Kinetics of Proton Transfer between Picric Acid and Two Azo Indicators in Acetonitrile

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The rate constants of proton transfer between picric acid and the two azo indicators methyl red and dimethylaminoazobenzene in acetonitrile ($<7 \times 10^{-5}$ M ionic strength, 25 °C) were determined by the electric field jump method. The rate constants of the ionic reactions picric acid + neutral indicator $\rightleftharpoons$ picrate anion + protonated indicator (k_1, k_{-1}) are $k_1 = 8.1 \times 10^8$ M^{-1} s^{-1}, $k_{-1} = 5.1 \times 10^9$ M^{-1} s^{-1} for methyl red and $k_1 = 4.7 \times 10^8$ M^{-1} s^{-1}, $k_{-1} = 4.2 \times 10^9$ M^{-1} s^{-1} for dimethylaminoazobenzene. The rate constants k_{-1} of the reactions between the ions are about a factor of 10 slower than that calculated for a diffusion-controlled reaction. Possible explanations for this behavior are discussed.

Introduction

The proton transfer reactions between acids and bases in water are fairly well understood.[2] On the other hand, recent work has shown that the mechanism of these reactions in organic solvents may be complex.[3] In halogenated hydrocarbon solvents such as chlorobenzene ion pairs are formed in a three-step reaction. It is assumed that the acid AH and the base B first form an encounter complex AH·B. The molecules in this complex then rotate to form the hydrogen bonded complex AH···B. The complete reaction scheme is[4]

$$AH + B \rightleftharpoons AH\cdot B \rightleftharpoons AH\cdots B \rightleftharpoons A^-\cdots HB^+ \qquad (1)$$

The observed rate constants of proton transfer in these solvents are smaller by a factor of roughly 10 than those calculated with the Smoluchowski theory for diffusion-controlled reactions.[5] It is assumed that the rotation of the molecules in the encounter complex is part of the rate-determining process.[5]

The mechanism of eq 1 can apply only when the interaction energy between the reactants in the encounter complex is larger than the interaction energy between the reactants and the solvent. In acetonitrile free ions are formed in acid–base reactions.[6] Therefore, in this solvent the solvent–solute interactions outweigh the solute–solute interactions and another reaction mechanism is expected.

No kinetic investigation of a proton transfer reaction in acetonitrile has been reported previously.

We have studied the kinetics of proton transfers between picric acid and the azo indicators methyl red and dimethylaminoazobenzene (DAB) in dry acetonitrile at 25 °C using the electric field jump (E-jump) relaxation method. Picric acid is a weak acid in acetonitrile with a pK = 11.0,[7] close to the pK values of protonated methyl red,[8] pK = 10.2, and protonated DAB,[9] pK = 10.05. Only the direct proton transfer between the acid and base can be observed with these compounds since the dissociation of the acids is negligible. No indication of ion pair formation was found by Kolthoff and co-workers in solutions of these molecules that were $\leq 10^{-3}$ M in picrate ion.[8] Therefore under our experimental conditions, where the concentrations of ions were always lower than 7×10^{-5} M, only free ions are formed:

$$AH + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + HB^+ \qquad (2)$$
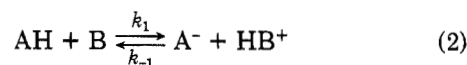
Experimental Section

Methyl red (MCB reagent, neutral) is, in fact, an acid salt and was therefore neutralized with KOH solution, extracted with chloroform, and recrystallized from toluene, mp 182 °C (lit.[10] 183 °C).

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Dimethylaminoazobenzene (Hartmann Deddon reagent) was recrystallized twice from methanol, mp 118 °C (lit.[11] 118 °C).

Picric acid (Mallinckrodt OR) was precipitated from hot water as the tetrabutylammonium salt. This was recrystallized from ethanol and dissolved in benzene, and the neutral acid was recovered by addition of sulfuric acid. The benzene solution was treated with neutral alumina and evaporated. The picric acid was recrystallized from benzene, mp 122.5 °C (lit.[12] 122–123 °C).

Acetonitrile was purified by a procedure modified from that of Walter and Ramalay,[13,14] dried over alumina, and fractionally distilled with a spinning band column. The acetonitrile was stored under nitrogen.

Stock solutions of picric acid and the indicators were prepared under nitrogen in a Pyrex apparatus consisting of containers for the solutions, burettes, and the mixing chamber. The acetonitrile was distilled in vacuo ($\sim10^{-4}$ torr) into the apparatus that had been dried by rinsing it with the solvent before preparing the solutions. Measured aliquots of the solutions were mixed and transferred into the measuring cell without opening the system to the atmosphere. The concentrations of the stock solutions were determined spectrophotometrically (Cary 14) using the following values for the extinction coefficients, determined in this work (extinction coefficient at the wavelength of maximum absorption in nm): picrate ion ϵ_{373}, 1.83×10^4; picric acid ϵ_{333}, 4.39×10^3; methyl red ϵ_{490}, 4.03×10^4. The extinction coefficient of DAB was taken from Kolthoff et al.,[8] ϵ_{410}, 2.8×10^4. Equilibrium concentrations were calculated using Kolthoff's pK values.[7-9] The equilibrium concentrations are accurate to within ±7%, if the unknown uncertainty of the pK values is neglected. Activity coefficients were neglected because the activity correction in no case exceeds 2%. The picric acid used for the experiments with methyl red contained 8.5% picrate ion. This was taken into account in the calculation of equilibrium concentrations. Introduction of this picrate ion was later recognized as having been caused by a pump used in drying the picric acid. The stock solution contained <0.2% picrate ion in the DAB kinetic experiments.

The E-jump apparatus has been described previously.[15] All measurements were done at 25.0 ± 0.1 °C. The signals were stored in a Tektronix R7912 transient digitizer and the relaxation times calculated with a nonlinear least-squares program using 190–240 data points that spanned at least four relaxation times. Often as many as 2–6 signals were averaged. The standard deviation between experimental and calculated data points was normally less than 1% of the relaxation amplitude. In order to check for a second relaxation the calculation was repeated with at least six different sections of the data. No indications of a second relaxation were found. Each of the experimental relaxation times (Table I) is the average of four to seven measurements. Relaxation times for a particular sample solution agreed typically within ±3% of the average relaxation time.

The sensitivity of Karl Fischer titrations of these deeply colored sample solutions is limited to 2×10^{-3} M water. The content of water in our solutions was lower than this and therefore could not be measured directly. Some indications however can be derived from two indirect observations. Acetonitrile is hydrolyzed in an acid-catalyzed process. In our stock solutions of picric acid 3×10^{-6} M picrate ion was formed within 10 days. In a reaction according to eq 2 the relaxation time is the same for all reactants. In the system picric acid/methyl red the relaxation could be measured by monitoring at both the
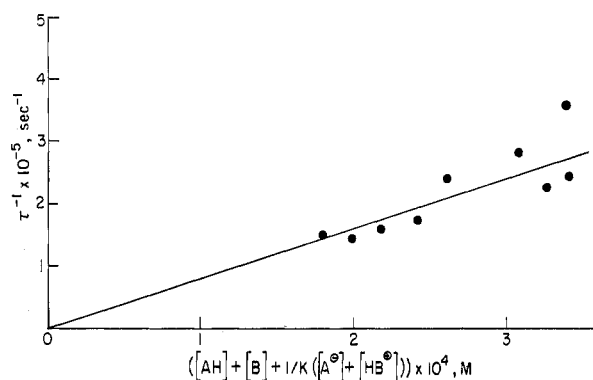
Figure 1. Plot of reciprocal relaxation times, τ^{-1}, vs. the concentration term of eq 3 for the system picric acid + methyl red in acetonitrile at 25 °C.
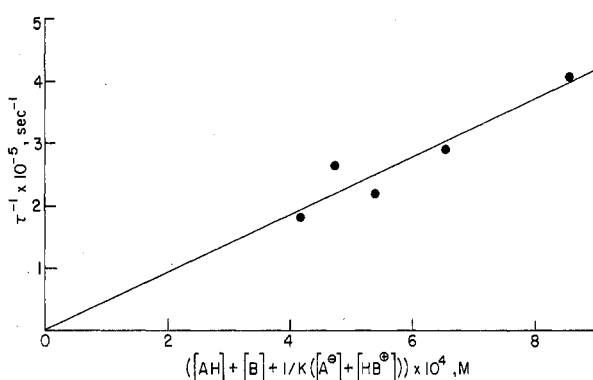
Figure 2. Plot of reciprocal relaxation times, τ^{-1}, vs. the concentration term of eq 3 for the system picric acid + DAB in acetonitrile at 25 °C.

absorption bands of protonated methyl red and the picrate ion. The relaxation times agreed to within 11–22%. When the E-jump experiment was performed without exclusion of air, the relaxation time for the methyl red ion was shortened by 10–20%. On the other hand, the relaxation time for the picrate ion was shortened by a factor between 1.5 and 2.6 over that observed under nitrogen. This shows that under air some contamination was immediately introduced that reacted mainly with the picric acid.

Results and Discussion

The relaxation time attributable to equilibrium 2 is given by[16]

$$1/\tau = k_1([AH] + [B] + (1/K)([A^-] + [BH^+])) \quad (3)$$

The experimental data (Table I, Figures 1 and 2) are in agreement with eq 3. Rate constants calculated from the slopes of the best straight lines through the origin according to eq 3 and from the equilibrium constants are $k_1 = 8.1 \times 10^8$ (M^{-1} s), $k_{-1} = 5.1 \times 10^9$ (M^{-1} s) for the reaction between picric acid and methyl red, and $k_1 = 4.7 \times 10^8$ (M^{-1} s), $k_{-1} = 4.2 \times 10^9$ (M^{-1} s) for the system picric acid/DAB. The standard deviations of these rate constants are 28% in the first and 18% in the second system. In both cases the reaction between the ions to form the neutral species is thermodynamically favored. If this process is assumed to be diffusion controlled its rate constant can be calculated with the Debye–Smoluchowski expression[17]

$$k_D = \frac{4\pi N_A Z_A Z_B e_0^2 (D_A + D_B)}{1000\epsilon kT(\exp(Z_A Z_B e_0^2/\epsilon\sigma kT) - 1)} \quad (4)$$

Here N_A is Avogadro's number, e_0 is the electron charge, Z_A and Z_B are the valencies of the ions A and B, D_A and D_B are their diffusion coefficients, ϵ is the dielectric

TABLE I: Electric Field Jump Relaxation Data for Proton Transfer between Picric Acid (AH) and the Azo Indicators (B)
Methyl Red and Dimethylaminoazobenzene in Acetonitrile at 25 °C

$C_{AH}{}^0$, 10^{-5} M	$C_B{}^0$, 10^{-5} M	([AH] + [B] + 1/K([A] + [HB])),[a] 10^{-5} M	τ, μs	no. of measrm	τ value max. dev,[c] %	τ value dev,[d] %
			Methyl Red			
3.03	5.19	19.9	7.03	7	3	b
1.54	7.58	18.0	6.78	6	6	22
17.12	1.07	21.8	6.26	6	3	11
5.39	4.18	24.1	5.69	7	2.5	b
15.83	1.61	32.6	4.42	6	3	17.5
7.77	3.17	26.0	4.14	7	2	b
10.67	3.76	34.0	4.09	6	6	16
6.91	5.33	30.8	3.51	6	2.3	b
11.20	3.54	33.9	2.79	6	4	b
		Dimethylaminoazobenzene (DAB)				
5.23	10.36	41.43	5.37	4	6	
9.23	9.94	53.87	4.52	5	3	
6.89	10.19	47.13	3.75	4	9	
14.44	9.38	65.48	3.43	4	3	
29.72	7.76	85.42	2.48	6	2	

[a] K = 0.158 for B = methyl red, K = 0.112 for B = DAB. [b] Relaxation time for picrate ion not measured. [c] Maximum deviation from the average of τ values from different measurements. [d] Deviation between τ values for methyl red and picrate ion.

constant of the solvent, k is the Boltzmann constant, and σ is the reaction radius of the ions. The diffusion coefficient D_A for the picrate ion can be estimated from its single ion limiting conductivity in acetonitrile[18] l_0 = 77.7 (cm²/mol ohm), to be D_A = 2.07 × 10^{-5} (cm²/s) using the Nernst–Hartley relation.[19] The conductances of salts of protonated methyl red and DAB are not known. However, diffusion coefficients with molecules with similar shape have been determined[20] in acetonitrile to be ~2 × 10^{-5} (cm²/s). Using $D_A + D_B$ = 4 × 10^{-5} and σ between 4 and 8 Å we calculate with eq 4 k_{-1} = (4.7–5.4) × 10^{10} (M^{-1} s). The observed rate constants are about a factor of 10 smaller than this limiting value. Similar results have been obtained in the reactions between neutral acids and bases in halogenated hydrocarbon solvents.[3] Only a limited fraction of the surface of organic molecules and ions is accessible for reaction. Therefore it is appealing to ascribe the observed rate lowering to a steric factor. It has been shown however that a steric factor cannot fully explain the rate data obtained in the halogenated hydrocarbon solvents.[21] In methanol the picrate ion is protonated with a reaction rate that is only 40% below the limiting value calculated with the Debye–Smoluchowski theory.[22] If the reaction in acetonitrile were mainly determined by steric effects the protonation rate should be smaller for methyl red, whose azo nitrogens are partly screened by the ortho carboxyl group, than for the sterically less hindered DAB.[23] In fact, k_{-1} has essentially the same value for methyl red and for DAB. From these arguments we may conclude that a steric factor cannot appropriately explain our observations.

The direct proton transfer between organic acids and bases in water is slower than diffusion controlled when the pK difference between acid and base is small.[2b] This is shown by the smooth transition in log k/Δ pK plots at ΔpK = 0 instead of the break at this point expected by theory. This has been explained by assuming that a certain amount of solvent reorientation around the anion is required to replace the hydrogen bond between the anion and the solvent by a new hydrogen bond to the protonating acid.[26] The same argument does not apply to acetonitrile solutions because anions are only weakly solvated in this solvent.[27] It has also been argued that the changes in the structure and electron distribution which are needed for the protonation of anions with delocalized charge are responsible for the slow protonation of these anions, es-

pecially carbanions.[2b] However, recently it was found that the trinitromethide ion, a carbanion with delocalized charge, is protonated at a diffusion-controlled rate in cyclohexanol and 2-methyl-2-propanol.[28] Therefore no appreciable activation energy for the protonation of the picrate ion can be expected in acetonitrile. On the other hand, cations are strongly solvated in acetonitrile. Kebarle has recently shown that alkali cations interact much more strongly with from one to four acetonitrile molecules in the gas phase than with the same number of water molecules.[29] In analogy to this it can be assumed that there is a strong solvation of the azo molecules around the site of the proton. For the proton transfer therefore some solvent reorganization around the cation is required that we assume accounts for our observations.

In all the solvents investigated so far, in nearly nonpolar as well as in the dipolar aprotic solvents and in water, the proton transfer between organic acids and bases is slower than the diffusion limit by about the same factor. It is obvious, however, that quite different effects are operating in the different solvents. Further work is in progress intended to elucidate the influence of cation solvation on fast kinetics in acetonitrile.

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(23) The situation is quite different for methyl red in acetonitrile from the one in water. In water the carboxyl group of methyl red is dissociated under the conditions for the protonation of the azo group and therefore

the solvation shell is favorably oriented for solvent mediated proton transfer. The anion of methyl orange, which is structurally very similar to the indicators studied here, is protonated exceptionally slowly in water.[24] Unfortunately, its protonation kinetics cannot be measured in acetonitrile because the protonated methyl orange is extremely insoluble in acetonitrile. The dissociation constant of methyl orange was determined by Kolthoff et al. by measuring absorbances immediately after mixing solutions.[25]
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Unimolecular Rate Constants for Ring Rupture and HCl Elimination from Chemically Activated 1-, 2-, and 3-Methylchlorocyclobutane and Chloromethylcyclobutane

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Chemically activated 1-, 2-, and 3-methylchlorocyclobutane were prepared with $\sim$110 kcal mol^{-1} of internal energy by the insertion of singlet methylene into the C–H bonds of chlorocyclobutane. Total decomposition rate constants for these molecules were measured as $7.6 \pm 3.8 \times 10^8$, $3.9 \pm 0.8 \times 10^8$ and $3.9 \pm 0.8 \times 10^8$ s^{-1}, respectively. Both HCl elimination and ring rupture are unimolecular reaction pathways for these vibrationally excited molecules and the rate constants for individual HCl-elimination and ring-rupture channels were extracted from the pressure dependence of the product yield ratios. These rate constants were interpreted according to RRKM theory and threshold energies for various unimolecular reaction channels were assigned. Chloromethylcyclobutane was prepared with 90 kcal mol^{-1} by the combination of cyclobutyl and chloromethyl radicals, which were formed by methylene abstraction of chlorine from chlorocyclobutane. The unimolecular ring-rupture and HCl-elimination rate constants for chloromethylcyclobutane were $4.7 \pm 0.2 \times 10^6$ and $4.8 \pm 4 \times 10^5$ s^{-1}, respectively. RRKM theory also was applied to the chloromethylcyclobutane reactions to assign threshold energies. The transition state models developed for the ring-rupture and HCl-elimination reactions fitted the experimental observation at both energies of activation. The methylchlorocyclobutane chemical activation rate constants are best fitted if $\Delta H_f^\circ(\mathrm{CH_2,^1A_1}) = 101$ kcal mol^{-1} is used to calculate the energy of activation.

Introduction

The HX (X = F, Cl and Br) elimination reactions from thermally and chemically activated halohydrocarbons have been extensively studied.[1-3] Both a three-centered and the more common four-centered decomposition pathways have been observed. The chemical and thermal activation studies include the hydrogen–deuterium isotope effects, temperature dependence of the rate constants, and variation of the rate constants with the length of the carbon chain and with position and extent of halogen substitution. Recently the chlorine isotope[4] and thermal fall-off effects[5] have been studied via thermal activation. In addition chemical activation has been used to study intramolecular competitive HX elimination[6] and the energy dependence of the rate constants.[7a,8] In the present work the chemical activation technique has been extended to study the competitive intramolecular HCl-elimination and ring-rupture pathways of methylchlorocyclobutane (MCCB)

and chloromethylcyclobutane (CMCB).

The chemical activation results for HX elimination from alkyl halides from this laboratory have been fitted to a common four-centered transition state model using the RRKM theory. The bond orders for the best model were 1.5, 0.9, 0.1, and 0.1 for C–C, C–X, C–H, and H–X, respectively. This model suggests that the hydrogen is only weakly bound to both the halogen and the carbon in the transition state. The sum of the bond orders is less than 3.0, which implies a polar transition state, in agreement with Maccolls' interpretation[9] of the lowering of E_0 with an α- or β-methyl substitution. The question of the stereochemistry of the elimination process, i.e., do the hydrogen and halogen originate from the same or opposite sides of the C–C bond, has not been answered experimentally; however, theoretical studies[9b,c] favor elimination via a syn transition-state geometry. Since the transition-state model for HCl elimination is well characterized, the present work offers the opportunity to compare the HCl-elimination channel to the less well understood ring-rupture channel in the 90–110-kcal mol^{-1} range. Our

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