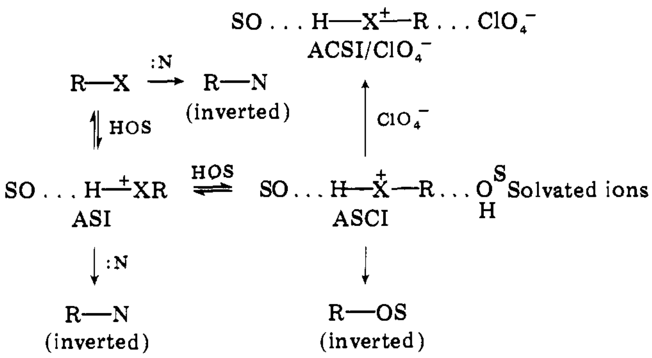
cation-stabilizing solvent molecule by the anion of the special salt (i.e., ClO_4^-) from the same side. This is plausible, since (a) the energy is not very sensitive to displacement (particularly lateral) of the cation stabilizing H_2O in H_2O + protonated isopropyl alcohol reaction, and (b) the very existence of a special salt effect implies that the interaction of ClO_4^- with the ACSI must be extremely stabilizing. Formation of this new ClO_4^-/ACSI should ultimately lead to loss of the leaving group followed by formation of product either with retained configuration (the nucleophile immediately takes the place of the leaving group) or racemization due to the formation of symmetrically solvated carbocations. The above description is summarized in Scheme I. This scheme has certain similarities and differences with those recently proposed by Sneen,[2] Bordwell,[5] and Schleyer.[13] In particular, only substitution with inversion is possible from the ACSI. Sneen[2] similarly suggested that the solvent-separated ion pair could collapse to product, but his scheme requires a product with retention of configuration. We have also included the direct S_N2 substitution, which may be particularly important in primary and methyl solvolyses. The structure of the ACSI bears a strong resemblance to the "solvated ion sandwich" proposed by Bordwell.[5] Schleyer[14] proposes that the solvent-separated ion pair can only give retained R-OS, but either inverted or racemized R-N. One should note that R-N could be formed with inversion using the scheme proposed in this paper if N^- acts as a special salt and forms an ACSI/N^- analogous to the ACSI/ClO_4^- of Scheme I.

Scheme I



N = any nucleophile (including HOS)

This scheme has the particular advantage of putting the nucleophilic "solvent assistance" proposed by Schleyer[14] into a general context. In addition it accommodates the suggestion that the low nucleophilicity of trifluoroacetic acid and the high degree of internal return in this solvent might be due to non-nucleophilic cation stabilization by the CF_3 group.[15]

Acknowledgment. The author gratefully acknowledges the hospitality of l'Universite Pierre et Marie Curie (Paris VI), the Centre de Mécanique Ondulatoire Appliquée, and particularly that of Professor R. Daudel. Also, many fruitful conversations with Dr. E. Evleth, Dr. O. Chalvet, and Professor F. Metras. He is also especially indebted to Drs. M. Chaillet, A. Dargelos, and D. Liotard for providing a copy of their geometrical optimization program.

References and Notes

(1) Professeur Associe a l'Universite Pierre et Marie Curie (Paris VI) 1974–1975; permanent address: Department of Chemistry, Hunter College of the City University of New York, 695 Park Avenue, New York, N.Y., 10021.
(2) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973), and references cited therein.
(3) For a comprehensive review, see D. J. Raber, J. M. Harris, and P. v. R. Schleyer, "Ions and Ion Pairs in Organic Reactions", M. Szwarc, Ed., Wiley, New York, N.Y., 1974, p 247.
(4) S. Winstein and G. C. Robinson, *J. Am. Chem. Soc.*, **80**, 169 (1958).
(5) F. G. Bordwell, P. F. Wiley, and T. G. Mecca, *J. Am. Chem. Soc.*, **97**, 132 (1975).
(6) P. Cremaschi, A. Gamba, and M. Simonetta, *Theor. Chim. Acta*, **25**, 237 (1972).
(7) A. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, **94**, 6730 (1972).
(8) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
(9) J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).
(10) J. J. Dannenberg and T. D. Berke, *Theor. Chim. Acta*, **24**, 99 (1972).
(11) M. Chaillet, A. Dargelas, and D. Liotard, to be published.
(12) J. P. Daudey, J. P. Malrieu, and O. Rojas, *Int. J. Quantum Chem.*, **8**, 17 (1974).
(13) Reference 3, p 363.
(14) F. L. Schadt and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 7860 (1973); P. v. R. Schleyer and C. J. Lancelot, *ibid.*, 91, 4297 (1969).
(15) J. J. Dannenberg, *Angew. Chem., Int. Ed Engl.*, **14**, 641 (1975).

Spiro Meisenheimer Complex from Catechol 2,4,6-Trinitrophenyl Ether. Rate-Limiting Proton Transfer as a Consequence of a Very Fast Intramolecular Nucleophilic Attack[1]

Claude F. Bernasconi* and Hsien-chang Wang

Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. *Received August 11, 1975*

Abstract: Temperature-jump experiments in 50% Me_2SO–50% water (v/v) show that the proton transfer is rate limiting in the formation of the spiro Meisenheimer complex (**9**) from catechol 2,4,6-trinitrophenyl ether. This is not because of an abnormally slow proton transfer but a consequence of a very fast rate of complex formation ($k_1 = 1.2 \times 10^9\ s^{-1}$). This rate is the highest measured to date for nucleophilic attack on an aromatic carbon.

The formation of spiro Meisenheimer complexes involves both intramolecular nucleophilic attack and proton transfer, as depicted in reaction 1. When Y = O, as in the prototype reaction 2, proton transfer is a rapid equilibrium step preceding the rate-limiting nucleophilic attack in all cases reported to date.[2-6] When Y = NR, however, as in the prototype reaction

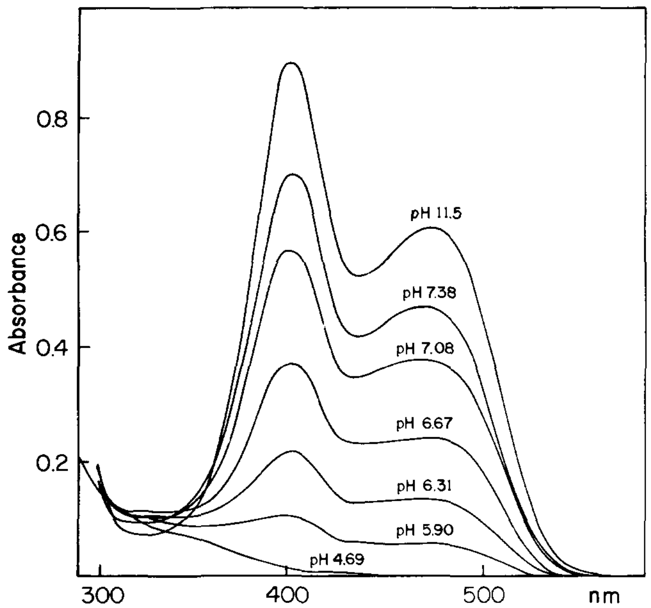
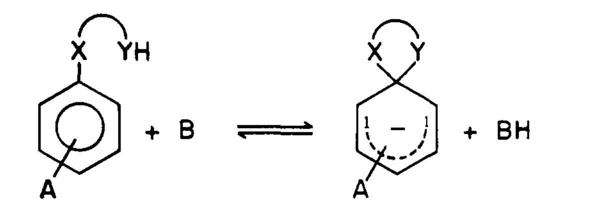
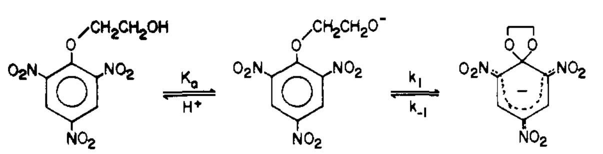


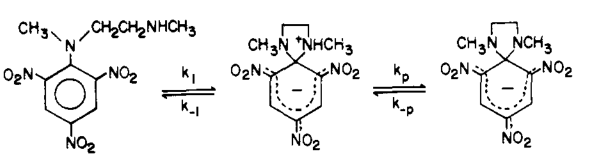
Figure 1. Spectra of **7** in equilibrium with **9** at various pH values in water. $[7]_o = 3.94 \times 10^{-5}$ M, ionic strength 0.5 M (NaCl), 25 °C.


(1)


(2)

1 2 3

3, proton transfer occurs after ring closure and is (partially) rate limiting;[1,7]


(3)

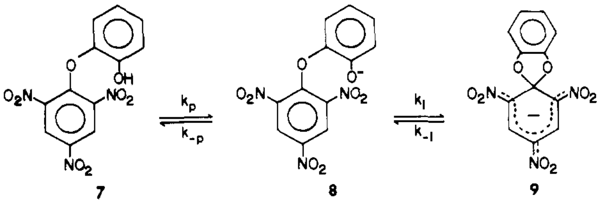
4 5 6

$$k_p = k_p^S + k_p^{OH}a_{OH^-} + k_p^B[B] \qquad (4a)$$

$$k_{-p} = k_{-p}^S a_{H^+} + k_{-p}^{OH} + k_{-p}^B[BH] \qquad (4b)$$

k_p^S, k_p^{OH}, and k_p^B refer to the deprotonation of **5** by the solvent, the hydroxide ion, and the buffer base, respectively, whereas k_{-p}^S, k_{-p}^{OH}, and k_{-p}^B refer to the protonation of **6** by the solvated proton, the solvent, and the buffer acid, respectively.

We now report data on reaction 5 in 50% Me_2SO–50% water


(5)

7 8 9

(v/v); note that k_p and k_{-p} are defined similarly as in eq 3, i.e., they are given by eq 4a and 4b, respectively. *System 5 is unique in that it is the first case of the general reaction 1 with Y = O, where proton transfer is rate limiting.*

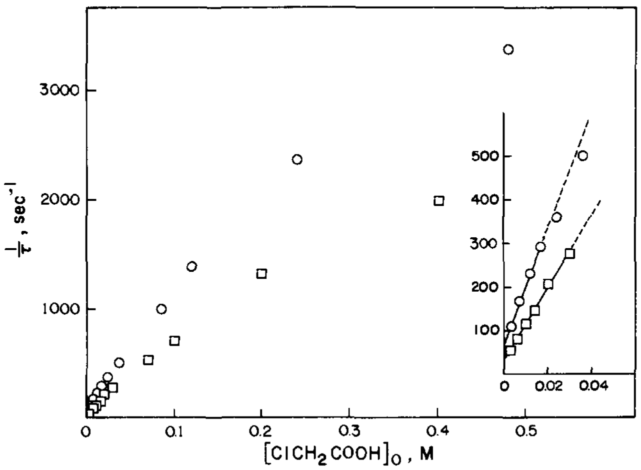


Figure 2. Representative plots of $1/\tau$ vs. total chloroacetate buffer concentration: ○ pH 4.06; □ pH 4.36.

Results

General Features. When catechol 2,4,6-trinitrophenyl ether (**7**) is dissolved in water, one observes partial formation of the spiro Meisenheimer complex **9** even in neutral solution, indicating a high apparent equilibrium constant K_aK_1, where K_a is the acid dissociation constant of **7** and $K_1 = k_1/k_{-1}$. This is borne out by the spectra taken as a function of pH, shown in Figure 1. A plot, at 470 nm, according to the equation

$$(OD_\infty - OD)/OD = a_{H^+}/K_aK_1 \qquad (6)$$

where OD is the optical density at a given pH and OD_∞ is the optical density in strongly basic solution where complex formation is quantitative, is linear, and affords $K_aK_1 = (1.39 \pm 0.02) \times 10^{-7}$ M at 25 °C and ionic strength of 0.5 M. By employing the same procedure in 50% Me_2SO–50% water (v/v) we obtain $K_aK_1 = (5.24 \pm 0.10) \times 10^{-6}$ M, at the same temperature and ionic strength.

Our initial plans called for a kinetic study in aqueous solution, but the rates were too high even for the temperature-jump relaxation method. When a reaction system is too rapid for the temperature-jump method, it is usually because of a very fast *unimolecular* step, the rate of which cannot be manipulated by a judicious choice of concentrations. In the case at hand, it is the k_{-1} step. However, by exploiting the well-known fact that the addition of Me_2SO decreases the dissociation rate (k_{-1}) of Meisenheimer complexes,[8] we were able to study the kinetics of system 5 in 50% Me_2SO–50% water (v/v).

Temperature-Jump Experiments. Solutions prepared by dissolving **7** in acetate, chloroacetate, or formate buffers were allowed to reach thermal equilibrium at 22.7 °C and subjected to temperature jumps of 2.3 °C, giving an end temperature of 25 °C. Chemical relaxation was monitored at 436 or 470 nm. A single relaxation time was observed and determined as a function of total buffer concentration at various pH values. The results are summarized in Table I. Figure 2 shows two representative plots of $1/\tau$ vs. total buffer concentration.

There are two noteworthy features about the kinetic data. (1) There is a very strong buffer dependence; e.g., at pH 5.74, $1/\tau$ increases 380-fold when the acetate buffer concentration is increased from 0.001 to 1.0 M. This is typical for proton-transfer reactions at pH values not too far from neutrality.[9] (2) All plots of $1/\tau$ vs. total buffer concentration are curved downwards, as shown in Figure 2. Such curvature usually indicates a mechanism where there is a change in the rate-limiting step. In our case the change is from rate-limiting proton

Table I. $1/\tau$ as Function of Buffer Concentration and pH in 50% Me_2SO–50% Water (v/v) at 25 °C, Ionic Strength 0.5 M (KCl)

pH	$10 \times [B]_o$,[a] M	$10^{-3}/\tau$, s^{-1}	pH	$10 \times [B]_o$,[a] M	$10^{-3}/\tau$, s^{-1}
		A. Acetate Buffer[b]			
5.43	0.036	0.174	5.74	0.20	1.07
5.43	0.072	0.321	5.74	0.40	2.06
5.43	0.120	0.530	5.74	2.00	7.87
5.43	0.168	0.729	5.74	6.00	18.5
5.43	0.240	1.02	5.74	10.0	26.2
5.43	0.360	1.60	6.04	0.036	0.224
5.43	0.840	2.99	6.04	0.072	0.482
5.43	1.20	4.73	6.04	0.120	0.715
5.43	2.40	7.45	6.04	0.240	1.55
5.43	4.80	11.8	6.04	0.360	2.17
5.74	0.010	0.069	6.04	0.840	4.95
5.74	0.020	0.139	6.04	1.20	7.50
5.74	0.040	0.221	6.04	2.40	11.6
5.74	0.10	0.532	6.04	4.80	24.2
		B. Formate Buffer[b]			
4.13	0.036	0.175	4.43	0.40	1.00
4.13	0.072	0.290	4.43	0.50	1.17
4.13	0.120	0.432	4.43	1.00	2.23
4.13	0.168	0.566	4.43	3.00	5.24
4.13	0.240	0.796	4.43	5.00	6.37
4.13	0.360	1.07	4.73	0.036	0.092
4.13	0.840	2.35	4.73	0.072	0.154
4.13	1.20	3.08	4.73	0.120	0.236
4.13	2.40	4.84	4.73	0.168	0.327
4.13	4.80	7.33	4.73	0.240	0.484
4.43	0.020	0.083	4.73	0.360	0.660
4.43	0.040	0.127	4.73	0.840	1.38
4.43	0.050	0.141	4.73	1.20	1.99
4.43	0.10	0.272	4.73	2.40	3.29
4.43	0.20	0.514	4.73	4.80	4.93
		C. Chloroacetate Buffer[b]			
4.06	0.036	0.108	4.36	0.030	0.055
4.06	0.072	0.167	4.36	0.060	0.081
4.06	0.120	0.231	4.36	0.100	0.115
4.06	0.168	0.293	4.36	0.140	0.144
4.06	0.240	0.359	4.36	0.200	0.208
4.06	0.360	0.502	4.36	0.300	0.276
4.06	0.840	1.00	4.36	0.700	0.537
4.06	1.20	1.38	4.36	1.00	0.712
4.06	2.40	2.36	4.36	2.00	1.26
4.06	4.80	3.37	4.36	4.00	1.99

[a] $[B]_o = [B] + [BH]$. [b] The pK_a's of the buffers are in Table V.

transfer (k_p, k_{-p}) to rate-limiting C–O bond formation/breaking (k_1, k_{-1}).

Data at High Buffer Concentration. The expression for the reciprocal relaxation time ($1/\tau$), derived under the assumption that **8** is a low concentration ("steady-state") intermediate, is given by

$$\frac{1}{\tau} = \frac{k_p k_1}{k_{-p} + k_1} + \frac{k_{-p} k_{-1}}{k_{-p} + k_1} \tag{7}$$

As shown in the Appendix, at relatively high buffer concentrations, eq 7 can be transformed into

$$\tau = \tau_{hi} + \tau_{hi} \frac{k_1}{k_{-p}{}^B [B]_o} \frac{K_a{}^B + a_{H^+}}{a_{H^+}} \tag{8}$$

where $K_a{}^B$ is the acid dissociation constant of the buffer acid, $[B]_o$ is the total buffer concentration, and τ_{hi} is the plateau value of τ which would be reached at very high buffer concentrations, i.e., when $k_{-p} \simeq k_{-p}{}^B[B] \gg k_1$; τ_{hi} is given by

$$\tau_{hi} = \left(\frac{K_a k_1}{a_{H^+}} + k_{-1}\right)^{-1} \tag{9}$$

All of our plots of τ vs. $[B]_o{}^{-1}$ were linear as required by eq 8; Figure 3 shows two representative examples. From the intercepts one obtains τ_{hi}, from the ratios of slope/intercept one obtains $k_1/k_{-p}{}^B$ according to the equation

$$\frac{\text{slope}}{\text{intercept}} = \frac{k_1}{k_{-p}{}^B} \frac{K_a{}^B + a_{H^+}}{a_{H^+}} \tag{10}$$

Table II summarizes the results of this analysis.

We can now estimate k_1 as follows. It is known that the rate constants for proton transfer between oxygen acids and bases reach the diffusion-controlled limit of $\simeq 10^{10}$ M^{-1} s^{-1} in the thermodynamically-favored direction when $\Delta pK = pK$(Acceptor) $- pK$(Donor) becomes large.[9a,10] As shown below, the pK_a of **7** is $\simeq 10.3$, while that of our strongest buffer acid, viz. chloroacetic acid, is 3.76 in the present medium. Hence for the reaction

$$\mathbf{8} + ClCH_2COOH \xrightarrow{k_{-p}{}^B} \mathbf{7} + ClCH_2COO^- \tag{11}$$

we have $\Delta pK = 10.3 - 3.76 = 6.54$, which is large enough to assure that the reaction is diffusion controlled. Thus, from

Table II. Analysis of Data According to Equations 8 and 10[a]

Buffer	pH	$10^5 \times \tau_{hi}$ = intercept, s	$10^5 \times$ slope, M s	k_1/k_{-p}^B, M
Acetate	6.04	1.4 ± 0.6	1.62 ± 0.03	0.39
Acetate	5.74	2.3 ± 0.2	1.84 ± 0.04	0.40
Acetate	5.43	3.5 ± 0.5	2.22 ± 0.05	0.42
Formate	4.73	8.0 ± 1.6	5.12 ± 0.08	0.21
Formate	4.43	8.2 ± 1.6	3.74 ± 0.04	0.23
Formate	4.13	8.5 ± 4.4	2.71 ± 0.06	0.21
Chloroacetate	4.36	20 ± 2	11.6 ± 0.2	0.12
Chloroacetate	4.06	17 ± 3	6.60 ± 0.14	0.13

[a] The pK_a^B values of the buffers are in Table V.

Table III. Analysis of Data According to Equations 12 and 14

Buffer	pH	Intercept, s^{-1}	$10^{-4} \times$ slope, $M^{-1} s^{-1}$	$10^{-9} \times k_{-p}^B$, $M^{-1} s^{-1}$
Acetate	6.04	[a]	6.26 ± 0.20	2.10
Acetate	5.74	19 ± 11	5.23 ± 0.07	3.10
Acetate	5.43	24.0 ± 4.2	4.18 ± 0.03	2.94
Formate	4.73	26.5 ± 3.2	1.79 ± 0.06	4.77
Formate	4.43	28.1 ± 5.7	2.43 ± 0.02	4.86
Formate	4.13	58.2 ± 6.4	3.02 ± 0.04	4.83
Chloroacetate	4.36	31.6 ± 1.9	0.90 ± 0.03	4.58
Chloroacetate	4.06	62.2 ± 5.1	1.40 ± 0.05	4.52

[a] Could not be determined due to too high experimental error.

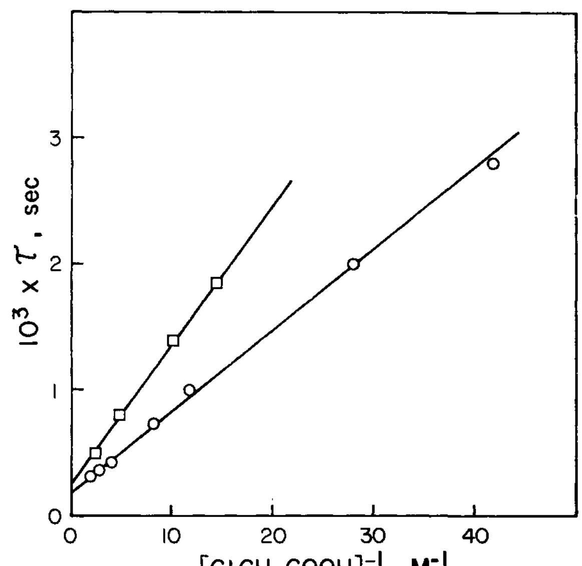


Figure 3. Representative plots of τ vs. $[B]_o^{-1}$ according to eq 8 for chloroacetate buffer: ○ pH 4.06; □ pH 4.36.

$k_1/k_{-p}^B = 0.12$ (Table II) and assuming k_{-p}^B (chloroacetate) $\simeq 10^{10}\ M^{-1}\ s^{-1}$, one calculates $k_1 \simeq 1.2 \times 10^9\ s^{-1}$.

From a plot (not shown) of $1/\tau_{hi}$ vs. $a_{H^+}^{-1}$ according to eq 9 we also obtain intercept = $k_{-1} = (1.0 \pm 0.3) \times 10^4\ s^{-1}$ and slope = $K_a k_1 = (5.5 \pm 1.0) \times 10^{-2}$ M s^{-1} We note that the ratio $K_a k_1/k_{-1} = 5.5 \times 10^{-2}/10^4 = 5.5 \times 10^{-6}$ is in excellent agreement with $K_a K_1 = 5.24 \times 10^{-6}$ determined spectrophotometrically.

Finally, combining $K_a k_1$ with k_1 calculated earlier affords $K_a \simeq 4.6 \times 10^{-11}$ M or $pK_a \simeq 10.34$ for **7**.

Data at Low Buffer Concentration. At low buffer concentration we have $k_1 \gg k_{-p}$, so that eq 7 simplifies to

$$1/\tau = k_p + (k_{-1}/k_1)k_{-p}$$
$$= k_p^S + k_p^{OH}a_{OH^-} + \frac{k_{-1}}{k_1}(k_{-p}^S a_{H^+} + k_{-p}^{OH})$$
$$+ \left(k_p^B \frac{K_a^B}{K_a^B + a_{H^+}} + \frac{k_{-1}}{k_1} k_{-p}^B \frac{a_{H^+}}{K_a^B + a_{H^+}}\right)[B]_o \quad (12)$$

Initial slopes and intercepts of plots of $1/\tau$ vs. $[B]_o$ (eq 12) are summarized in Table III. They can be exploited as follows. At pH ≤ 5 the k_p^{OH}, k_{-p}^{OH} pathway becomes negligible compared to the k_p^S, k_{-p}^S pathway. Hence the intercept of the plot according to eq 12 is

$$\text{intercept} = k_p^S + (k_{-1}/k_1)k_{-p}^S a_{H^+}$$
$$= k_p^S + (k_p^S/K_a K_1)a_{H^+} \quad (13)$$

A plot according to eq 13 (not shown) is linear. The intercept of this new plot affords $k_p^S = 5 \pm 2\ s^{-1}$, i.e., a value with a rather high uncertainty; however the slope is more accurate and, in conjunction with the known $K_a K_1$, affords $k_p^S = 3.9 \pm 0.5\ s^{-1}$. From this we also obtain $k_{-p}^S = k_p^S/K_a = 8 \times 10^{10}\ M^{-1}\ s^{-1}$.

Now we turn to the slopes of the plots according to eq 12. Taking into account that $k_p^B = k_{-p}^B K_a/K_a^B$ the slopes can be written as

$$\text{slope} = \left(\frac{K_a}{K_a^B + a_{H^+}} + \frac{k_{-1}}{k_1}\frac{a_{H^+}}{K_a^B + a_{H^+}}\right) k_{-p}^B \quad (14)$$

with k_{-p}^B being the only remaining unknown. The k_{-p}^B values calculated on the basis of eq 14 are also summarized in Table III.

Discussion

All rate and equilibrium constants of system 5 are summarized in Tables IV and V.

Reliability of Analysis. In view of several potential sources of error in our data analysis, it is important to get some idea of the reliability of the calculated parameters. One such source is that the intercepts of the inversion plots according to eq 8 (Figure 3) are relatively small and thus have a relatively high uncertainty. A second is that in changing from a medium of low buffer concentration to one of high concentration a differential salt effect may somewhat distort our data even though the ionic strength was kept constant. The third is the assumption of $k_{-p}^B = 10^{10}\ M^{-1}\ s^{-1}$ when B = chloroacetate.

Table IV. Equilibrium and Rate Constants for Reaction 5 in 50% Me_2SO–50% Water (v/v) at 25 °C

Constant	Comments
$K_aK_1 = (5.24 \pm 0.10) \times 10^{-6}$ M	Spectrophotometric (eq 6)
$K_aK_1 = (5.5 \pm 2.0) \times 10^{-6}$ M	Kinetic (eq 9)
$K_a \simeq 4.6 \times 10^{-11}$ M ($pK_a \simeq 10.34$)	From K_ak_1 and k_1
$K_ak_1 = (5.5 \pm 1.0) \times 10^{-2}$ M s^{-1}	From eq 9
$k_1 \simeq 1.2 \times 10^9$ s^{-1}	From $k_1/k_{-p}{}^B$ (B = chloroacetate, $k_{-p}{}^B \simeq 10^{10}$ M^{-1} s^{-1})
$k_{-1} = (1.0 \pm 0.3) \times 10^4$ s^{-1}	From eq 9
$K_1 \simeq 1.2 \times 10^5$	From $K_1 = k_1/k_{-1}$
$k_p{}^S = 3.9 \pm 0.5$ s^{-1}	From eq 13
$k_{-p}{}^S$ 8×10^{10} M^{-1} s^{-1}	From $k_{-p}{}^S = k_p{}^S/K_a$
$k_p{}^{OH} \simeq 10^{10}$ M^{-1} s^{-1}	Estimated (ref 9a)
$k_{-p}{}^{OH} \simeq 1.7 \times 10^5$ s^{-1}	From $k_{-p}{}^{OH} = k_p{}^{OH}K_s/K_a$ ($K_s = a_{H^+}a_{OH^-} \simeq 8 \times 10^{-16}$, ref 22)

Table V. Rate Constants for Reaction **7** + B $\rightleftarrows$ **8** + BH in 50% Me_2SO–50% Water (v/v) at 25 °C

B	$pK_a{}^B$ [a]	ΔpK [b]	$10^{-4} \times k_p{}^B$, [c] M^{-1} s^{-1}	$10^{-9} \times k_{-p}{}^B$, M^{-1} s^{-1}
Acetate	5.74	4.60	6.8[d]	2.71[d](3.0)[e]
Formate	4.43	5.91	0.59[d]	4.82[d](5.45)[e]
Chloroacetate	3.76	6.58	0.12[d]	4.55[d](10.0)[f]

[a] Determined potentiometrically. [b] $\Delta pK = pK_a - pK_a{}^B$. [c] $k_p{}^B = K_ak_{-p}{}^B/K_a{}^B$. [d] $k_{-p}{}^B$ from eq 14, average of two or three values from Table III. [e] $k_{-p}{}^B$ from $k_1/k_{-p}{}^B$ and $k_1 = 1.2 \times 10^9$ s^{-1}. [f] Estimated, ref 9a and 10.

It is rewarding that our data offer some ways to check for internal consistency and thus to exclude the possibility of gross errors. We first note the close agreement between K_aK_1 determined kinetically at *high* buffer concentration, with K_aK_1 determined spectrophotometrically at *low* buffer concentration. Second, there is satisfactory to good agreement between $k_{-p}{}^B$ calculated from eq 14 (data at *low* buffer concentration) and $k_{-p}{}^B$ calculated from $k_1/k_{-p}{}^B$ ratios (data at high buffer concentration). Thus we estimate that the parameters summarized in Tables IV and V are reliable within a factor of two or better.[11]

Comparison with Literature Data. Our pK_a of **7** is about one unit more acidic than that of phenol in the same solvent,[12] a result which is in agreement with the expected acidifying effect of the picryl group.

On the other hand, Drozd et al.[13] report a spectrophotometrically determined $pK_a = 5.83$ ($K_a = 1.48 \times 10^{-6}$) for **7** in 50% ethanol–50% water. This value is totally unreasonable. It appears that what these authors assume to be K_a is in fact K_aK_1; with this interpretation their value of 1.48×10^{-6} comes rather close to our $K_aK_1 = 5.24 \times 10^{-6}$. That K_aK_1 is somewhat higher in 50% Me_2SO–50% water compared to 50% ethanol–50% water is expected.

Rate-Limiting Proton Transfer. It is instructive to analyze the reasons why proton transfer is rate limiting in reaction 5, but not in any other case of the general reaction 1 with Y = O reported to date. Let us compare our data with those of reaction 2. For this latter, $K_ak_1 = 1.6 \times 10^{-8}$ M s^{-1} [5,14] and $k_{-1} = 0.095$ s^{-1} [5] in water at 25 °C. Although K_a is not known, a reasonable estimate is $K_a \simeq 3 \times 10^{-15}$ M;[15] this then leads to an estimated $k_1 \simeq 5 \times 10^6$ s^{-1}.

If one defines k_p and k_{-p} for reaction 2 the same way as for reaction 5, the requirement for rate-limiting proton transfer is that $k_1 > k_{-p}$. In reaction 2 there are no experimental conditions where such a relation between k_1 and k_{-p} is possible. This is mainly because of the low $K_a \simeq 3 \times 10^{-15}$, which implies that the protonation of **2** even by the weakest acid in the system, viz. the solvent, is very fast, with $k_{-p}{}^{OH} \simeq 10^9$ s^{-1}.[9a] Thus k_{-p} can never be lower than $\simeq 10^9$ s^{-1}. Since furthermore $k_1 \simeq 5 \times 10^6$ s^{-1} is appreciably smaller than k_1 in system 5, we have $k_1 \ll k_{-p}$ by a wide margin under all experimental conditions.

Similar arguments apply to all other reported systems of the type of eq 1 with Y = O. On the other hand, in reaction 5 $k_{-p}{}^{OH} = 1.7 \times 10^5$ s^{-1} is relatively small, as a consequence of the relatively high acidity (K_a) of **7**. In fact the value of $k_{-p}{}^{OH}$ is so low that under typical reaction conditions of this study the protonation of **8** occurs mainly through the $k_{-p}{}^S$ and $k_{-p}{}^B$ steps. Even though these latter are diffusion controlled or nearly so, proton transfer is rate limiting under typical conditions because k_1 is very high (1.2×10^9 s^{-1}) and the $k_{-p}{}^S$ and $k_{-p}{}^B$ steps are bimolecular reactions and thus become very fast only at high a_{H^+} or high buffer acid concentrations.[16]

Reactivity of 8. Even though spiro Meisenheimer complexes are known to form several orders of magnitude faster than comparable *inter*molecular complexes,[2-6] presumably on entropy grounds, the value of $k_1 = 1.2 \times 10^9$ s^{-1} in reaction 5 is remarkably high; it is the highest rate of a nucleophilic attack on an aromatic carbon measured to date. Though the phenolate oxygen in **8** is much less basic than the glycolate oxygen in **2**, **8** cyclizes (in 50% Me_2SO–50% water) about 200 times faster than **2** (in water). The rate enhancing effect of Me_2SO undoubtedly accounts for a considerable portion of this difference;[17] the greater conformational rigidity of **8** compared to **2** may be an additional factor which enhances k_1 for **8** (entropy effect).

In the absence of the two mentioned factors the k_1 values in the two systems would probably be of comparable magnitude. This is consistent with phenoxide ion in water attacking picryl chloride[18] about sevenfold faster than methoxide ion in methanol,[19] or the very similar rates of the attack of picryl fluoride by the phenoxide and methoxide ions in water.[20]

The k_{-1} values on the other hand greatly reflect the difference in basicity of the two oxygens ($k_{-1} = 10^4$ s^{-1} for **9**, $k_{-1} = 0.095$ s^{-1} for **3**).

Experimental Section

Materials. Catechol 2,4,6-trinitrophenyl ether (**7**) was prepared by the procedure of Drozd et al.,[21] mp 128 °C (lit.[21] 128.5 °C). Me_2SO, KCl, and the buffers were commercial products and used without further purification except for chloroacetic acid, which was recrystallized from hexane.

Spectra and Kinetics. Spectra were taken on a Cary 14 spectrophotometer which was thermostated at 25 ± 0.2 °C; pH measurements were carried out on a Corning 110 digital pH meter; in 50% Me_2SO–50% water the pH meter was calibrated at 20 °C with acetate and chloroacetate buffers, using the tables of Hallé et al.[12]

The temperature-jump experiments were carried out on a Messanlagen (Göttingen) transient spectrophotometer. Each reported relaxation time represents the average of at least four oscilloscope pictures.

Acknowledgment. We thank the National Science Foundation for financial support.

Appendix: Derivation of Equation 8

Except at the very lowest buffer concentrations the $k_p{}^B[B]$ and $k_{-p}{}^B[BH]$ terms in eq 4a and 4b, respectively, are dominant. This permits eq 7 to be written as

$$\frac{1}{\tau} = \frac{k_1 k_p{}^B[B]}{k_{-p}{}^B[BH] + k_1} + \frac{k_{-1} k_{-p}{}^B[BH]}{k_{-p}{}^B[BH] + k_1} \qquad (15)$$

Inverting and rearranging leads to

$$\tau = \frac{k_{-p}{}^B[BH] + k_1}{k_1 k_p{}^B[B] + k_{-1} k_{-p}{}^B[BH]} \qquad (16)$$

Dividing both the numerator and the denominator of eq 16 by $k_{-p}{}^B[BH]$ affords

$$\tau = \frac{1 + k_1/k_{-p}{}^B[BH]}{k_1 k_p{}^B[B]/k_{-p}{}^B[BH] + k_{-1}} \qquad (17)$$

Since the relation

$$k_p{}^B[B]/k_{-p}{}^B[BH] = K_a/a_{H^+} \qquad (18)$$

holds, eq 17 becomes

$$\tau_{hi} + \tau_{hi}(k_1/k_{-p}{}^B[BH]) \qquad (19)$$

with τ_{hi} given by eq 9. Substituting $[B]_0 a_{H^+}/(K_a{}^B + a_{H^+})$ for [BH] then affords eq 8.

References and Notes

(1) This is part 15 in the series "Intermediates in Nucleophilic Aromatic Substitution". Part 14: C. F. Bernasconi and F. Terrier, *J. Am. Chem. Soc.*, **97**, 7458 (1975).

(2) M. R. Crampton, *J. Chem. Soc., Perkin Trans. 2*, 2157 (1973).

(3) C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, **38**, 500 (1973).

(4) C. F. Bernasconi and H. S. Cross, *J. Org. Chem.*, **39**, 1054 (1974).

(5) M. R. Crampton and M. J. Willison, *J. Chem. Soc., Perkin Trans. 2*, 1681, 1686 (1974).

(6) M. R. Crampton and M. J. Willison, *J. Chem. Soc., Perkin Trans. 2*, 155 (1976).

(7) C. F. Bernasconi and C. L. Gehriger, *J. Am. Chem. Soc.*, **96**, 1092 (1974).

(8) For recent reviews, see (a) M. R. Crampton, *Adv. Phys. Org. Chem.*, **7**, 211 (1969); (b) M. J. Strauss, *Chem. Rev.*, **70**, 667 (1970).

(9) (a) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964); (b) C. F. Bernasconi, "Relaxation Kinetics", Academic Press, New York, N.Y., 1976, Chapter 4.

(10) M.-L. Ahrens and G. Maass, *Angew. Chem., Int. Ed. Engl.*, **7**, 818 (1968).

(11) The error limits given in Table IV are standard deviations and thus do not take into account the potential source of error from a salt effect and a possibly somewhat erroneous value of $k_{-p}{}^B$ (B = chloroacetate).

(12) J.-C. Hallé, R. Gaboriaud, and R. Schaal, *Bull. Soc. Chim. Fr.*, 2047 (1970). Note that the comparison is somewhat crude because the temperature and ionic strength are not identical in the two systems.

(13) V. N. Knyazev, A. A. Klimov, N. G. Yaryshev, and V. N. Drozd, *Zh. Org. Khim.*, **10**, 2587 (1974).

(14) $K_a k_1$ calculated by multiplying Crampton and Willison's[5] $K_{OH}k_1$ (K_{OH} = [**8**]/[**7**]a_{OH^-}) with 10^{-14}

(15) P. Ballinger and F. A. Long, *J. Am. Chem. Soc.*, **82**, 795 (1960).

(16) It is interesting to note that the situation in reaction 3 is somewhat intermediate between that of reactions 2 and 5. Deprotonation of **5** occurs mainly by the $k_p{}^{OH}$ and $k_p{}^B$ steps because $k_p{}^S$ is small (like $k_{-p}{}^{OH}$ in system 5). However $k_{-1} \approx 2 \times 10^5\ s^{-1}$ is only moderately high (like k_1 in system 2); as a consequence proton transfer is rate limiting ($k_{-1} > k_p$) at low pH and low [B], but becomes very fast ($k_{-1} \ll k_p$) at high pH and/or high [B].

(17) For the system 1-(β-hydroxyethoxy)-2,4-dinitrobenzene, $K_{OH}k_1$ (K_{OH} defined analogously as in ref 14) is 67-fold larger in 50% Me_2SO–50% water compared to water,[4] presumably mainly due to an increase in k_1.

(18) J. J. Ryan and A. A. Humffray, *J. Chem. Soc. B*, 1300 (1967).

(19) L. H. Gan and A. R. Norris, *Can. J. Chem.*, **52**, 18 (1974).

(20) J. Murto, *Acta Chem. Scand.*, **20**, 303 (1966).

(21) V. N. Drozd, V. N. Knyazev, and A. A. Klimov, *Zh. Org. Khim.*, **10**, 826 (1974).

(22) J.-C. Hallé, R. Gaboriaud, and R. Schaal, *Bull. Soc. Chim. Fr.*, 1851 (1969). Note that the value of K_s given is only approximate, since our conditions of temperature and ionic strength are different.

Triphase Catalysis. Kinetics of Cyanide Displacement on 1-Bromooctane[1]

Steven L. Regen

Contribution from the Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233. *Received February 4, 1976*

Abstract: The kinetics of the triphase-catalyzed displacement of cyanide ion (aqueous phase) on 1-bromooctane (organic phase) employing cross-linked polystyrene resins (solid phase) bearing a variety of quaternary ammonium groups has been investigated. The rate of the displacement exhibited a first-order dependency on the 1-bromooctane concentration and was linearly dependent on the amount of catalyst used. Comparison of the catalytic activity for resins having 1, 10, and 21% ring substitution indicates that within this range of ring substitution, resin activity is directly related to the number of quaternary ammonium groups present. Examination of the activity displayed by various other polystyrene ion-exchange resins further revealed that, at the 8–10% ring substitution level, the structure of the quaternary ammonium group bound to the polymer backbone has little influence in determining the catalyst's activity. Polystyrene in the "popcorn" form yielded a resin catalyst which exhibited activity similar to that produced from the microporous form; macroporous polystyrene afforded a significantly less active catalyst. Increasing the level of ring substitution in microporous polystyrene with $CH_2N(CH_3)_3Cl$ groups to 46, 70, and 76% resulted in a sharp drop in catalyst activity accompanied by a significant change in swelling properties of the resin.

A new type of heterogeneous catalysis termed "triphase catalysis" has recently been introduced.[2] The underlying feature which distinguishes this from other forms of heterogeneous catalysis is that both the catalyst and each one of a pair of reactants are located in separate phases. This principle has been successfully applied to certain *aqueous phase–organic phase* reactions employing a *solid phase* catalyst.

In the present work we have examined in detail the kinetics of one such triphase-catalyzed process. The system chosen was the displacement of cyanide ion (aqueous phase) on 1-bromooctane (organic phase) catalyzed by one of several different types of polystyrene ion-exchange resins (solid phase); an illustration of the three-phase system is presented in Scheme I. This investigation was carried out for the dual purpose of (1)