and ΔH_3; thus the hydrogen bond formed between a phenol and a homoconjugated anion is very weak.

The heat evolved in the formation of the first hydrogen bond between a phenolate ion and a phenol ΔH_4 is significantly larger than that of the proton transfer from the phenol to the acridine orange base (Table 2). Therefore, the energetics of reaction (2) are mainly determined by this association. The association tendency of the phenolate ions in benzonitrile is much stronger than in acetonitrile. This is due to a larger reaction enthalpy ΔH_4. The difference of about 8 kJ mol^{-1} between ΔH_4 in these solvents may be ascribed to different hydrogen bond energies of hydrogen bonds between the phenol monomers and the solvents since benzonitrile is a weaker hydrogen bond acceptor than acetonitrile.

The solvent dependence of the *AO/NP* system reveals a surprising effect of the homoconjugation. At the ionic strength 0.1 M, K_1 has almost the same value in both solvents. This is a fortuitous coincidence, since the dependence of K_1 on the ionic strength in these solvents is quite different. The concentration of ions in a benzonitrile solution of *AO* and *NP* at the ionic strength 0.1 M is significantly larger than in a solution with the same starting concentrations in acetonitrile. This is due solely to the stronger anion association which shifts the overall equilibrium to the side of the ions in spite of the smaller dielectric constant of benzonitrile.

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Acid Base Reactions Between Acridine Orange and Substituted Phenols in Benzonitrile Part II. Kinetics: An Extended Eigen Mechanism of Proton Transfer

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Chemical Kinetics / Elementary Reactions / Molecular Interactions / Solutions

The kinetics of proton transfer between five substituted phenols (AH) and the acridine orange base (B) are studied in benzonitrile solution using the temperature jump method. In the overall reactions (1) – (3)

$$n = 1 \quad (1)$$

$$n\,\mathrm{AH} + \mathrm{B} \underset{k_{bn}}{\overset{k_{fn}}{\rightleftharpoons}} \mathrm{A}^-(\mathrm{AH})_{n-1} + \mathrm{HB}^+; \quad n = 2 \quad (2)$$

$$n = 3 \quad (3)$$

the formation and dissociation of an intermediate ion pair $A^- \ldots HB^+$ is rate determining. The rate constants of the bimolecular recombination of the ions to the ion pair are k_{b1}, k_{b2}, and k_{b3}. Their values are in the range $(0.18-1.7)\cdot 10^9\ M^{-1}\ s^{-1}$ (25°C, I = 0.1 M). k_{b2} and k_{b3} do not depend on the pK of the phenol involved, although these rates are not diffusion controlled. The rate of proton transfer from the protonated acridine orange (BH^+) to the free anions (A^-) does depend to some degree on the acidity of the corresponding phenol. In the case of the 3-methyl-4-nitrophenolate ion this rate is diffusion controlled, as shown by the dependence of k_{b1} on the temperature and the ionic strength. Lower limits for the formation constants of the ion pairs are estimated from the rate data. The equilibria and the kinetics are discussed in terms of an extended Eigen scheme of proton transfer, and the separate steps of anion solvation by hydrogen bonding to phenol molecules shown to depend in different ways on the basicity of the anion.

1. Introduction

Proton transfer reactions between organic acids and bases in aqueous solutions were among the first classes of chemical reactions to be extensively studied by relaxation methods [1, 2]. Diffusion controlled rates are a general feature of these reactions [3]. In organic solvents different mechanisms of proton transfer are observed. The rate constants of ion pair formation of many amines with phenols in halogenated hydrocarbon solvents are ten to hundred times less than the calculated values for diffusion control, and do not correlate with the equilibrium constants [4, 5]. This is explained by diffusion controlled formation of weakly bound intermediate complexes with sufficient lifetime to allow rotation of the reactants within the complex [5]. Recently we have found that proton transfers between protonated nitrogen bases and phenolate ions in dry acetonitrile are kinetically hindered by the need for solvent reorientation at the site of the proton, whereas there is no measurable energy barrier for the transfer of the proton within the hydrogen bonded complex [6, 7].

Similar effects could be expected to be operative in benzonitrile solution, since the dipole moment of the benzonitrile molecule is almost equal to that of the acetonitrile molecule and since molecular reorientation is slower in benzonitrile because of its larger viscosity. A strong solvation of ions by benzonitrile is indicated by the solubility of many salts in this solvent, in spite of its relatively low dielectric constant (ε = 25.2 at 25°C). No investigation of the kinetics of proton transfer reactions in benzonitrile has previously been reported.

The following is a report of the conclusions of a study of the kinetics and energetics of proton transfers between 3-chloro-4-nitrophenol *CNP*, 4-nitrophenol *NP*, 3-methyl-4-nitrophenol *MNP*, 4-chloro-3,5-dimethylphenol *CMP*, and 3,5-dimethylphenol *DMP* and the indicator base acridine orange in benzonitrile. Depending on the concentration of the phenol AH proton transfer is observed in three different overall reactions [8]. At concentrations $c_{AH} < 10^{-3}$ M free ions are formed by protonation of the base B

$$AH + B \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} A^- + HB^+ \qquad (1)$$

together with the homoconjugate anions AHA^-

$$2\,AH + B \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} AHA^- + HB^+ \qquad (2)$$

At higher concentrations of the phenol reaction (1) could not be observed; however, in addition to reaction (2), further association of the anions occurred according to

$$3\,AH + B \underset{k_{b3}}{\overset{k_{f3}}{\rightleftharpoons}} A(AH)_2^- + HB^+ . \qquad (3)$$

These reactions are all exothermic. Some of them are nevertheless endergonic because of the large negative entropy connected with ion formation in benzonitrile. The equilibrium- and thermodynamic data of the acid base and association reactions have been given in the preceding paper [8].

2. Experimental

Purification of the solvent and of the other chemicals has been described [8]. The kinetic measurements were done with a Meßanlagen temperature jump transient spectrometer. The ionic strength of the sample solutions was kept constant by adding Bu_4NPF_6 *TBHP*. The viscosities of solutions of *TBHP* in benzonitrile were measured at 25°C

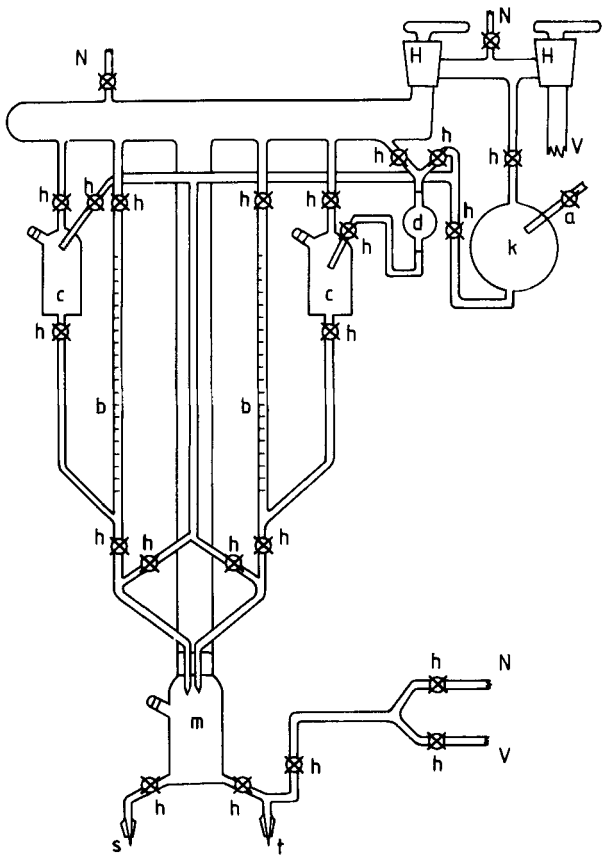


Fig. 1
Buret system for preparing sample solutions in an inert atmosphere. The freshly distilled benzonitrile is filled into the storage bulb k through valve a by aid of a teflon tubing; b = burets; c = stock flask for preparing reagent solutions; d = calibrated flask that allows filling a measured volume of solvent into c; h = teflon valve; H = 15 mm glass valve; m = mixing chamber with outlets s to spectrophotometric cell and t to T-jump cell; N = nitrogen inlets; V = connections to vacuum line

with an Ubbelohde viscosimeter. Contamination of the sample solutions with moisture was avoided by preparing stocks and the samples in the closed all glass apparatus shown in Fig. 1. This apparatus was dried before each preparation by evacuating it for at least 12 hours at about 10^{-2} Pa. In each sample solution the equilibrium concentration of HB^+ was checked spectrophotometrically. The solution was not used to evaluate kinetic data when the equilibrium constant calculated from this measurement deviated by more than ± 10% from the value previously obtained [8].

The *T*-jump cell was thermostatted by circulating water through the upper electrode. The temperature before the jump was measured by means of a Si-diode sealed in a teflon tubing dipping into the solution near to the upper electrode. Charging voltages of 30 kV and 35 kV were used, resulting in respective temperature increases of 3.2°C and 4.4°C. The signals were stored in a Biomation transient recorder Model 805, and evaluated with a non-linear least squares program, which allows data fitting with one or two exponentials. 800 to 1200 data points were taken for each signal. In calculating the relaxation times τ_2 the heating process was taken into account as the first exponential (τ_1). The heating times were calculated from the measured resistance as [9]

$$\tau_e = 1/2\,RC\,.$$

In some instances both the relaxation times τ_1 and τ_2 were calculated by curve fitting. τ_1 obtained in this way agreed to within a few percent with τ_e. A typical signal is shown in Fig. 2. Between three and six signals were taken for each sample solution. The relaxation times for a particular sample solution agreed typically better than ± 5% of the average relaxation time.

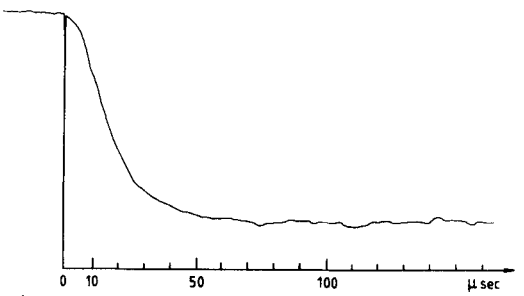


Fig. 2
Relaxation curve for the proton transfers between *AO* and *NP*, τ = 10.9 μsec

3. Results

3.1. Proton Transfer Between Acridine Orange and Nitrophenols

For the protonation of the acridine orange base B by *CNP*, *NP* and *MNP* concentrations of $10^{-5}-10^{-4}$ M of both reactants were used. The reaction was monitored with the absorption of the protonated acridine orange BH^+ at 20000 cm^{-1}. In all solutions only one chemical relaxation signal was observed. It is ascribed to the parallel reactions (1) and (2). These are coupled by the hydrogen bond association of the phenolate anion A^- to the homoconjugate ion AHA^-:

$$A^- + AH \underset{k_{b4}}{\overset{k_{f4}}{\rightleftharpoons}} AHA^- \,. \qquad (4)$$

This reaction was studied independently. Solutions containing *NP* and its tetrabutylammoniumsalt show a relaxation time after a temperature jump which is very close to the heating time.

Therefore only a lower limit for k_{f4} could be determined; k_{f4}^{NP} is greater than $4 \cdot 10^8$ M^{-1} s^{-1}. Under the conditions used to study the acid base reactions (1) and (2) the equilibration of (4) is rapid compared with that of (1) and (2). The reciprocal relaxation time, $1/\tau$ for reactions (1) and (2) is calculated by standard methods of relaxation kinetics [1]

$$1/\tau = k_0 F_1\,. \qquad (6)$$

In (6) the concentration term

$$F_1 = K_1 \cdot \left(c_{AH} + \frac{c_B(2\,c_{AH} + K_4^{-1})}{c_{AH} + c_{A^-} + K_4^{-1}} \right) + c_{A^-} + \frac{c_{HB^+}(2c_{A^-} + K_4^{-1})}{c_{AH} + c_{A^-} + K_4^{-1}}$$

accounts for the preequilibrium, and the observed rate constant k_0 is defined by

$$k_0 = k_{b1} + k_{b2} \cdot K_4 \cdot c_{AH}\,.$$

Values of k_{b1} and k_{b2} are obtained from intercept and slope of linear plots of Eq. (7)

$$(\tau \cdot F_1)^{-1} = k_{b1} + k_{b2} \cdot K_4 \cdot c_{AH} \qquad (7)$$

shown in Fig. 3. The equilibrium relations $k_{f1} = K_1 \cdot k_{b1}$ and $k_{f2} = K_2 \cdot k_{b2}$ can be used to calculate k_{f1} and k_{f2}. The results are given in Table 2. The τ values are listed in Table 1. The agreement between experimental and calculated values is very good.

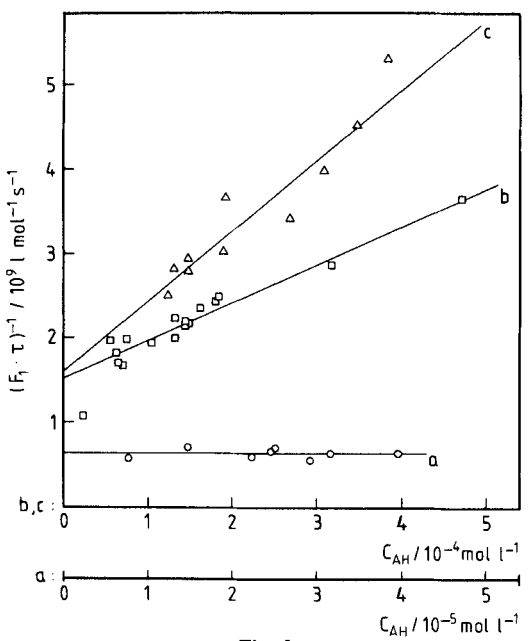


Fig. 3
Dependence of the relaxation times of proton transfers between nitrophenols and Acridine Orange on the phenol concentration. Plot of the rate expression Eq. (7) vs. the equilibrium concentration of a) CNP, b) NP, and c) MNP

In the experiments with *CNP* the concentration of the phenol had to be kept very low in order to avoid complete protonation of the base. Under these conditions reaction (2) did not make a measurable contribution to the observed relaxation. This is evident from Fig. 3, where the plot of Eq. (7) for the *CNP* system produces a zero slope. The standard errors of the estimated relaxation times are σ = 0.068, 0.066, and 0.066 for *CNP*, *NP* and *MNP* respectively.

The rates of proton transfer between *MNP* and acridine orange were measured also at 18°C, 35°C, and 50°C (Fig. 4). Rate constants were calculated using Eqs. (6) and (7) and the equilibrium relations as before. In this temperature range we obtain (Fig. 5)

$$k_{b1} = (3.19 \pm 0.09) \cdot 10^{11} \exp(-12.8 \pm 1.8\,\text{kJ mol}^{-1}/RT)\,M^{-1}\,s^{-1}$$

and

$$k_{b2} = (2.82 \pm 0.08) \cdot 10^{15} \exp(-40.0 \pm 2.6\,\text{kJ mol}^{-1}/RT)\,M^{-1}\,s^{-1}.$$

Table I
Reactions of Acridine Orange base with Nitrophenols

$10^4\ c^0_{AH}$ [a] M	$10^5\ c^0_B$ [b] M	τ µsec
3-Cl-4-nitrophenol, T = 25°C, I = 0.1 M		
0.608	3.19	29.3
0.365	4.13	26.4
0.632	5.97	19.7
1.00	7.19	18.2
0.807	10.2	13.9
1.03	13.2	13.6
0.909	16.6	11.1
0.469	25.1	7.7
4-Nitrophenol, T = 25°C, I = 0.1 M		
0.378	1.09	52.5
1.80	1.40	51.1
1.28	2.90	46.0
2.10	2.56	36.1
1.81	3.66	35.0
2.17	2.94	34.1
0.842	10.2	25.0
1.93	6.67	24.8
1.84	8.44	21.6
2.02	13.0	18.1
1.28	19.3	17.0
1.04	14.7	16.9
1.25	18.7	16.5
3.92	5.86	16.5
2.24	16.2	14.8
1.22	27.6	12.5
5.66	0.624	10.9
3-CH_3-4-nitrophenol, T = 25°C, I = 0.1 M		
2.86	1.45	72.6
1.67	2.92	63.3
3.86	3.17	36.5
3.72	1.36	44.7
2.48	10.61	30.4
1.98	14.6	27.4
3.64	6.94	27.4
1.74	21.3	25.3
2.23	14.7	25.1
4.53	5.65	24.1
1.83	18.9	23.3
6.75	3.88	20.9
3-CH_3-4-nitrophenol, T = 18°C, I = 0.1 M		
1.29	3.62	79.3
2.29	1.96	72.9
2.71	4.44	46.0
4.50	8.09	25.1
4.39	12.5	21.3

Table I *(Continued)*

$10^4\ c^0_{AH}$ [a] M	$10^5\ c^0_B$ [b] M	τ µsec
3-CH_3-4-nitrophenol, T = 35°C, I = 0.1 M		
1.21	4.33	50.7
2.45	3.50	42.2
3.54	5.84	26.2
5.62	6.38	18.1
4.61	4.28	24.8
4.61	8.77	17.9
6.59	8.48	14.4
7.09	12.1	12.0
6.16	15.6	11.2
3-CH_3-4-nitrophenol, T = 50°C, I = 0.1 M		
4.07	2.23	29.8
6.07	2.82	20.4
7.90	4.06	13.8
10.3	4.67	9.5
11.3	6.58	8.3
3-CH_3-4-nitrophenol, T = 25°C, I = 0.025 M		
1.74	4.46	42.5
2.32	2.81	39.4
3.00	2.21	38.0
3.69	5.47	20.0
4.50	4.19	19.2
5.48	5.80	16.5
3-CH_3-4-nitrophenol, T = 25°C, I = 0.05 M		
1.79	3.35	52.0
2.75	1.90	49.2
2.79	2.11	44.8
2.74	6.69	25.9
4.53	3.85	24.2
3.98	4.40	24.0
3.26	11.1	18.5
3.53	10.5	18.3
7.51	3.87	14.8
3-CH_3-4-nitrophenol, T = 25°C, I = 0.2 M		
1.03	4.46	82.7
1.75	2.73	77.6
2.66	4.42	44.5
1.77	9.78	44.2
2.10	7.50	43.0
2.27	11.7	31.4

[a] Total concentration of phenol.
[b] Total concentration of Acridine Orange.

Table II
Rate and Equilibrium Constants for the Reactions of Acridine Orange with Nitrophenols in Benzonitrile [a]

Phenol	T °C	I M	$10^{-7}\ k_{f1}$ $M^{-1}\ s^{-1}$	$10^{-8}\ k_{b1}$ $M^{-1}\ s^{-1}$	$K_1 = k_{f1}/k_{b1}$ [b]	$10^{-10}\ k_{f2}$ $M^{-2}\ s^{-1}$	$10^{-8}\ k_{b2}$ $M^{-1}\ s^{-1}$	$K_2 = k_{f2}/k_{b2}$ [b] M^{-1}
CNP	25	0.1	39.0 ± 4	5.9 ± 0.6	0.66	–	–	15600
NP	25	0.1	4.0 ± 0.08	14.6 ± 0.3	0.0276	13.3 ± 0.3	1.9 ± 0.07	690
MNP	25	0.1	1.1 ± 0.05	16.9 ± 0.6	0.0064	4.9 ± 0.1	3.1 ± 0.07	155
	18	0.1	1.4 ± 0.06	16.6 ± 0.8	0.0084	4.5 ± 0.3	1.8 ± 0.1	253
	35	0.1	1.3 ± 0.03	24.4 ± 0.5	0.0055	3.2 ± 0.06	4.0 ± 0.1	80
	50	0.1	1.0 ± 0.1	26.4 ± 2.6	0.0040	3.3 ± 0.2	10.2 ± 0.4	32
	25	0.025	1.2 ± 0.1	39.7 ± 3.9	0.0030	5.0 ± 0.3	5.7 ± 0.3	88
	25	0.05	1.0 ± 0.02	25.1 ± 0.5	0.0040	5.6 ± 0.06	4.8 ± 0.05	117
	25	0.2	1.0 ± 0.05	8.7 ± 0.5	0.011	6.5 ± 0.3	2.5 ± 0.15	260

[a] The errors are standard errors. [b] From Ref. [8].

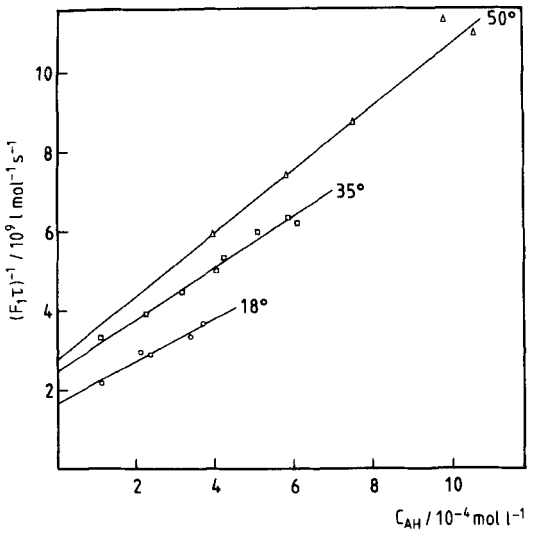


Fig. 4
Temperature dependence of the relaxation time for proton transfers between MNP and Acridine Orange. Plot of the rate expression Eq. (7) vs. equilibrium concentration of MNP

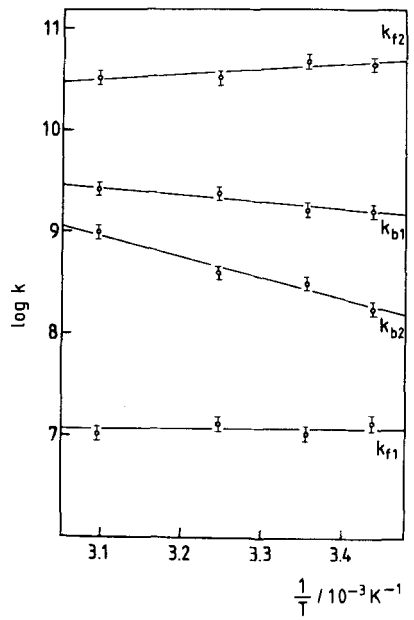


Fig. 5
Arrhenius plot of the rate constants in the Acridine Orange-MNP system

The errors are standard errors of the parameters of the best straight lines. The activation enthalpy $\Delta\ddot{H}_1^{\neq} = E_a - RT = 10.4$/kJ mol^{-1} calculated from this result is within the confidence limits equal to the negative value of the corresponding reaction enthalpy $-\Delta H_1 = 14.5$/kJ mol^{-1}, and $\Delta\ddot{H}_2^{\neq} = 37.7$/kJ mol^{-1} is even smaller than the negative of the reaction enthalpy $-\Delta H_2 = 50.4$/kJ mol^{-1} [8]. Thus the forward rate constant k_{f1} is practically independent of temperature, whereas k_{f2} decreases with increasing temperature, as shown in Fig. 5. The activation parameters are listed in Table 3.

The dependence of the rates on the ionic strength I was investigated at 25°C by varying the amount of the inert salt *TBHP* (Tables 1 and 2, Fig. 6). Rate constants were calculated as before using the equilibrium constants K_1 and K_2 measured independently at the same ionic strength.

The dependence of a diffusion controlled reaction rate on the viscosity and the ionic strength can be expressed in terms of the rate constant k_D^0 at zero ionic strength, the viscosities of the solvent η_0 and solutions η, and the activity term Π_f [10]

Table III
Activation parameters and thermodynamic data for the reactions (1) and (2) of 3-Methyl-4-nitrophenol *MNP*

	AH + B ⇌ A^- + HB^+	2 AH + B ⇌ AHA^- + HB^+
$\Delta\ddot{H}^{\neq}$	10.4	37.7
$\Delta\ddot{H}^{\neq}$	−4.1	−12.7
$-\Delta H$	14.5	50.4
$\Delta\ddot{S}^{\neq}$	−25	+51
$\Delta\ddot{S}^{\neq}$	−115	−76
$-\Delta S$	90	127

Dimensions: ΔH, kJ mol^{-1}; ΔS, JK^{-1} mol^{-1}.

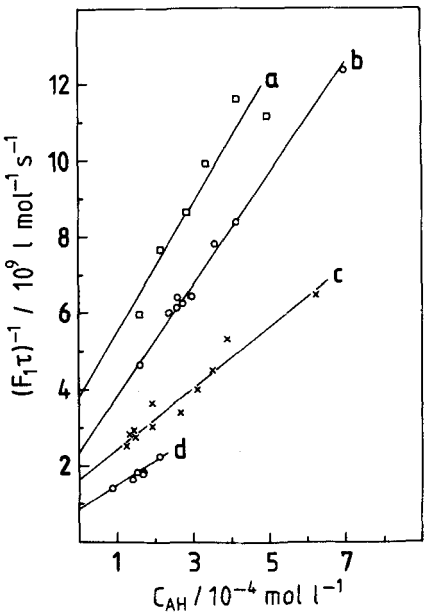


Fig. 6
Ionic strength dependence of the relaxation time for proton transfers between MNP and Acridine Orange at 25°C. Plot of the rate expression Eq. (7) vs. the equilibrium concentration of MNP at ionic strength I: a) 0.025 M; b) 0.05 M; c) 0.1 M; d) 0.2 M

$$k_D = \frac{\eta_0}{\eta} \cdot k_D^0 \cdot \Pi_f, \qquad \Pi_f = \frac{f^+ f^-}{f^{\neq}} \tag{8}$$

where f^+, f^-, and $f^{\neq}$ denote the ionic activity coefficients of the cation, the anion and the activated complex respectively. By fitting the experimental rate constants k_{b1} to Eq. (8) using the Debye Hückel formula

$$-\log f = \frac{A \cdot \sqrt{I}}{1 + B \cdot r \cdot \sqrt{I}}$$

for the ionic activity coefficients f^+ and f^-, and taking $f^{\neq} = 1$ a value $k_D^0 = k_{b1}^{0,MNP} = 1.8 \cdot 10^{10}$ M^{-1} s^{-1} and the ionic radius $r = 0.43$ nm were calculated for the *MNP*/acridine orange system. The same calculation results in $k_{b2}^{0,MNP} = 1.8 \cdot 10^9$ M^{-1} s^{-1} and $r = 0.89$ nm for the reaction of HB^+ with the homoconjugate anion of *MNP*. The forward rates are independent of the ionic strength, as is expected for reactions between neutral molecules (Fig. 7).

In all calculations the ionic strength was assumed to be constant, and completely determined by the concentration of the inert salt *TBHP*. No activity terms need to be included in the kinetic Eqs. (6) and (9), because in no case the concentration of the reacting ions exceeded $3 \cdot 10^{-5}$ M, whereas the smallest concentration of *TBHP* was $2.5 \cdot 10^{-2}$ M.

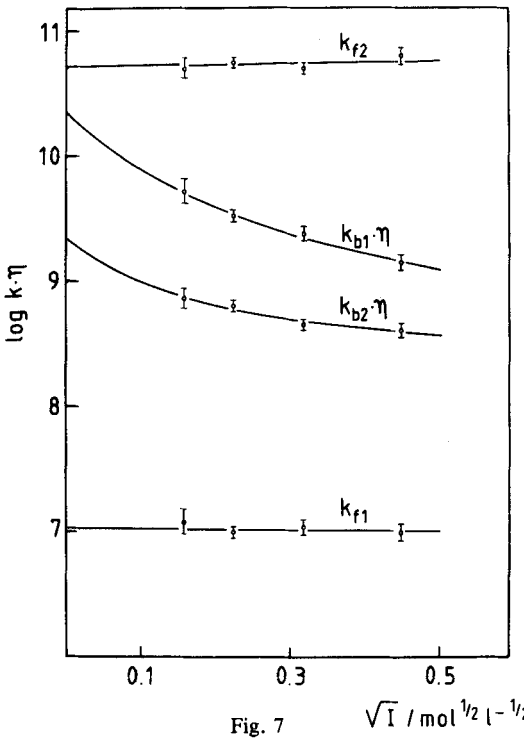


Fig. 7

Dependence of the apparent rate constants k_{f1} and k_{f2}, and of the rate constants k_{b1} and k_{b2}, corrected for the viscosity dependence, on the ionic strength I. The curves through $k_{b1}\eta$ and $k_{b2}\eta$ are the best fits of Eq. (8)

3.2. Protonation of Acridine Orange by Weakly Acidic Phenols

A 10^2 – 10^3 – fold excess of the weak acids *CMP* and *DMP* is necessary to protonate the acridine orange base to a measurable extent. Under these conditions only reactions (2) and (3) are observable [8]. As with the nitrophenols, only one chemical relaxation with a time constant in the 10 – 50 µsec range was found (Table 4). This was attributed to the parallel reactions (2) and (3), which are coupled by the hydrogen bond association of the homoconjugate anion

$$AHA^- + AH \underset{k_{b5}}{\overset{k_{f5}}{\rightleftharpoons}} A(AH)_2^- \,. \qquad (5)$$

If it is assumed that $k_{f5} \geq 10^7\ M^{-1}\ s^{-1}$ holds, the relaxation time of (5) is outside the timescale of our measurement for all phenol concentrations used. Thus the reciprocal relaxation time $1/\tau$ for reactions (2) and (3) is given by

$$1/\tau = k_0 F_2 \,, \qquad (9)$$

with

$$F_2 = K_2\left[c_{AH}^2 + \frac{c_{AH}\,c_B(6\,c_{AH} + 4\,K_5^{-1})}{c_{AH} + c_{AHA^-} + K_5^{-1}}\right] + c_{AHA^-} + \frac{c_{HB^+}(3\,c_{AHA^-} + K_5^{-1})}{c_{AH} + c_{AHA^-} + K_5^{-1}}$$

accounting for the rapid pre-equilibrium. The observed rate constant k_0 is defined by

$$k_0 = k_{b2} + k_{b3}\cdot K_5 \cdot c_{AH} \,,$$

which allows the determination of k_{b2} and k_{b3} from intercept and slope of linear plots of Eq. (10)

$$(\tau F)^{-1} = k_{b2} + k_{b3}\cdot K_5 \cdot c_{AH} \qquad (10)$$

shown in Fig. 8.

Table IV
Reactions of Acridine Orange with Methylphenols at 25°C, ionic strength I = 0.1 M

$10^2\,c_{AH}^0$ [a] M	$10^5\,c_B^0$ [b] M	τ µsec
	4-Cl-3,5-dimethylphenol	
0.983	35.2	45.3
2.45	2.08	42.6
1.36	24.9	34.5
2.61	4.46	25.9
2.20	12.4	22.0
1.77	23.3	21.5
2.60	17.8	17.9
4.03	3.00	17.3
3.19	10.8	13.8
3.69	8.63	13.2
3.70	12.0	12.7
4.56	1.62	10.9
	3,5-Dimethylphenol	
8.27	2.11	58.6
9.92	2.68	38.2
12.4	1.91	30.5
7.94	13.1	25.9
12.2	4.16	23.3
9.71	9.77	22.2
6.86	28.2	22.2
8.50	18.4	21.5
11.1	7.44	21.0
10.2	13.5	19.1
10.7	11.6	18.9
12.8	7.33	17.3
9.45	25.4	14.8
15.4	6.26	13.1

[a] Total concentration of phenol.
[b] Total concentration of Acridine Orange.

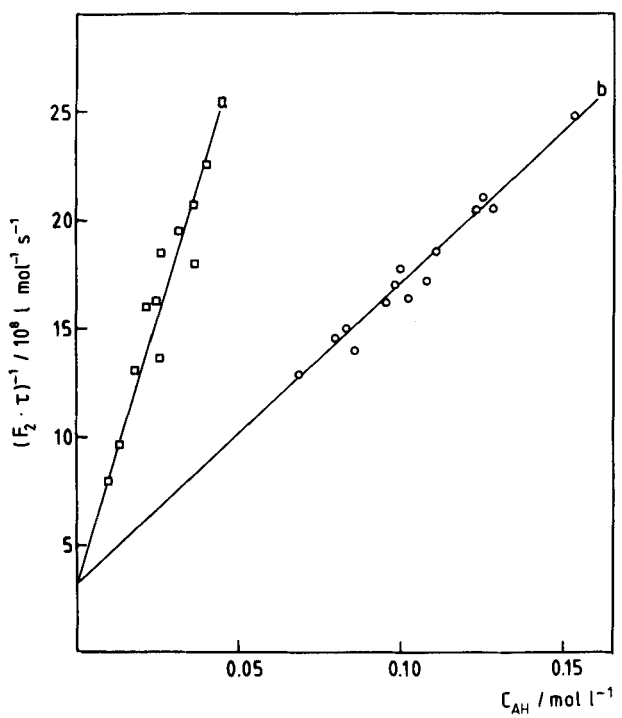


Fig. 8

Dependence of the relaxation time of proton transfers between Methylphenols and Acridine Orange on the phenol concentration. Plot of the rate expression Eq. (10) vs. the equilibrium concentration of a) CMP and b) DMP

The equilibrium relations then give $k_{f2} = K_2 \cdot k_{b2}$ and $k_{f3} = K_3 \cdot k_{b3}$ (Table 5). The standard errors of the estimated relaxation times are $\sigma = 0.094$ and 0.033 for the systems with *CMP* and *DMP* respectively.

Table V
Rate and equilibrium constants for the reactions of acridine orange with methylphenols in benzonitrile[a])

	CMP	DMP
k_{f2} (10^5 M^{-2} s^{-1})	25 ± 10	1.5 ± 0.12
k_{b2} (10^8 M^{-1} s^{-1})	3.1 ± 0.8	3.1 ± 0.22
$K_2 = k_{f2}/k_{b2}$ (M^{-1})[b])	$8.3 \cdot 10^{-3}$	$5.0 \cdot 10^{-4}$
k_{f3} (10^6 M^{-3} s^{-1})	436 ± 22	7.0 ± 0.1
k_{b3} (10^8 M^{-1} s^{-1})	9.8 ± 0.5	8.2 ± 0.1
$K_3 = k_{f3}/k_{b3}$ (M^{-2})[b])	0.45	$8.6 \cdot 10^{-3}$

[a]) The indicated errors are standard errors; [b]) from Ref. [8].

The reactions (2), (3), and (5) form a coupled system with two relaxation modes [9]. The amplitudes of both relaxation processes at the wavelength of observation were calculated by standard methods [11, 12]. Our formalism is identical to that used previously for an analogous system [13]. Different trial values of the unknown rate constant k_{f5} were tested. With values $k_{f5} = 10^8$ M^{-1} s^{-1} or larger we calculated that the amplitude of the faster process contributes less than 1% to the total amplitude under our experimental conditions. This is the reason why only one relaxation was observed throughout. A value of k_{f5} of the same order of magnitude as k_{f4} is reasonable, since in reaction (5) as in (4) a hydrogen bond is formed.

The titration curves obtained by adding *DMP* or *CMP* to solutions of acridine orange were equally well described by a scheme consisting of the acid base reaction (1) and following association of the free anion with two molecules of phenol:

$$2\,AH + A^- \rightleftharpoons A(AH)_2^- \qquad (11)$$

as by the scheme of reactions (2) and (3). If a combination of (1) and (11) is used to evaluate the kinetic data, no correlation between the relaxation times and the appropriate rate expression is obtained [14]. Therefore, this mechanism was excluded.

4. Discussion

The observed single steps of proton transfer between acridine orange and the phenols spanning an estimated acidity range of 7.5 pK units [8] in benzonitrile are very fast. We may compare their rate constants with k_D, the rate constant of a diffusion controlled reaction given by Eigen [10] and Weller [15]

$$k_D = k_D^0 \Pi_f, \qquad (12)$$

with

$$k_D^0 = \sigma_A \sigma_B \cdot k_S \cdot \Phi, \quad k_S = 4 \cdot \pi \cdot N_L \cdot D \cdot r_{AB},$$

$$\Phi = \frac{\varphi}{e^{\varphi} - 1}, \qquad \varphi = \frac{z_A \cdot z_B \cdot e^2}{r_{AB} \cdot \varepsilon \cdot k \cdot T}.$$

Here k_D is expressed in terms of k_S, Φ, Π_f, and $\sigma \cdot k_S$ is the rate constant of the Smoluchowski theory for the diffusion controlled recombination of particles A and B with a reaction radius r_{AB} and mutual diffusion coefficient D. The Debye factor Φ accounts for the coulomb interaction of ionic reactants at zero ionic strength, and the screening of this interaction by counter-ions at higher ionic strength is taken into account by the activity term Π_f introduced by Eigen. Steric factors σ were used by Weller in comparing experimental with calculated rates of diffusion controlled reactions between organic ions with a small reactive site in aqueous solution. The calculated values are $\sigma = 1/2$ for several organic acids and $\sigma = 1/3$ for acridine [15].

Factors of about the same magnitude should apply to our reactants, i.e. $\sigma_A \cdot \sigma_B \sim 1/6$. In the following it is shown that a larger factor is appropriate for ionic reactions in benzonitrile.

The diffusion coefficients D_i of the reactants in benzonitrile are not known. They are estimated with an empirically modified Stokes-Einstein relation appropriate for reactants of similar size to the solvent [16]

$$D_i = \frac{k \cdot T}{4 \cdot \eta \cdot r_i}.$$

If the radii of the reactants are taken as equal

$$k_S = \frac{4 \cdot R \cdot T}{\eta}. \qquad (13)$$

For 0.1 M solutions of *TBHP* at 25°C, $k_S = 8.0 \cdot 10^9$ M^{-1} s^{-1}. With reasonable parameters the Wilke and Chang procedure for estimating diffusion coefficients [17] leads to a range of values for k_S which includes the one given here. Using this value and r_{AB} between 1.0 and 0.4 nm we calculate $k_D^0 = (2.2-4.5) \cdot 10^{10}$ M^{-1} s^{-1}; with $r_{AB} = 0.43$ nm a value $k_D^0 = 4.2 \cdot 10^{10}$ M^{-1} s^{-1} is obtained.

The rate constants k_{b1}^{MNP} of the recombination of protonated acridine orange with the anion of *MNP* at different ionic strengths are about 40% of the values of k_D calculated for the same ionic strength using $r_{AB} = 0.43$ nm. The reaction is, therefore, clearly diffusion controlled and exhibits a steric factor $\sigma_A \sigma_B = 0.4$. This result is confirmed by the value of the activation energy $E_a = 12.8$ kJ mol^{-1}, which agrees very well with the activation energy of viscous flow in benzonitrile $E_v = 11.3$ kJ mol^{-1} [18]. Typically the rate constants of diffusion controlled recombination reactions of ions in organic solvents like benzene [19] and methanol [20] are about half the theoretical values of k_D.

The formation of the ions, with rate constant $k_{f1}^{MNP} = 1.1 \cdot 10^7$ M^{-1} s^{-1} may be formulated as a two step process

$$\underset{1}{AH + B} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{2}{A^- \,..\, HB^+} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{3}{A^- + HB^+} \qquad (14)$$

in which the ion pair **2** equilibrates very fast with the neutral reactants **1**. The apparent forward rate constant is then given by $k_{f1} = k_{23} \cdot k_{12}/k_{21}$ and the reverse rate constant by $k_{b1} = k_{32}$. The equilibrium constant $K_{12} = k_{12}/k_{21}$ for the formation of the ion pair is assumed to decrease with increasing temperature. The independence of k_{f1}^{MNP} on temperature is then the result of the compensation of the decrease of K_{12}^{MNP} against the increase of k_{23}^{MNP}.

Similar arguments hold for the reaction path leading to the homoconjugate anion. The values $k_{f2}^{NP} = 1.3 \cdot 10^{11}$ M^{-2} s^{-1} and $k_{f2}^{MNP} = (3-6) \cdot 10^{10}$ M^{-2} s^{-1} are larger than k_D in a bi-

molecular reaction. They may be accounted for by a two step process

$$\underset{\mathbf{1}}{AH + B} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\mathbf{2}}{A^- \ldots HB^+} \underset{k_{42}}{\overset{k_{24}[AH]}{\rightleftharpoons}} \underset{\mathbf{4}}{AHA^-} + HB^+ \qquad (15)$$

in which the intermediate reacts with a second molecule of the phenol. Thus $k_{f2} = k_{24} \cdot k_{12}/k_{21}$, and $k_{b2} = k_{42}$. The intermediate is described as the ion pair as in (14). The negative value of E_a for the forward reaction **1** → **4** in the *MNP*/acridine orange system implies that K_{12}^{MNP} decreases more strongly with increasing temperature than k_{24}^{MNP} increases.

Recently it has been suggested that a decrease of proton transfer rates with increasing temperature may be due to the decrease of diffusion induced proton tunneling rates [21]. In this model the proton transfer is assumed to occur either by a classical jump mechanism or by tunneling between equivalent energy levels of the reactants moving in an essentially uncorrelated manner. With typical microscopic and macroscopic parameters a tunneling rate $k_T \sim 10^{10}\ s^{-1}$ was calculated [21]. The tunneling rates decrease rapidly when the proton donor and acceptor become non-equivalent [22]. We cannot adopt this model to explain the temperature dependence of the forward rate constants k_{f1}^{MNP} and k_{f2}^{MNP}, since the larger one with a value of $5 \cdot 10^{10}\ M^{-2}\ s^{-1}$ at 25°C describes the rate of a formally termolecular process between non-equivalent partners. We are forced to the conclusion that there exists along the reaction path an intermediate complex with highly correlated motions of the heavy particles, which is described here as the ion pair. The proton transfer within the complex involves fast proton tunneling. A one step reaction between the base and a hydrogen bonded dimer of the phenol can also not account for pathway **1** → **4** for two reasons. In the measurements with *NP* and *MNP* the phenol concentrations were so small that phenol dimers could make only a negligible contribution to the observed rates. Nor can the constancy of k_{b2} for phenols of widely differing acidity be explained by this type of mechanism. The latter result will be discussed below.

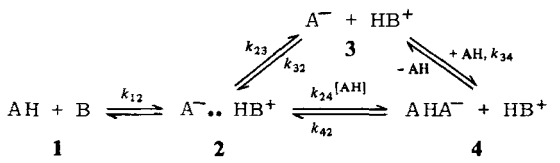
Although at least one intermediate must be present in pathway **1** → **4**, the detailed formulation of this pathway needs further consideration, as formation of an aggregate **4'** may occur prior to the rate determining dissociation:

$$\underset{\mathbf{1}}{AH + B} \rightleftharpoons \underset{\mathbf{2}}{A^- \ldots HB^+} \overset{+AH}{\rightleftharpoons} \underset{\mathbf{4'}}{AHA^- \ldots HB^+} \rightleftharpoons \underset{\mathbf{4}}{AHA^-} + HB^+ .$$

The potential energies of the activated states in reactions **1** → **3** and **1** → **4** with respect to the neutral reactants are given by (AH = *MNP*) $\Delta H_{13} + \Delta \tilde{H}_1^{\neq} \sim -4.1\ kJ\ mol^{-1}$ and $\Delta H_{14} + \Delta \tilde{H}_2^{\neq} \sim -12.7\ kJ\ mol^{-1}$ respectively. Thus the second molecule of phenol makes a stabilizing contribution of ca. 8.5 kJ mol^{-1} to the energy of the activated state in the latter pathway. On the other hand, the association step **4** → **4'** can hardly be ascribed an activation energy as high as the measured $E_a = 40\ kJ\ mol^{-1}$ since it involves only the formation of a hydrogen bond. Thus there can be no doubt that **4'** is not a kinetically important intermediate, and that the strong hydrogen bond of AHA^- is partly opened in the activated state. It must be pointed out that in spite of the negative $\Delta \tilde{H}^{\neq}$ the values of $\Delta \tilde{G}^{\neq}$ in both pathways **1** → **3** and **1** → **4** are positive. In contrast to the situation in more polar solvents, the activation in benzonitrile is controlled by a large negative activation entropy of ionic dissociation.

The rate constants k_{b2}^{CMP} and k_{b2}^{DMP} may contain contributions from both the direct reaction **4** → **2** and a pathway **4** → **3** → **2** with the free anion as a low concentration intermediate (Scheme I)

Scheme 1



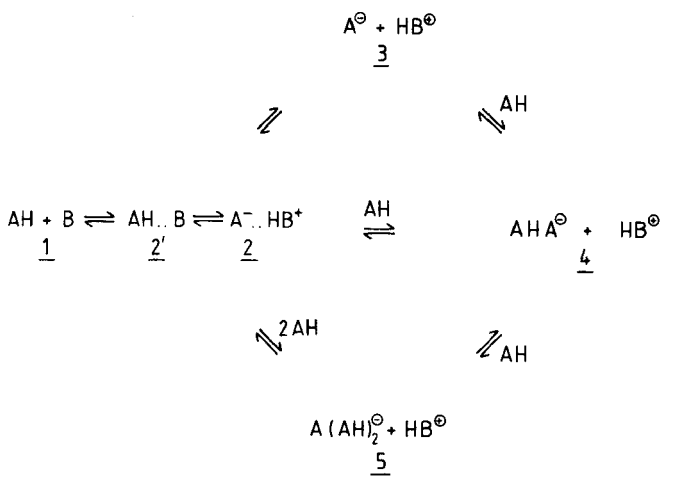
The relative contributions of the two pathways to the overall rate are given by k_{42} and $k_{32}/K_{34} \cdot c_{AH}$, respectively. Homoconjugation constants K_{34} depend little on the acidity of the phenol [8, 23, 24], and may be estimated to be of the order of $10^4\ M^{-1}$ for both *CMP* and *DMP*. Assuming this value and $k_{32} = k_D$ we calculate that the contribution of pathway **4** → **3** → **2** to the observed rates was less than 1% in most of our experiments, and in no case exceeded 10%. If the homoconjugated anion would not recombine directly with the protonated base, or if this reaction were slow compared with the pathway involving the free anion, then the rates of equilibration of the acid base system would be slowed down by a factor between 10 and more than 100 below the observed values. It is important to note that the rate constants k_{42} are very large, although in all cases the homoconjugated ions are thermodynamically much more stable than the free anions, and in the case of *MNP* a large activation energy was measured. In this case the reason is the large positive entropy of activation of **4** → **2** corresponding to the large positive reaction entropy of **4** → **1**.

The energetics of the non-diffusion controlled step **4** → **2** must be almost identical in all systems studied, for otherwise the observed identical values of k_{42} cannot be explained. We may assume that the forward reaction is diffusion controlled $k_{24} = k_D$. This leads to an estimate of $K_{24} \sim 30$ independent of the phenol. When $\Delta \tilde{H}_{24}^{\neq}$ is taken as identical with the activation enthalpy of viscous flow of benzonitrile as a consequence of the assumption $k_{24} = k_D$, we obtain estimates of the formation enthalpy and entropy of the ion pair from the neutral reactants $\Delta H_{12}^{MNP} \sim -20\ kJ\ mol^{-1}$ and $\Delta S_{12}^{MNP} \sim -50\ JK^{-1}\ mol^{-1}$. These are reasonable values, since they imply that in the reactions of *MNP* both the diffusion controlled formation of the homoconjugate anion from the ion pair **2** → **4** and the diffusion controlled recombination of the ions A^- and HB^+ to the ion pair **3** → **2** are exothermic and exergonic (whereas the overall reaction **3** → **1** is endothermic). Using $K_{24} = 30$ formation constants of the ion pairs $K_{12} = 500$, 16, 6, $3 \cdot 10^{-4}$, and $2 \cdot 10^{-5}\ M^{-1}$ are calculated for *CNP*, *NP*, *MNP*, *CMP*, and *DMP* respectively*). Accordingly the ion pair dissociation constant is

*) From these data we can estimate that under our experimental conditions never more than 0.5% of the protonated *AO* was present as the ion pair.

$K_{23} = \frac{C_{A^-} \cdot C_{HB^+}}{C_{A^-..HB^+}} = 1.3 \cdot 10^{-3}$ M. Because of the hydrogen bond interaction in the ion pair K_{23} is significantly smaller than the purely electrostatic value $2.8 \cdot 10^{-2}$ M calculated with the Fuoß-Eigen equation [10].

The full mechanism of proton transfer may be interpreted in the framework of an extended Eigen scheme including the different hydrogen bonded complexes (Scheme II).



The original Eigen mechanism, which is valid for proton transfer in protic solvents, consists of the elementary steps **1** ⇌ **2'** ⇌ **2** ⇌ **3**. In benzonitrile the formation of hydrogen bonded complexes by direct reaction of the intermediate ion pair with acids in **2** ⇌ **4** and **2** ⇌ **5** makes an important contribution to the overall rate. At phenol concentrations larger than 10^{-2} M only the latter steps are observed. Under these conditions the free anion is not even an intermediate in the acid base reaction.

According to Eigen only the proton transfer within the complex **2'** ⇌ **2** depends on the difference of the pK-values of acid and protonated base ΔpK. The same argument has been used by Marcus in the treatment of proton transfer reactions, in which the transfer step and not diffusion is rate limiting [25].

Marcus obtained a relation between the free energy of activation and the free energy of reaction in terms of the intrinsic energy barrier of height $\lambda/4$ which must be overcome in the proton transfer step **2** ⇌ **2'** on the one hand and the work W required to bring the reactants (or products) together to form the reaction complex on the other hand. The intrinsic barrier $\lambda/4$ is associated with the need for electron redistribution and alterations of bond length and bond angles during the course of the proton transfer. The work term W also includes the entropy of localization, the free energy of solvation, and the energies due to steric and statistical factors which are required in order to form the reaction complex. When the dependence of proton transfer rates on the structure of the reactants is interpreted along these lines, the assumption is generally made that only λ depends on ΔpK, the work term W being treated as a constant [26, 27].

Our results provide for the first time direct experimental evidence related to these assumptions, and they also indicate possible limitations. As is shown in the previous sections the stability constant of the ion pair K_{12} parallels almost exactly the acidity of the phenol, whereas the rates and the equilibrium constants of the dissociation of the ion pair to the free ions **2** ⇌ **3** and of the formation of the hydrogen bonded anion **2** ⇌ **4** are constant. This allows one to attribute the dependence of the overall forward rate constants k_{f1} and k_{f2} and of K_{13} and K_{14} to the change of K_{12} with the acidity of the phenol. This was predicted by Eigen, and is in agreement with Marcus treatment since the barrier height $\lambda/4$ depends on ΔG^0, the difference in free energies of the proton in **2'** and **2**. It must be noted, however, that the reaction **2** → **4** includes the solvation of the anion by a phenol molecule, whose proton donating ability decreases to the same extent as the basicity of the anion increases in a series of related substances. If, instead, a proton donor with constant properties would solvate the anions, no constancy of either k_{24} or K_{24} within the series could be expected.

Also, the second step of anion solvation shows a significantly different structure reactivity relationship. In **2** ⇌ **5** the loose hydrogen bonded complexes $A(AH)_2^-$ ($\Delta H_{45} \sim 0$ kJ mol^{-1}) react with the protonated acridine orange HB^+ at almost a diffusion controlled rate. The observed rate constants k_{b3} may be interpreted as k_{52} in analogy to the other ion recombinations. Since k_{52} does not depend on the acidity of the phenol, whereas K_{45} does, the forward rate constants k_{25} are different for different phenols in contrast to the assumed constancy of k_{24}. Certainly, an additional hydrogen bonded intermediate is involved in **2** ⇌ **5**; the detailed formulation of this pathway does not change the argument, however. Since the separate elementary steps of anion solvation by hydrogen bonding depend in a different way on the properties of the proton donor constancy of solvation terms in the energetics of proton transfer in a protic solvent may occur only by fortuitous cancellation of different effects.

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Absorption and Fluorescence Spectra, pK_a Values, and Fluorescence Lifetimes of Monohydroxyflavones and Monomethoxyflavones

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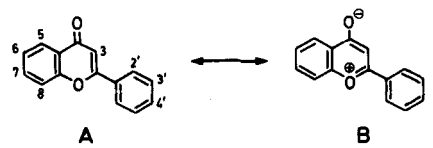
The absorption and fluorescence spectra of all isomeric hydroxyflavones and methoxyflavones, except for the photolabile 3-methoxyflavone, have been measured in organic solvents and in aqueous solutions of various acidity. With the exception of 5-hydroxyflavone, all are found to be fluorescent in methanol and water solution. On the other hand, there is virtually no fluorescence observed in cyclohexane solution, a fact that is interpreted in terms of high intersystem crossing rates and the El-Sayed selection rules. – Except for the 3-hydroxy and 7-hydroxy isomers, the anions of hydroxyflavones are non-fluorescent, whereas the protonated forms exhibit strong fluorescence emission. Methoxyflavones have higher fluorescence quantum yields than the corresponding hydroxyflavones and have fluorescence decay times ranging from 1.3 to 6.9 ns in methanol at room temperature. – The ground state pK_a values of the hydroxyflavones range from 7.8 to 9.8, except for the 5-hydroxy isomer (11.6). The pK_a's governing the protonation step range from -1.22 to -1.55, again with the exception of the 5-hydroxy isomer (-3.1). The dissociation constants of the first excited singlet state were calculated with the help of the Förster-Weller equation. The results predict a reversal of the most basic and most acidic sites of the hydroxyflavones. In aqueous solutions, this should result in the formation of excited state tautomers which, however, could be detected only for the 3-hydroxy and 7-hydroxy isomers. Apparently, the lifetimes of the other isomers are too short to allow the establishment of excited state equilibria.

Introduction

The flavones form one of the largest group of organic natural products [1–3]. Their occurrence is practically confined to the plant kingdom, being partially responsible for deep yellow colors of certain flowers. Among their biological activities [1, 2], flavones have been shown to act against blood cell adhesion and aggregation.



Scheme 1
Chemical structure of the flavone chromophore (A) and its dipolar resonance structure B

The structure and numbering of flavone is shown in Scheme 1. By analogy to the behavior of pyrones, flavone (A) can be formulated as a zwitterion (B), which contributes significantly to the flavone structure and can explain the relative basicity of the carbonyl groups.

Most natural flavones bear either hydroxy or methoxy groups or are linked to a sugar residue ("glycones"). Due to their importance, the absorption spectra have been studied in great detail [3, 5], since absorptiometry is one of the most suitable methods for the structure elucidation and identification of flavonoids [3, 5]. Interestingly, most of the data are confined to methanol as a solvent. The published spectra [6, 7] for the 6- and 8-hydroxy isomers do not agree with ours.

Except for our previous work on the pH-dependent fluorescence of flavonol [8], 7-hydroxyflavone [9] and 4'-hydroxy-