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Kinetic Studies on the Decolorization Reaction of Rosaniline in Aqueous Acidic Medium*

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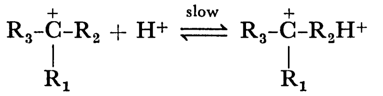
The reaction responsible for the decolorization of rosaniline in acid medium has been studied spectrophotometrically. The rate-determining step has been found to be the reaction of the protonated dye cation with water molecule. Kinetic data have been analyzed on the basis of rate equations which were derived considering the complete protolytic scheme involving all the steps of the reaction of rosaniline in acid and alkaline media. The rate constant k_1 for the ion-molecule reaction has been found to be independent of the dye concentration and hydrogen ion concentration. The apparent rate constant k at various hydrogen ion concentrations has been utilized for calculating the equilibrium constant for the fast protonation step. Effect of ionic strength in the range 0—0.27 indicates no substantial effect on the rate constant k_1. Anomalous solvent effects were obtained suggesting the solvated nature of the reactants. The average energy of activation for the reaction of rosaniline in aqueous medium corresponded to 10.52 kcal. Chemical and kinetic evidence has been presented to prove the participation of water molecule in the rate-determining step.

The mechanism for the color fading of the basic triphenylmethane dyes in acidic medium put forward by Biddle and Porter[1] indicates that in the rate-determining step the dye cation reacts with proton giving



$$\underset{\displaystyle R_1}{R_3\text{-}\overset{+}{C}\text{-}R_2} + H^+ \underset{}{\overset{\text{slow}}{\rightleftharpoons}} \underset{\displaystyle R_1}{R_3\text{-}\overset{+}{C}\text{-}R_2H^+}$$

a protonated product. Later on working with malachite green Katiyar[2] found almost linear dependence of rate constant on the proton concentration as well as increase in rate constant with the increase in ionic strength of the medium and decrease in rate with decrease in dielectric constant of the medium. These data apparently agreed with the mechanism given by Biddle and Porter. However, it was difficult for us to conceive the idea of a protonation rection of an amino group being slower than the reaction of the protonated dye cation with water. A careful analysis of the data on the variation of the rate constant with hydrogen ion concentration in the color fading reaction of rosaniline as well as the earlier data[2] showed that the values of the so-called bimolecular rate constant obtained by dividing the apparent rate constant with $[H^+]$ are not identical. This raised suspicion as to the validity of the ion-ion step as the rate determining step in the reaction-leading to decolorization of triphenylmethane dyes in acid solutions.

In some of the investigations,[3–7] all the possible reactions of the dye with various other species present in the aqueous acidic solutions have been considered in interpreting the observed kinetic data. But in these studies where the reaction was treated as an ion-molecule reaction, the authors did not make any attempt to find out the effect of dielectric constant or ionic strength on the reaction rate. Existing literature also revealed complete absence of such studies on the ion-molecular type reaction of triphenylmethane dyes. Apart from this, no direct chemical evidence has been cited for the suggested mechanism.

In view of the above mentioned facts, we decided to undertake the investigation of the reaction of color fading of rosaniline (C.I. Basic violet 14), a primary member of the triphenylmethane dyes, in acidic medium. These studies have been utilized to establish the nature of the reacting species and to provide a possible explanation for the misleading effect of dielectric constant and ionic strength on the reaction rate.

Experimental

Materials. Rosaniline hydrochloride (C. I. No. 42510, Basic violet-14) was obtained from Eastman Organic Chemicals. Paraffin wax used for coating the inside of the reaction vessels was a B. D. H. laboratory grade material (congealing point 60—62 °C). Dioxane, a B. D. H. analytical grade reagent was purified further[8] before use. All other chemicals needed for buffer solutions were either B. D. H. AnalaR or E. Merck "pro analysi" grade reagents. Deionized all glass distilled water was used for all the experiments.

Methods. Investigations were carried out spectrophotometrically using Beckman DU or Cary model 14 spectrophotometers by the method described earlier.[9]

Rosaniline has an absorption maximum at 546 nm in water solution. It follows Beer's law at 546 nm satisfactorily up to the concentration of 2.5×10^{-5} M ($\varepsilon'=66500$). It was observed that the absorption maximum remains unchanged by the addition of a neutral electrolyte such as 1.0 M solution of KCl. All the measurements, when pure water was used as solvent, were made at 546 nm and the concentration of the dye taken was less than 2.5×10^{-5} M. The decolorization reaction of rosaniline in the presence of acid was found to be reversible in nature. In the presence of small amounts of acid (pH>4), therefore, the fading reaction did not proceed to completion. The backward reaction was minimized by taking the concentration of acid in large excess (pH<2) over that of the dye (2.5×10^{-5} M), which shifted the equilibrium to the side of the product. Further, the kinetic data were recorded in the first few minutes of the reaction.

Fitting of data to straight lines by method of least squares and calculations of the standard derivations to assess the error limits were done with the help of an I. B. M. 7044 digital computer.

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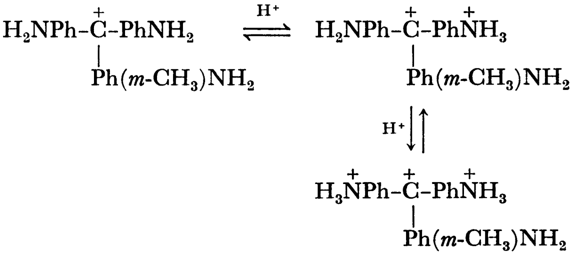
Results and Discussion

Chemical and Kinetic Evidence for the Reactant and Product. In order to get a direct chemical evidence for the nature of reactants, we carried out the protonation of rosaniline in complete absence of water. It was observed that when pure dry HCl gas was passed into a solution of rosaniline (4×10^{-4} M) in pure dry acetonitrile, the solution instantaneously changed its color from red to reddish violet. Further passage of dry HCl gas changed the color to yellowish green, which remained stable in the absence of moisture. These colored species are due to the protonation of the first and second amino groups respectively. Earlier spectral investigations[10,11] also indicated that out of three amino groups only two get protonated. That one *p*-amino grouping is never protonated in all these cases is due to the fact that only one of the benzene rings is involved in resonance interactions, thus giving a difference in base strength of one amino group with respect to the other two. It has been also reported that 68% of the carbonium ions from crystal violet add two protons in 1 M hydrochloric acid.[12] These protonations of amino groups in rosaniline may be represented as follows:



$$\mathrm{H_2NPh\text{-}\underset{Ph(\mathit{m}\text{-}CH_3)NH_2}{\overset{+}{C}}\text{-}PhNH_2 \;\overset{H^+}{\rightleftharpoons}\; H_2NPh\text{-}\underset{Ph(\mathit{m}\text{-}CH_3)NH_2}{\overset{+}{C}}\text{-}Ph\overset{+}{N}H_3} \quad \text{(I)}$$

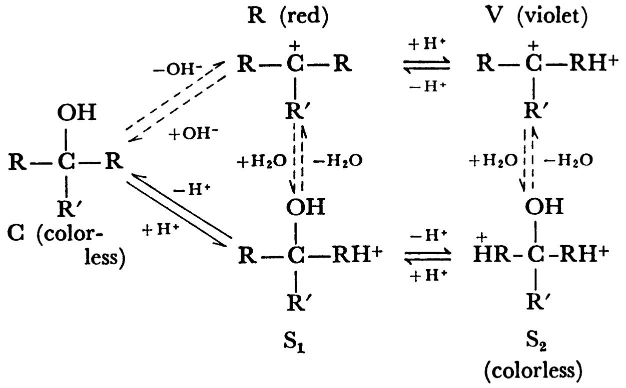
$$\mathrm{H^+}\downarrow\uparrow$$

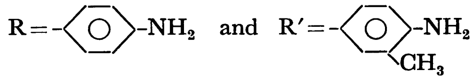
$$\mathrm{H_3\overset{+}{N}Ph\text{-}\underset{Ph(\mathit{m}\text{-}CH_3)NH_2}{\overset{+}{C}}\text{-}Ph\overset{+}{N}H_3} \quad \text{(II)}$$

A drop of water in the violet (I) or green (II) solution thus obtained changed them to colorless solution. This demonstrates that colorless product is obtained from the reaction of water with the protonated species and not from the protonation of the dye.

Now in order to establish the rate-determining step, the rate of decolorization of the protonated species in the presence of water was compared with the rate of unprotonated rosaniline in aqueous acidic medium under identical conditions. The overall rate constants, k, for these protonated and unprotonated solutions were found to be 0.207 and 0.202 $\mathrm{min^{-1}}$ respectively at pH 1.35. Similarly at pH 2.4, k corresponedd to 0.026 and 0.018 $\mathrm{min^{-1}}$ for these protonated and unprotonated rosaniline solutions. It is thus esablished that under the identical conditions of temperature, solvent and hydrogen ion concentration the rates of reaction responsible for the decolorization of protonated and unprotonated dye are the same within reasonable limits. This finding augments the earlier evidence that water is one of the reactants and further proves that the rate-determining step in the decolorization reaction of basic triphenylmethane dye in aqueous-acidic medium is definitely not the protonation process, but is the reaction of water molecule with the protonated dye cation giving protonated carbinol, whose existence is reported in the literature.[13-15]

Rate Expression for the Decolorzation of Rosaniline. Evidence presented above shows that protonation of rosaniline is the fast equilibrium step and subsequent reaction of water molecule with the protonated dye cation is the slow rate-determining step. On the basis of the protolytic scheme given by Cigen[3] and taking into account only the protonation of one amino group, as the concentration of acid used in all the cases was not that much as to cause further protonation, all the steps of the reaction of the rosaniline in acid and alkaline media can be shown as follows. The solid lines in the scheme indicate that the reactions proceed instantaneously whereas broken lines indicate that the reactions take place with measurable velocity.



where 

Now let us define the following constants:

$K_1=\dfrac{[V]}{[R][H^+]}$, where [R] is the concentration of rosaniline

k_1=pseudo first order rate constant for the reaction; $V+H_2O\rightarrow S_2$

k_2=first order rate constant for the reaction; $S_2\rightarrow H_2O+V$.

The investigations were carried out spectrophotometrically. Therefore, the concentrations of the dye are given in the form of specific absorptions. The following symbols are used:

ε_R, ε_V=The molar absorptivity of R and V respectively.

e_R, e_V=The specific absorbance of a solution containing only R and V respectively.

e_0, e_t, e_∞=The specific absorbance of the solution at times 0, t and at equilibrium.

C_M=The total concentration of rosaniline.

If protonation equilibrum is achieved instantaneously, one can obtain the following equations by the method of Cigen.

$$\frac{[H^+]}{(e_R-e_0)}=[H^+]\cdot\frac{1}{(e_R-e_V)}+\frac{1}{K_1(e_R-e_V)} \qquad (1)$$

And the overall rate constant k at pH<2 is given as

$$k=\frac{1}{t}\ln\frac{e_0-e_\infty}{e_t-e_\infty}=k_1\frac{K_1[H^+]}{1+K_1[H^+]}+k_2 \qquad (2)$$

neglecting the other equilibrium terms except the protonation and subsequent water addition step. Thus a plot of $[H^+]/(e_R-e_0)$ against $[H^+]$ will give a straight line. The intercept, C, of this line on the Y axis and its slope, m, give $(e_R-e_V)=1/m$ and thus giving $K_1=m/C$ hence, the value of K_1 can be obtained from Eq. 1.

Table 1.[a] Rate constants at varying concentration of rosaniline

$[H^+]=1.89\times10^{-2}$ M

Rosaniline concn mol/l $\times 10^6$	k, $s^{-1}\times10^2$
19.6	0.21
17.7	0.20
15.7	0.21
13.7	0.22
11.8	0.21
9.8	0.21
5.9	0.22

a) Temperature = 25 °C.

The value of k_1, the rate of hydration, can be obtained from the slope of a plot of k *versus* $K_1[H^+]/(1+K_1[H^+])$ and that of k_2 from the intercept of this plot.

Effect of Rosaniline Concentration on the Reaction Rate. The dependence of rate on the concentration of rosaniline was studied by recording the kinetic runs at varying dye concentrations in the range 19.6×10^{-6} M to 3.9×10^{-6} M and a fixed amount of hydrochloric acid (1.89×10^{-2} M). Value of e_∞ was obtained by measuring the absorbance after the lapse of four hours. Analysis of the results from the graphical method yielded linear first order plots with almost the same slope, giving a constant value of k for all the rosaniline concentrations as shown in Table 1. This indicates that the value of k is independent of the initial concentration of rosaniline. As the equilibrium constant k_1 and the hydrogen ion concentration are constant, the value of k_1, the true rate constant for hydration, will remain unchanged for all rosaniline concentrations in accordance with Eq. 2. Thus, k_1 is independent of initial concentration of rosaniline. Since the concentration of the reactant, namely, water is in great excess as compared to that of the dye, the first order nature of the reaction is in agreement with the suggested mechanism.

Effect of Hydrogen Ion Concentration on Reaction Rate. As in the aqueous solution of the dye there exist more than one species, it is not possible to determine the values of ε_R, ε_V, e_R, e_V directly from the measured absorption curves. For simplicity, aqueous solution of dye of pH 6.5 was taken. In such a solution, the concentration of the red form, R, is about 80—90% of the total dye concentration. If the apparent molar extinction coefficient of such a solution is denoted by ε'_R and the specific extinction by e'_R, then $e'_R/e_R=e'_V/e_V$. From this relation and Eq. 1, the value of K_1 can be determined by substituting e'_R, the measured specific extinction, for e_R and e'_V for e_V. For the determination of equilibrium constant the rates of decolorization of rosaniline were measured at various hydrogen ion concentrations at constant ionic strength. The equilibrium $R+H^+ \rightleftharpoons V$ is reached instantaneously during the mixing, whereupon the color of the solution fades owing to the reaction $V+H_2O \rightleftharpoons S_2$. By determining the fading rate and extrapolating the extinction to $t=0$, e_0 was obtained. The measurements were carried out at the wavelength, 546 nm, where the absorption curve of the red component has a sharp maximum. The plots of $\log(e_t-e_\infty)$

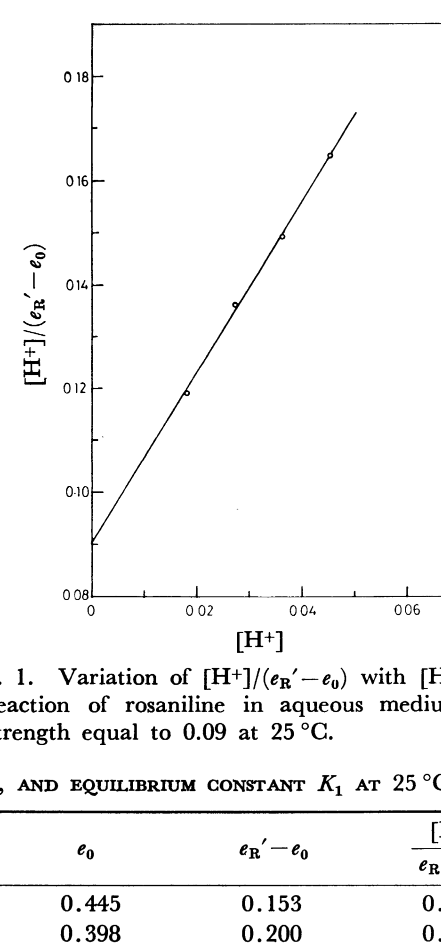


Fig. 1. Variation of $[H^+]/(e_R'-e_0)$ with $[H^+]$ for the reaction of rosaniline in aqueous medium at ionic strength equal to 0.09 at 25 °C.

Table 2.[a] Rates of hydration of rosaniline k_1, k_2, and equilibrium constant K_1 at 25 °C

e_R'	$[H^+]$	$\log(e_0-e_\infty)$	e_∞	e_0	$e_R'-e_0$	$\frac{[H^+]}{e_R'-e_0}$
0.598	0.0182	1.594	0.052	0.445	0.153	0.119
0.598	0.0272	1.558	0.037	0.398	0.200	0.136
0.598	0.0363	1.513	0.029	0.355	0.243	0.149
0.598	0.0454	1.491	0.015	0.325	0.275	0.165

$K_1=18.13\pm0.15\ M^{-1}$

k, $s^{-1}\times10^3$	$\frac{K_1[H^+]}{1+K_1[H^+]}$	k_1, s^{-1}	k_2, s^{-1}
3.99	0.248		
5.22	0.330		
6.18	0.397	1.7×10^{-2}	0.4×10^{-3}
7.31	0.452		

a) Ionic strength = 0.09.

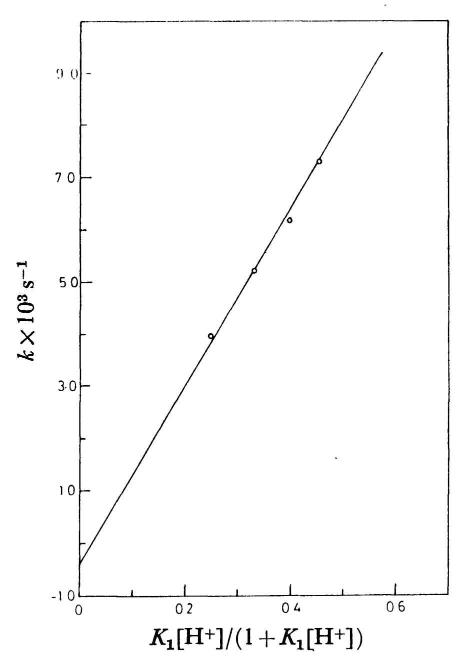


Fig. 2. Plot of k *vs.* $K_1[H^+]/(1+K_1[H^+])$ for the reaction of rosaniline at $\mu=0.091$.

vs. time at various hydrogen ion concentrations were linear indicating the first order nature of the reaction as expected from Eq. 2. The values of apparent rate constants, k, were found to increase with increasing concentration of the acid (Table 2). In order to find out the equilibrium constant K_1 of the protonation step using Eq. 2, a plot of $[H^+]/(e'_R-e_0)$ against $[H^+]$ was made as shown in Fig. 1. The slope and intercept from this graph gave a value of 18.1 ± 0.15 M^{-1} for the equilibrium constant K_1. As is evident from Eq. 2, a plot of $K_1[H^+]/(1+K_1[H^+])$ *vs.* k should give a straight line with slope equal to k_1 and intercept k_2. Such plot shows the linear variation of $K_1[H^+]/(1+K_1[H^+])$ with k giving the value of $k_1=1.7\times10^{-2}$ s^{-1} and $k_2=0.40\times10^{-3}\pm0.05\times10^{-3}$ s^{-1} which are independent of the hydrogen ion concentrations (Fig. 2). It is evident from the values of k_1 and k_2 that the rate of forward reaction is much greater than that of backward reaction under the experimental conditions but still k_2 is quite significant. Hence, in all the measurements of k_1, the backward reaction has been taken into account.

Effect of Ionic Strength on the Rate Constant k$_1$. Usually for a reaction between an ion and a neutral molecule, the electrostatic effects are small in very dilute solution. If the reacting species in the rate determining step in the present case are ionic type the rate constant should increase with increase in ionic strength.[9,16] The effect of ionic strength ion dipole interaction can be expected from considerations of interactions of the ion atmosphere with the dipole moment of the reactant molecule in the free state and in the complex.[17]

Studies were done taking fixed concentration of the dye (0.72×10^{-5}M) and varying HCl concentration at a constant ionic strength of 0.27. The values of rate constants and equilibrium constants obtained from Eqs. 1 and 2 are reported in Table 3. It is of interest to note that the equilibrium constant K_1 is 34.9 ± 0.15 M^{-1} and it is considerably higher that the value obtained at $\mu=0.091$ which is 18.13 ± 0.15 M^{-1} (Table 2). The equilibrium constant at higher ionic strength increases as expected, since the effect of ionic strength on the association constant follows the Bjerrum-Brønsted relationship.[18] The values of k_1 at $\mu=0.27$ was found to be 2.08×10^{-2} s^{-1}. Comparing this value to k_1 obtained at $\mu=0.091$ (1.7×10^{-2} s^{-1}), it is evident that it does not change much in accordance with the equation valid for ionic reactions,[9,16] and given below:

$$\ln k = \ln k_0 + \frac{2Z_AZ_BA\sqrt{\mu}}{1+\beta a_i\sqrt{\mu}} \tag{3}$$

The increase in the value of k_1 even after a three-fold increase in ionic strength is too small to get any meaningful quantitative correlation. In view of the limitation that the acid concentration cannot be decreased above pH 2 and the overall rate becomes faster with increase in ionic strength, the study could not be extended to higher ionic strength. But, the above studies clarifies the cause of apparent increase of the overall rate constant with increase in ionic strength which led to the false inference about the nature of reactants, by previous workers. No doubt the overall rate constant k is markedly dependent on the ionic strength of the medium but this is because of the change in value of K_1 and the rate constant k_1 is only slightly effected. Thus, the above observations further supports the nature of reacting species as given in the protolytic scheme.

Effect of Dielectric Constant on the Rate Constant k$_1$. Experiments were carried out at different dioxane–water compositions keeping the ionic strength of the solution constant using suitable HCl–KCl mixtures in all the experiments. It was observed that the wavelength of maximum absorption shifted to 543 nm in dioxane–water mixtures, the studies were therefore carried out at 543 nm. The values of e'_R were determined prior to the experiment at each solvent percentage. Rate constants and equilibrium constants at different dixane–water concentrations are sum-

Table 3.[a] Rate constants and equilibrium constants at constants at $\mu=0.27$

$[H^+]$	k, s$^{-1}\times10^3$	$\frac{[H^+]}{e_R'-e_0}$	K_1	$\frac{K_1[H^+]}{1+K_1[H^+]}$	k_1, s$^{-1}\times10^2$	k_2, s$^{-1}\times10^3$
0.0145	3.46	0.112	34.91 ± 0.25 M^{-1}	0.336	2.08 ± 0.06	0.40 ± 0.05
0.0218	5.30	0.131		0.432		
0.0291	6.77	0.151		0.504		
0.0363	8.28	0.169		0.559		

a) Temperature = 25 °C.

Table 4. Rate constants and equilibrium constants in dioxane-water mixtures at 25 °C

$[H^+]$	k, $s^{-1}\times10^3$	$\frac{[H^+]}{e_R'-e_0}$	K_1	$\frac{K_1[H^+]}{1+K_1[H^+]}$	k_1, $s^{-1}\times10^2$
			5% (v/v) Dioxane-Water		
0.0908	7.67	0.211	$(11.43\pm0.20)M^{-1}$	0.509	(1.58 ± 0.10)
0.0726	6.91	0.188		0.453	
0.0636	6.50	0.180		0.421	
0.0545	5.76	0.168			
			10% (v/v) Dioxane-Water		
0.0908	8.06	0.317	$(18.01\pm0.2)M^{-1}$	0.620	(2.80 ± 0.15)
0.0817	7.04	0.296		0.595	
0.0726	6.39	0.275		0.566	
0.0545	4.32	0.237		0.495	
			15% (v/v) Dioxane-Water		
0.0908	5.04	0.404	$(21.23\pm0.20)M^{-1}$	0.658	(1.70 ± 0.15)
0.0817	4.61	0.376		0.634	
0.0726	5.06	0.349		0.606	
0.0545	3.20	0.298		0.536	

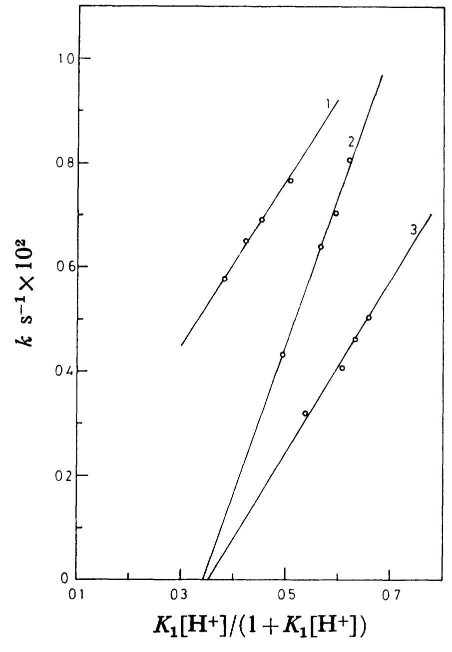


Fig. 3. Plot of $K_1[H^+]/(1+K_1[H^+])$ vs. k in dioxane-water media at 25 °C.
1 : 5% dioxane; 2 : 10% dioxane; 3 : 15% dioxane.

marized in Table 4. It is of interest to note that the values of equilibrium constant K_1 increase with increase in solvent percentage or decrease in dielectric constant of the medium. It corresponded to 11.43 M^{-1} in 5%, 18.01 M^{-1} in 10% and 21.23 M^{-1} in 15% dioxane–water mixture. This increase in equilibrium constant with decrease in dieletric constant is understandable and is in accordance with the formulation discussed elsewhere. Figure 2 represents the plot of $K_1[H^+]/(1+K_1[H^+])$ vs. k, the total reaction rate. As expected from Eq. 2, the plot is a fairly straight line. It may be seen from Fig. 3 that the slope increases in 5% to 10% and then decreases in 15%, 2.8×10^{-2} s^{-1} in 10% and $1.7\times10^{-2} s^{-1}$ in 15% dioxane–water mixture, even though total rate generally decreases with decrease in dielectric constant of the medium. Several treatments are available for interpreting the influence of the solvent on electrostatic force which modifies the rate process between ion and dipolar molecules. The equation derived by Amis and Jaffe[20)] and modified by Amis[21)] is as follows:

$$\ln k_D' = \ln k_\infty' + \frac{Z_A m_0 \varepsilon}{kTr^2 D} \tag{4}$$

where k_D' and k' are specific reaction rates at dielectric constant D and m_0 is the moment at $\mu=0$. Further modification of the Eq. 4 was done by Quinlan and Amis[22)] to obtain a relation which also predicts linear dependence of ln $k'_{\mu=0}$ on $1/D$. Laidler and Landskroener[23)] proposed a relation for such type of reaction based on Kirkwood[24)] and Kirkwood and Westheimer's[25)] theory which also predicts that the dependence of ln k' on $1/D$ should be linear. Thus,

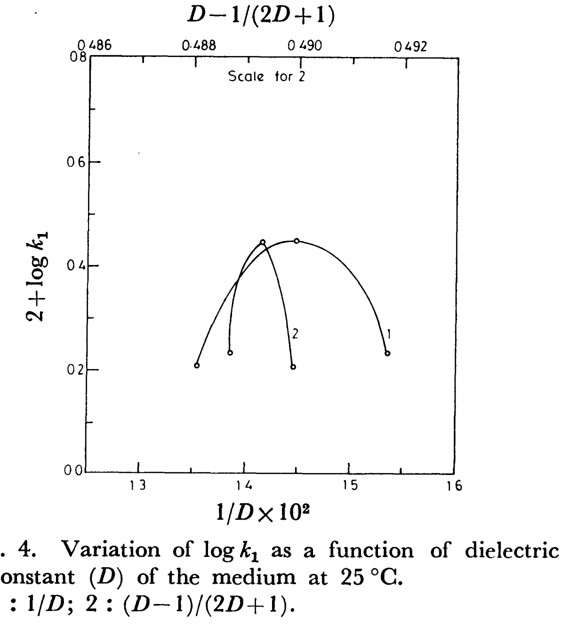


Fig. 4. Variation of $\log k_1$ as a function of dielectric constant (D) of the medium at 25 °C.
1 : $1/D$; 2 : $(D-1)/(2D+1)$.

almost all the models suggest that on the basis of electrostatic considerations the plot of $\ln k'$ *vs.* $1/D$ should be linear with positive slope if the charge on the reacting ion is positive for reaction between an ion and a neutral molecule. Figure 4 represents the dependence of $\log k_1$ on $1/D$. The plot, contrary to expectation, does not show any linear behavior and after 10% dioxane–water composition, the slope also becomes negative. The inconsistency with the predicted behavior can be analyzed on the basis of Laidler and Eyring[26] equation according to which the plot of $\ln k_1$ *vs.* $1/D$ will be straight line only when the Kirkwood term in the equation is only slightly affected with change in dielectric constant of the medium and the change in ϕ's (the non-electrostatic term) is insingnificant. In the present case, since the reacting species are water and protonated triphenylmethane carbonium ion, the effect on Kirkwood term due to change in dielectric constant is apparently significant.

For a bimolecular reaction of dipolar molecule (A) with dipolar molecule (B) the specific velocity constant is given as follows:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{M}^* \rightarrow \mathrm{X} + \mathrm{Y}$$

$$\ln k' = \ln\left(\alpha \frac{\bar{k}T}{h} K_0{}^*\right) - \frac{1}{\bar{k}T}\,\frac{D-1}{2D+1}\left(\frac{\mu_{\mathrm{A}}{}^2}{a_{\mathrm{A}}{}^3} + \frac{\mu_{\mathrm{B}}{}^2}{a_{\mathrm{B}}{}^3} - \frac{\mu_{\mathrm{M}^*}{}^2}{a_{\mathrm{M}^*}{}^3}\right) + \frac{\phi_{\mathrm{A}} + \phi_{\mathrm{B}} - \phi_{\mathrm{M}^*}}{\bar{k}T} \tag{5}$$

where k' is the specific velocity constant, α is the transmission coefficient, $\bar{k}$ is the Boltzmann constant, h is Planck's constant, T is the temperature in degrees Kelvin, D is the dielectric constant of the final solution, and for dilute solutions D is effectively the dielectric constant of the pure solvent. a_{B} is the average distance of closest approach of B to A, a_{A} is the average distance of closest approach of A to B, ϕ_{A}, ϕ_{B} and ϕ_{M^*} are the sum of the non-electrostatic terms considered by Laidler and Eyring.[26] $K_0{}^*$ is defined by Laidler and Eyring as $K_0{}^* = F'_{\mathrm{M}^*}/F_{\mathrm{A}}F_{\mathrm{B}}$, where F_{A} and F_{B} are the partition function of A and B and F'_{M^*} is the part of the partition function of complex, F_{M} which refers to the degrees of translational freedom corresponding to decomposition. According to this equation, if the non-electrostatic terms are negligibly small, a plot of $\ln k'$ *vs.* $(D-1)/(2D+1)$ should give a straight line. Laidler and Eyring[26] used Eq. 5 to interpret the solvent effects on the hydrolysis of esters. They plotted $\ln k'$ *vs.* $(D-1)/(2D+1)$ for acid and alkaline hydrolysis of some esters and obtained good straight line plots. Figure 4 (plot 2) represents the variation of $\log k_1$ with $(D-1)/(2D+1)$. It may be seen that this plot is also not linear. There are several reactions[27] where the solvent effect cannot be accounted for satisfactorily by electrostatic considerations only. Basic triphenylmethane dyes, as reported earlier,[9] exhibit specific solvent effect also in the case of carbinol formation in alkaline medium. The explanation of specific effects can be formulated in terms of the noneletrostatic terms, ϕ's. Probably, the most important factor contributing to these terms is the solvating power of the solvents.

Effect of Temperature on Rate Constant k_1. Kinetic runs were further carried out at 20 and 30 °C maintaining the ionic strength for the solution constant using suitable HCl–KCl mixture. The data obtained are summarized in Table 5. It is interesting to note that increase in temperature decreased the value K_1 from 25.33 M^{-1} at 20 °C to 19.71 M^{-1} at 30 °C. This indicates that the equilibrium is shifted towards the reactants. Thus, even if the total rate increases with increase in temperature, the values of e_0 and e_∞ are also increased. This decrease in equilibrium constant with increase in temperature is well expected for the exothermic reaction of protonation of amino group. From the slopes of the plots of $K_1[\mathrm{H}^+]/(1+K_1[\mathrm{H}^+])$ *vs.* k at 20 and 30 °C the values of rate constants k_1 were obtained and were found to be $1.12\times10^{-2}\ \mathrm{s}^{-1}$ at 20 °C and $2.03\times10^{-2}\ \mathrm{s}^{-1}$ at 30 °C. Taking the value of k_1 at 25 °C equal to $1.7\times10^{-2}\ \mathrm{s}^{-1}$ as obtained earlier in aqueous medium, although this value is at slightly different ionic strength but the change due to this can be ignored as discussed earlier, dependence of $\log k_1$ on $1/T$ was plotted. This plot shows a fairly good straight line indicating that ΔE remains constant in this narrow temperature range. The average value of apparent ΔE was found to be 10.52 kcal. These studies suggest that the protolytic scheme is valid at higher temperatures also. Raising the temperature has the effect of displacing the equilibrium constant towards

TABLE 5. VARIATION OF RATE CONSTANT AND EQUILIBRIUM CONSTANT WITH TEMPERATURE

$[\mathrm{H}^+]$	k, $\mathrm{s}^{-1}\times10^2$	$\dfrac{[\mathrm{H}^+]}{e_{\mathrm{R}}'-e_0}$	$\dfrac{K_1[\mathrm{H}^+]}{1+K_1[\mathrm{H}^+]}$	k_1, $\mathrm{s}^{-1}\times10^2$
		Temperature 20 °C		
0.0908	0.728	0.242	0.697	1.12±0.06
0.0726	0.639	0.207	0.647	
0.0545	0.574	0.174	0.579	
0.0363	0.490	0.143	0.479	
		Temperature 30 °C		
0.0908	1.27	0.250	0.642	2.03±0.10
0.0726	1.16	0.218	0.589	
0.0545	1.02	0.188	0.518	
0.0363	0.79	0.154	0.417	

the colored, dehydrated form. The dissociation constant increases with temperature if they are defined as acid constants that is, as $1/K_1$. Due to specific solvent effect exhibited by the system, the different contributions to the energy of activation and thereby the true energies and entropies of activation could not be calculated.

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