HA represents the undissociated hydrochloric acid, S the organic solvent (dioxane, ethanol, or propan-2-ol), SH^+ the solvated proton, DE the arenediazo methyl ether, DEH^+ its conjugate acid, and D^+ the diazonium ion.

Since in dilute solution the concentration of diazo ether, c_{DE}, is small compared with that of H_2O and S, equilibrium (c) can be replaced by the two equilibria (d) & (e), as such

$$\text{(d)}\quad DE + H_3O^+ \rightleftharpoons DEH^+ + H_2O$$

$$\text{(e)}\quad DE + SH^+ \rightleftharpoons DEH^+ + S$$

As a result, two possibilities arise; either the proton transfer according to (d) & (e), or the decomposition of the protonated substrate to the diazonium ion in agreement with (f) may be regarded as the rate determining step. If the latter possibility was justified, then the rate of reaction may be formulated by the transition state theory as

$$v = k_f [\mathrm{DEH}^+] f_{\mathrm{DEH}^+} / f_{x_f} \qquad (12)$$

Where the k's represent rate constants, the f's repesent activity coefficients and x_f refers to the transition state of reaction (f).
The rate constant of the total reaction (k_{obs}) is given by eq. (13)

$$k_{obs} = v / [\mathrm{DE}] = k_f [\mathrm{DEH}^+] f_{\mathrm{DEH}^+} / [\mathrm{DE}] f_{x_f} \qquad (13)$$

If the activity coefficients of the protonated diazo ether, DEH^+, and the transition state have the same value, which is likely to be the case, then eq. (13) is reduced to

$$k_{obs} = k_f [\mathrm{DEH}^+] / [\mathrm{DE}] \qquad (14)$$

Equation (14) implies that the observed first-order rate constant of the reaction is equal to the rate constant of the actual decomposition of DEH^+ to the diazonium ion, D^+ multiplied by the ratio $[\mathrm{DEH}^+]/[\mathrm{DE}]$. The logarithm of this ratio is in a linear relationship to Hammett's acidity function which is defined by

$$H_o = -\log a_{H^+} f_B / f_{BH^+} = pK_a^B - \log (c_{BH^+} / c_B) \qquad (15)$$

where a_{H^+} represents the activity of the hydrogen ion, K_a^B is a constant (the equilibrium constant of the reaction $BH^+ \rightleftharpoons B + H^+$), and B is any neutral base (16). At constant temperature log k_{obs} should be linearly realted to H_o. This has been shown also to be the case for the variation of k_{obs} with hydrochloric acid concentration in a medium of constant dioxane or ethanol concentration (1), where values of the acidity function for HCl in these media are available.

If, on the other hand, the protonated substrate formation according to (d), (e) were the rate determining steps, application of Christiansen's equation (16) yields

$$k_{cbs} = \frac{k_d k_f a_{H_3O^+} f_{DE}}{k_f / f_{x_d} + k_{-d} a_{H_2O}} + \frac{k_e k_f a_{SH^+} f_{DE}}{k_f / f_{x_e} + k_{-e} a_S} \qquad (16)$$

Since $k_f >> k_d$, k_e on the present assumption, it could be approximately assumed that eq. (16) becomes

$$k_{obs} = \frac{k_d \, a_{H_3O^+} \, f_{DE}}{f_{x_d}} + \frac{k_e \, a_{SH^+} \, f_{DE}}{f_{x_e}} \qquad (17)$$

In medium of a constant low water content, where $[SH^+] >> [H_3O^+]$, eq. (17) is reduced to

$$k_{obs} = \frac{k_e \, a_{SH^+} \, f_{DE}}{f_{x_e}} = k_e \, [SH^+] \, \frac{f_{SH^+} \, f_{DE}}{f_{x_e}}$$

$$= \alpha \; k_e \; [SH^+] \qquad (18)$$

where

$$\alpha = \frac{f_{SH^+} \, f_{DE}}{f_{x_e}}$$

Since SH^+ is itself an oxomium ion, α should be inappreciably affected by change in acid concentration (17), and the rate constant should be proportional to $[SH^+]$, i.e., with the stoichiometric acid concentration.

It has been previously shown (1) that in the case of the present reaction log k_{obs} is not proportional to lcg [HCl]. In any case, $a_{SH^+} \, f_{DE}/f_{x_e}$ is not proportional to H_o since the latter differs from the former by the factor $f_B f_{x_e} / f_{BH^+} f_{DE}$. This factor being not constant, a reaction verified by eq. (14) is therefore unlikely to obey eq. (18).

Accordingly, it may be elucidated that the assumption which occurs in agreement with the decomposition (f) rather than the proton transfer proposition realised by (d) & (e), is the rate determining step in the reaction under investigation.

In conclusion, the variations in k_{obs} with solvent composition at a constant acid concentration are thus to be ascribed primarily to changes in the equilibrum symbolised by (e), as well as to the ratio values of $[DEH^+]/[DE]$. This may be attributable to changes in the proton affinity of the solvent.

EXPERIMENTAL

Materials. The arenediazo methyl ethers used in this investigation, namely benzenediazo methyl ether, and 4-nitrobenzenediazo methyl ether and a purified sample of β-naphthol were available as was mentioned in previous work (1). Solvents were purified by standard methods and dried as was described earlier (1). Likewise, acid solutions were prepared, dried and estimated by titration with sodium borate (1). Deionised water utilised in the kinetics was obtained as previously mentioned (17).

Kinetic measurements. Rates of reaction were determind by spectrophotometric analysis for azo dyes using a Unicam SP 600 spectrophotometer. The technique of such kinetic measurements employed is similar to that previously described (1). x % by volume of water stands for a medium obtained by mixing x ml of water and (100 - x) of organic solvent containing the appropriate amount of hydrochloric acid to give a 0.1 M or 1 M solution. β-Naphthol and the diazo ethers 2a and 2f (1) were used under this investigation. In practice, aqueous solutions were prepared by mixing x ml of water, (80 - x) ml of organic solvent, and 10 ml of 1 M or 10 M hydrochloric acid. Solutions of β-naphthol (5 ml of 0.09 M) in the required solvent was then added, diluted to 99 ml with the organic solvent and kept for 20 min to come to a temperature of 25°C. 1 ml of the diazo ether solution was dropped into the reaction flask and the procedure was followed as was described earlier (1). The percentage mole fraction, symbolised by 'm' in Table and Fig., of water is then given by $100\ M\ x\ /[\ M\ x + (100 - x)\ .\ 18\ d]$, where d and M are the density and the molecular weight of the organic solvent, respectively. Anhydrous solutions were freshly prepared before use and carefully protected from moisture. The percentage mole fraction of dioxane or propan-2-ol in ethanol - dioxane or ethanol - propan -2-ol mixtures is given by $46 \times d\ /[46 \times d + (100 - x)\ M\ 0.8)$, where d and M are the density and the molecular weight of dioxane or propan-2-ol, respectively, and x is the "ml" of dioxane or propan-2-ol.

After taking into consideration the molecular weight as well as the density, the above may be exemplified as follows

1) In the case of an ethanol - dioxane binary mixture where, % volume of dioxane = 10 ml,

$$m = \frac{100 \times 46 \times 10 \times 1.03}{46 \times 10 \times 1.03 + 90 \times 88 \times 0.8} = 7.0$$

2) In the case of an ethanol - propan-2-ol binary mixture where, % volume of propan-2-ol = 10 ml,

$$m = \frac{100 \times 46 \times 10 \times 0.8}{46 \times 10 \times 0.8 + 90 \times 60 \times 0.8} = 7.9$$

REFERENCES

1. N.K. Masoud and M.F. Ishak, J. Chem. Soc., Perkin Trans, II, 927 (1988).
2. H.T.S. Britton, "Hydrogen Ions", Vol. 1, 4th ed., Chapman & Hall, London, (1955).
3. E. Grunwald and B.J. Berkowitz, J. Am. Chem. Soc., **73**, 4939 (1951); B. Gutbezahl and E. Grunwald, ibid, **75**, 559 (1953).
4. N.F. Hall and J.B. Canant, J. Am. Chem. Soc., **49**, 3047 (1927); N.F. Hall and T.H. Werner, ibid. **50**, 2367 (1928); N.F. Hall, ibid. **52**, 5115 (1930).
5. R.T. Hardman and A. Lapworth, J. Chem. Soc., **99**, 2242 (1911).
6. P.S. Danner, J. Am. Chem. Soc., **44** 2832 (1922); B.O. Heston and N.F. Hall, ibid. **56**, 1462 (1934).
7. E.A. Braude and E.S. Stern, Nature (London), **161**, 169 (1948).
8. L.P. Hammett and M.A. Paul, J. Am. Chem. Soc., **56**, 830 (1934).

9. R.G. Bates and G. Schwarzenbach, Helv. Chim. Acta, **38**, 699 (1955); K. Schwabe, Chimia, **13**, 385 (1959).
10. P. Salomaa, Acta Chem. Scand., **11**, 125 (1957).
11. R.G. Bates and R.A. Robinson, "Chemical Physics of Ionic Solution", Wiley, New York, (1966).
12. E.A. Braude and E.S. Stern, J. Chem. Soc., 1976 (1948).
13. C. Eaborn, J. Chem. Soc., 3148 (1953).
14. H. Sadek, M.S,. Abu Hamayem and I.M. Sidahmed, Suomen Kemistilehti, **11** (39B), 225 (1966).
15. C.H. Rochester, "Acidity Functions", Academic Press, London and New York, (1970); F.A. Carey and R.J. Sundberg, "Advanced Organic Chemistry", Part A, 3rd ed., Plenum Publishing Corporation, New York, Ch.4 & 5 (1980).
16. J.A. Christiansen, Z. Phys. Chem. (Leipzig), **33B**, 145 (1936); idem., ibid., **37B**, 347 (1937); L.P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, (1970).
17. N.K. Masoud, J. Chem. Soc., Perkin Trans. II, 1312 (1975).