

Dissociation Kinetics of Picric Acid and Dipicrylamine in Methanol

Steric Effect on a Proton Transfer Rate

BY FRANK STROHBUSCH,† DAVID B. MARSHALL, F. ARCE VAZQUEZ,§
ARTHUR L. CUMMINGS‡ AND EDWARD M. EYRING*

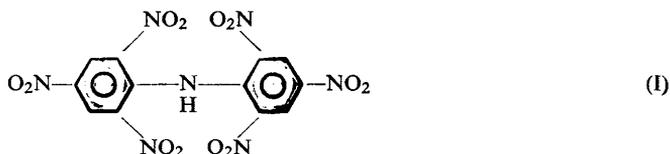
Department of Chemistry, University of Utah,
Salt Lake City, Utah 84112, U.S.A.

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The acid-base dissociation kinetics of picric acid and 2,2',4,4',6,6'-hexanitrodiphenylamine(I) in methanol at 25°C have been investigated using the electric field jump method. The rate constants for the reaction $A^{\ominus} + H^{\oplus} \xrightleftharpoons[k_{-1}]{k_1} HA$, where HA denotes picric acid, are $k_1 = 4.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{-1} = 9.2 \times 10^6 \text{ s}^{-1}$. For (I) the corresponding values are $k_1 = 2.28 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{-1} = 1.31 \times 10^5 \text{ s}^{-1}$. The dissociation constant of (I) in methanol was determined to be $K = 5.4 \times 10^{-5}$ in agreement with the value derived from the kinetics. The protonation rate constant k_1 of the picrate ion indicates a diffusion controlled reaction. It is suggested that the surprisingly small value of k_1 for the protonation of the anion of (I) can be ascribed to steric shielding of the acidic nitrogen atom by the adjacent nitro groups in this compound.

The reasons why proton transfer reactions in some cases, especially the protonation of carbanions, do not reach diffusion controlled rates, is a subject of continuing discussion.¹ Among the various effects that can influence the rates of these reactions, the delocalization of charge in carbanions and the inability of these ions to form hydrogen bonds to a proton donor are regarded as the most important.^{1, 2} Recently this view has been questioned because the analysis of rate data with the Marcus theory of proton transfer³ reveals large kinetic effects of solvent reorientation.⁴ The protonation of tertiary amines at a localized electron pair takes on the characteristics of carbanion protonation in the solvent dimethyl sulphoxide. This and related evidence show that solvent-solute interactions play a crucial role in determining protonation rates.⁵

We have studied the protonation-deprotonation kinetics according to eqn (1):



† Present address: University of Freiburg, West Germany.

§ Present address: Departamento de Química Física, Facultad de Ciencias, Santiago de Compostela, Spain.

‡ Present address: National Bureau of Standards, Gaithersburg, Maryland, U.S.A.

of the two acids HA = picric acid and 2,2',4,4',6,6'-hexanitrodiphenylamine [dipicrylamine, (I)] in methanol at 25°C using the electric field jump technique.

The picrate ion is protonated at a diffusion controlled rate, as expected. In contrast to this the specific rate of protonation of the anion of (I) is anomalously slow. This is not readily explained by either charge delocalization or solvent-solute interaction effects. We assume that steric screening of the site of protonation lowers the rate in this particular case.

EXPERIMENTAL

Picric acid (Mallinckrodt O.R.) was recrystallized once from acetic acid and twice from benzene. Light yellow plates, m.p. 122.5°C (rep. 122-3).⁶

2,2',4,4',6,6'-hexanitrodiphenylamine (dipicrylamine) (Eastman Kodak) decomposes at $\approx 245^\circ\text{C}$ as reported in the literature.⁷ Solutions of picric acid and of dipicrylamine in Baker absolute methanol were prepared by dilution of stocks made up by weight. Karl Fischer titration of some of the solutions verified that the water content was $< 0.1\%$.

EQUILIBRIUM MEASUREMENTS

Absorbances of methanolic solutions of dipicrylamine and of solutions containing excess quantities of NaOH, KOH and tetrabutylammoniumhydroxide were measured at $25.0 \pm 0.1^\circ\text{C}$ using a 1 cm path length cell in a Cary 14 spectrophotometer.

KINETIC MEASUREMENTS

The spectrophotometric electric field jump apparatus has been described previously.⁸ At least seven relaxation curves were recorded photographically for each sample solution. The reproducibility of the relaxation time τ , determined from the photographs for a particular sample solution, was typically $\pm 6\%$ for dipicrylamine and $\pm 10\%$ for picric acid. In some of the measurements with picric acid the signal was stored with a Tektronix R7912 transient digitizer and the relaxation time calculated using a nonlinear least squares computer program. Because of the short relaxation times involved the decay time of the high field pulse of about 32 ns was taken into account in the program by including Eigen's formula for an exponential forcing function.⁹ The relaxation times determined from the photographs were corrected using the relation¹⁰, $\tau_{\text{obs}}^2 = \tau_{\text{chem}}^2 + \tau_{\text{elect}}^2$. No systematic differences between the relaxation times taken from photographs and those computed were observed.

RESULTS AND DISCUSSION

DISSOCIATION CONSTANTS

The $\text{p}K_a$ value for picric acid in methanol has been determined potentiometrically by Juillard,¹¹ $\text{p}K_a = 3.67$. For dipicrylamine a spectrophotometric $\text{p}K_a = 3.5$ in 99.8% methanol has been reported.¹² This value was derived by extrapolating measured data* covering a $\text{p}K_a$ range of 3.83 to 4.23. We found that solutions of dipicrylamine that had been made alkaline by addition of sodium hydroxide or potassium hydroxide do not obey Beer's law. The same observation, indicating a spectral change by ion association, had been made previously by Kolthoff and

* In ref. (12) a strong dependence of the observed $\text{p}K_a$ of dipicrylamine on the concentration is reported. We found similar effects when using dipicrylamine concentrations lower than $3.5 \times 10^{-5} \text{ mol dm}^{-3}$. The concentration dependence is opposite to the one expected from the Debye-Hückel limiting law for the dependence of K_a on the ionic strength. Therefore, we suspect that either the water or traces of base present in the solvent (certified to contain not more than 2 p.p.m. base) cause the observed deviations. Those of our measured K_a values that would be affected to $< 10\%$ by $0.4 \times 10^{-6} \text{ mol dm}^{-3}$ of base were given weights inversely proportional to the uncertainty caused by such an amount of base and averaged, resulting in the value reported in the text.

Bendix on aqueous solutions.¹³ The extinction coefficients of the dipicrylamine anion in solutions of its tetra-*n*-butylammonium salt are independent of concentration and higher than those obtained with the alkali salts. In all spectroscopic and kinetic measurements reported below dilute solutions of dipicrylamine without admixtures were used. The concentrations of the anion in these solutions were determined using $\epsilon = 2.50 \times 10^4$ at $\lambda = 450$ nm. The absorbance of the free acid at this wavelength is negligible. Using the spectrophotometric data and the Debye-Hückel limiting law with an ionic radius of 5 Å to calculate activity coefficients, we determined the thermodynamic dissociation constant $K_a = a_{H^+}a_{A^-}/a_{HA} = f_{\pm}^2[H^+][A^-]/[HA] = (5.42 \pm 0.43) \times 10^{-5}$ at 25°C.*

TABLE 1.—ELECTRIC FIELD JUMP RELAXATION DATA FOR THE PROTONATION DEPROTONATION REACTIONS OF PICRIC ACID AND DIPICRYLAMINE IN METHANOL AT 25°C. ACTIVITIES CALCULATED FROM K_a AND THE DEBYE-HÜCKEL LAW

$10^5 C_0/\text{mol dm}^{-3a}$	$10^5 C_A\ominus/\text{mol dm}^{-3b}$	$10^{-5}\tau^{-1}/\text{s}^{-1c}$
picric acid		
5.9	4.9	140
6.3	5.1	120
6.5	5.3	99 ^d
9.0	6.9	150
10.8	8.0	160
12.5	9.0	175
16.2	11.0	170
17.6	11.7	205
18.0	11.9	188
21.6	13.7	210
25.0	15.2	220
31.3	17.9	190
32.4	18.3	215
36	19.7	230
43.1	22.3	265
53.9	26.0	320
dipicrylamine		
2.7	2.0	2.0
5.6	3.5	2.6
10.8	5.5	4.0
11.2	5.7	3.8
18.2	7.8	4.7
21.6	8.7	5.1
36.4	12.0	5.9
43.2	13.3	6.9

^a Total molar concentration of acid. ^b Concentration of anion, assumed to be equal to the proton concentration. Calculated from the total concentration using $pK_a = 3.67$. ^c Experimental reciprocal relaxation time. ^d This point was omitted in the calculation of the rate constants because it deviates more than 3 times the standard deviation from the best correlation.

*See footnote page 2138.

KINETIC MEASUREMENTS

Changes in ionic strength accompanying relaxation can be neglected.¹⁴ The relaxation time for the equilibrium (1) is then given by¹⁵

$$\frac{1}{\tau} = k_1 f_{\pm}^2 ([A^{\ominus}] + [H^{\oplus}]) + k_{-1} \quad (2a)$$

or the equivalent formula

$$\frac{1}{\tau} = k_1 f_{\pm}^2 ([A^{\ominus}] + [H^{\oplus}]) + k_1 K_a. \quad (2b)$$

Under our experimental conditions the mean ionic activity coefficients f_{\pm} can be calculated with the Debye-Hückel limiting law, and are used to calculate the concentration terms in table 1. The relaxation data are consistent with the simple equilibrium (1) (table 1, fig. 1 and 2). The rate constants for picric acid were calculated with (2b) using $pK_a = 3.67$: $k_1 = (4.3 \pm 0.35) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{-1} = (9.2 \pm 0.75) \times 10^6 \text{ s}^{-1}$. In the case of dipicrylamine the standard deviation for the kinetic data (5.6 %) is even smaller than that of the equilibrium constant (8.0 %). Therefore, eqn (2a) was used to calculate $k_1 = (2.28 \pm 0.13) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_{-1} = (1.31 \pm 0.20) \times 10^5 \text{ s}^{-1}$. From these rate constants an equilibrium constant $K_a = (5.7 \pm 1.3) \times 10^{-5}$ is calculated that agrees with the spectrophotometrically determined value.

An upper limit for the rate constants of reaction in the thermodynamically favoured direction k_1 can be calculated with the Debye-Smoluchowski theory.¹⁶ From the single ion limiting conductivities of the proton,¹⁷ $l_0 = 146.2 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$ and the picrate ion,¹⁷ $l_0 = 47.1 \text{ cm}^2 \text{ mol}^{-1} \Omega^{-1}$ diffusion coefficients can be deduced using the Nernst-Hartley relation.¹⁸ With an estimated reaction distance of 5 Å and these diffusion coefficients a value $k_1 = 6.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C

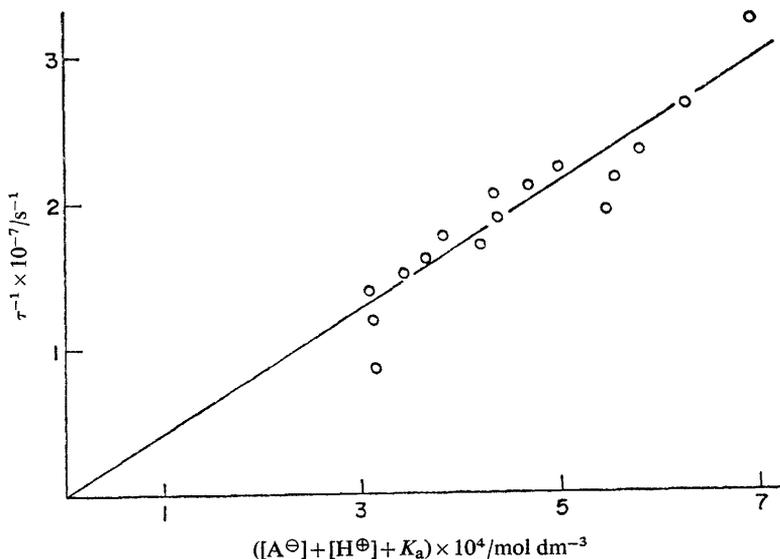


FIG. 1.—Dependence of reciprocal relaxation time τ^{-1} on concentration of picrate ions and protons in methanol at 25°C.

is calculated. The experimental k_1 for picric acid is 40 % lower than this limiting value for ions that can react with their total surface. A reduction of the rate of this order of magnitude is usually observed in reactions of organic molecules¹⁹ and is expected when a surface factor ≤ 1 and the hydrodynamic interaction between the reacting particles is taken into account.²⁰

The limiting conductivity of the dipicrylamine ion in methanol is not known. For reactions of the proton with anions in methanol no k_1 value $< 5 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ can be calculated with the Debye-Smoluchowski theory, even when the diffusion coefficient of the anion is set equal to zero. Thus, there is no means to reconcile the experimental k_1 of (I) with a diffusion controlled reaction.

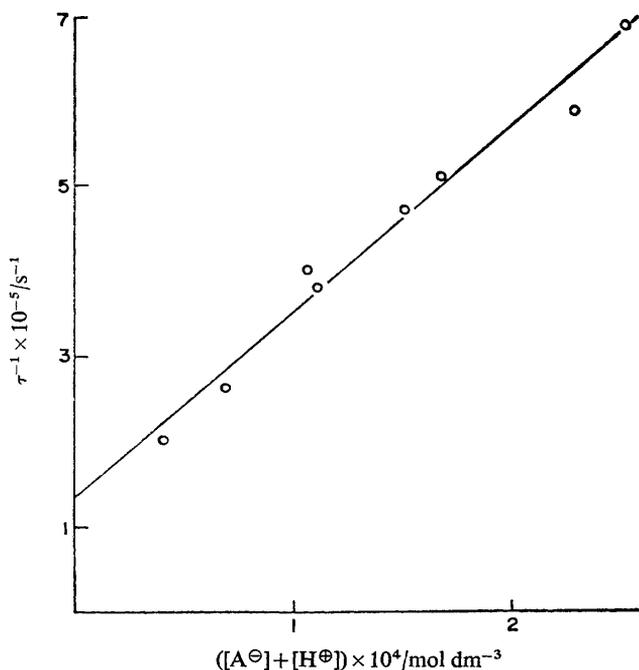


FIG. 2.—Dependence of reciprocal relaxation time τ^{-1} on concentration of dipicrylamine anions and protons in methanol at 25°C.

For the protonation of neutral nitrogen compounds rate constants $k_1 = (1.5-1.9) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ are calculated using the same values for diffusion coefficients and reaction distance as above. The experimental rate data for trimethylamine,²¹ *p*-toluidine²² and substituted pyridines²³ in methanol [$k_1 = (0.6-1.2) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$] agree with this upper limit. Therefore no appreciable activation energy is necessary for the transfer of a proton from the methanol oxygen to a nitrogen atom.

The charge of the dipicrylamine anion is strongly delocalized. This gives rise to three different effects. (1) Dispersion interactions with the organic solvent are increased. Grunwald and Fong²⁴ have shown that this interaction dominates the dissociation equilibrium of dipicrylamine in mixtures of water with organic solvents. By admixture of the organic solvent to water the dissociation constant of dipicrylamine increases, although the dielectric constant of the mixture decreases.²⁴ Analogous effects have been observed with the picrate ion.²⁵ Therefore, it is not very likely that this effect is kinetically significant in only one of the two systems. (2) The electronic and molecular structure is changed on protonation more than in the case

of an ion with localized charge. (3) The ability of the anion to form hydrogen bonds is decreased. These latter two effects should also apply to a lesser extent to the picrate ion. Kresge and coworkers have demonstrated that there is no influence of conjugation upon the rates of protonation of highly resonance stabilized nitrogen compounds.² Because in these other cases there is lack of evidence that electron delocalization influences the protonation kinetics another possible explanation for the relatively slow reaction of the dipicrylamine anion should be considered. The four *ortho* nitro groups effectively shield the site of protonation in this anion in any possible conformation. Therefore, the approach of the proton may be sterically hindered by these groups. In fast proton transfer reactions typically steric factors of ≈ 0.5 are found for organic molecules in water.²⁶ On the other hand in special cryptates synthesized by Lehn the proton inside the molecular cavity is so efficiently shielded from the environment, that deprotonation is extremely slow even in strong base.²⁷ Therefore, steric effects of different magnitudes on proton transfer rates are conceivable. The steric effect should influence both the protonation and the deprotonation rate constants of dipicrylamine. Unfortunately, no data about closely related systems are available that allow a comparison.

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