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Quaternization Kinetics. IV. Pyridine and 4-Picoline in Ethylene Carbonate and 4-Picoline in Mixtures of Propylene Carbonate and Diphenyl Ether[1a]

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Rates of quaternization by *n*-butyl bromide at 50, 75 and 100° have been measured for the following systems: pyridine and 4-picoline in ethylene carbonate and 4-picoline in mixtures of diphenyl ether and propylene carbonate. The latter cover the range 3.6–65 in dielectric constant. The kinetics are quantitatively second order in all cases except diphenyl ether; here, second order obtains during the first 10% of reaction. Beyond this point, salt separates and the rate decreases. The dependence of rate on dielectric constant in the mixtures shows the presence of a partially ionized transition state, but comparisons of rates among various solvents of high dielectric constant show that specific short range forces are involved, in addition to the electrostatic forces.

Introduction

The quaternization of pyridine bases has been studied in several solvents of high dielectric constant[2-4]; second-order kinetics were followed quantitatively to substantial completion of the reaction. No unambiguous correlation could be found, however, between rate and dielectric constants: The rate in tetramethylene sulfone ($D = 42$), for example, is nearly twice that in propylene carbonate ($D = 65$). This case represents a reversal of the generalization that increase in dielectric constant of solvent favors quaternization. Clearly, specific short range forces which depend on molecular structure in a detailed way superpose their effects on those of long range electrostatic forces. These observations also strongly support the suggestion that the activated transition state is a solvated complex, which presumably is the precursor of the solvated ions which constitute the products of the reaction. The purpose of this paper is to present data on the rate of quaternization in ethylene carbonate ($D = 73$) and in mixtures of diphenyl ether and propylene carbonate. The latter cover the range $3.6 \leqslant D \leqslant 65$. Intercomparison among the four solvents tetramethylene sulfone,[2] dimethylsulfolane,[4] ethylene carbonate and propylene carbonate[3] give further examples of the specificity of solvation effects. In the mixtures, the electrostatic term in the rate equation controls up to about 50% propylene carbonate; beyond this point, the rate increases more rapidly than predicted by theory.

Experimental

Materials.—Middle fractions of pyridine, 4-picoline and *n*-butyl bromide were used. Propylene carbonate and ethylene carbonate (Jefferson Chemical Company) were distilled under reduced pressure: boiling points, 120° at 18 mm. and 126° at 17 mm., respectively. Diphenyl ether (Dow Chemical Company) was washed with 3 *M* sodium hydroxide and water, dried with calcium chloride and fractionally recrystallized; m.p. 27.00°.

Densities were determined in a 20-ml. pycnometer. Within about 0.1%, the following formulas summarize the densities of mixtures of propylene carbonate and diphenyl ether; w is weight per cent. of propylene carbonate in the mixture

$$\rho\ (50°) = 1.0483 + 0.001225w$$
$$\rho\ (75°) = 1.0266 + 0.001178w$$
$$\rho\ (100°) = 1.0076 + 0.001134w$$

The density of ethylene carbonate is given by

$$\rho\ (t°) = 1.3084 - 0.00111(t° - 50°)$$

Dielectric constants were measured at 200 kc. in a guarded cell.[5] The results are given in Table I. Ethylene carbonate melts at 36°, so measurements on the mixtures containing it were made at 50°; those for propylene carbonate were made at 25°. The capacity of our cell when filled with ethylene carbonate was beyond the range of the bridge capacitor; the value of 73 in Table I is estimated by empirical extrapolation of the D-w curve. Over most of the range for the propylene carbonate–diphenyl ether mixtures, the polarization

$$P_{12} = \frac{(D-1)(2D+1)}{9D}\,\frac{x_1M_1 + x_2M_2}{\rho_{12}}$$

is linearly additive on a volume basis, as shown in Fig. 1, where P_{12} is plotted against the volume fraction of propylene carbonate.

TABLE I

DIELECTRIC CONSTANTS OF MIXTURES WITH DIPHENYL ETHER

	Ethylene carbonate (50°)				
w	24.7	50.0	72.4	100	
D	11.75	32.6	50.8	(73)	
	Propylene carbonate (25°)				
w	0.00	1.08	3.50	10.1	20.0
D	3.60	4.13	4.99	7.51	11.90
w	30.4	40.2	53.0	77.2	100.0
D	17.16	22.8	30.6	47.8	65.1

Methods for determining the rate constants have been described in previous papers[2-4] of this series. One change was made: the ethylene carbonate samples solidified at room temperature and hypodermic syringes naturally could not be used for sampling. Instead, the entire contents of a test ampoule were quantitatively transferred to the titration beaker with methanol.

Results and Discussion

All of the systems investigated followed second-order kinetics exactly to well over 90% completion of the quaternization with the single exception of solutions in diphenyl ether. Here the rate was found to decrease with time; it was also observed that a second phase appeared beyond about 10% conversion. The product, N-*n*-butyl-4-picolinium bromide, has a quite low solubility in diphenyl ether. Consequently, the values for the rate constant in this solvent are based on the initial rates

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(1b) Department of Chemistry, The University of Akron. A travel grant from the Fulbright Exchange Program is gratefully acknowledged.

(2) B. D. Coleman and R. M. Fuoss, THIS JOURNAL, **77**, 5472 (1955).

(3) P. L. Kronick and R. M. Fuoss, *ibid.*, **77**, 6114 (1955).

(4) E. Hirsch and R. M. Fuoss, *ibid.*, **77**, 6115 (1955).

(5) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5897 (1954).

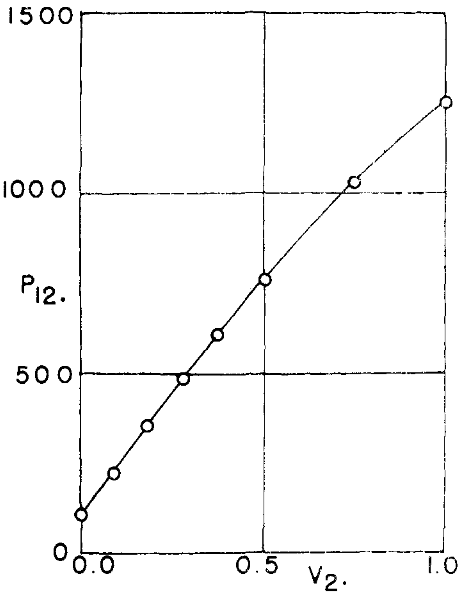

Fig. 1.—Polarization plot for mixtures of diphenyl ether and propylene carbonate.

for reactions which were discontinued at less than 10% completion. A summary of the results is given in Tables II and III; a and b are initial concentrations of butyl bromide and base in moles/g. solution and k_2 is the rate constant (l./mole min.). In Table III, the weight per cent. of propylene carbonate (% PC) in the mixed solvent is given for each set of data. All of the systems studied gave linear Arrhenius plots; the values of the constants of the equation

$$k_2 = A \exp(-\Delta E/RT) \quad (1)$$

are summarized in Table IV, together with the values of ΔS^*, which is defined by the equation[6]

$$\Delta S^* = R \ln k_2 + \Delta E/T - R \ln (ekT/h) \quad (2)$$

TABLE II

QUATERNIZATION BY n-BUTYL BROMIDE IN ETHYLENE CARBONATE

t, °C.	$10^4 b$	$10^4 a$	$10^3 k_2$
	Pyridine		
50	0.988	0.980	5.19
50	1.002	1.987	5.19
50	2.172	1.149	5.23
75	0.988	0.980	34.0
75	1.002	1.987	31.4
100	0.988	0.980	150
99	1.002	1.987	148
100	2.172	1.149	148
	4-Picoline		
50	0.862	0.868	8.87
50	0.945	1.903	8.87
50	1.965	0.906	8.90
75	0.906	0.911	50.6
75	1.130	2.456	49.3
75	1.965	0.906	48.0
100	0.906	0.911	212
100	0.958	1.957	210
100	1.965	0.906	206

TABLE III

QUATERNIZATION OF 4-PICOLINE BY n-BUTYL BROMIDE IN MIXTURES OF PROPYLENE CARBONATE AND DIPHENYL ETHER

t, °C.	$10^4 b$	$10^4 a$	$10^3 k_2$
	0.0% PC		
50	0.949	0.949	0.147
75	.949	.949	0.76
98	.949	.949	2.83
	10.1% PC		
50	1.002	0.995	0.70
75	1.002	.995	3.52
100	1.002	.995	13.3
	20.0% PC		
50	0.988	0.988	1.06
75	.988	.988	6.37
98	.988	.988	24.6
	30.4% PC		
50	0.991	0.991	1.53
75	.991	.991	8.72
98	.991	.991	33.1
	40.2% PC		
50	1.012	1.012	1.90
75	1.012	1.012	11.4
98	1.012	1.012	47.6
	53.0% PC		
50	0.972	0.980	2.26
75	.946	.950	14.7
100	.946	.950	70.0
	77.2% PC		
50	0.990	0.955	3.24
75	.990	.955	19.8
98	.990	.955	80.7
	100% PC		
50	0.758	1.191	3.90
75	.670	0.987	24.3
98	.953	0.953	106

TABLE IV

REACTION CONSTANTS FOR MIXTURES

% PC	log A	ΔE	ΔS^*_{323}
0.0	6.10	14.70	−40.8
10.1	6.38	14.10	−39.5
20.1	7.57	15.60	−34.1
30.4	7.50	15.25	−34.4
40.2	8.09	16.00	−31.7
53.0	8.47	16.45	−30.0
77.2	8.35	16.05	−30.5
100.0	8.61	16.25	−30.5

The system 4-picoline–n-butyl bromide has now been studied in five solvents: tetramethylene sulfone, dimethylsulfolane, ethylene carbonate, propylene carbonate and diphenyl ether. As expected, the rate of reaction is by far the slowest in diphenyl ether. The activation energy is lowest in this solvent, but this favorable factor is more than compensated by the low value of the statistical factor A. The other four solvents all give rapid quaternization, in conformity with their highly polar nature. But within this group, specific differences appear which must be correlated with details

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[6] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 197–199.

of solvation of the activated complex; the dielectric constants are so high that the continuum term has very little influence. For the reaction A + B $\rightleftarrows$ M*, the following equation has been proposed[7]

$$\ln k_2 = \ln k_0 - \frac{1}{kT}\frac{D-1}{2D+1}\left(\frac{\mu_A{}^2}{r_A{}^3} + \frac{\mu_B{}^2}{r_B{}^3} - \frac{\mu^{*2}}{r^{*3}}\right) + \frac{\Sigma\varphi}{kT} \qquad (3)$$

where D is the dielectric constant of the medium in which reaction occurs and μ and r are dipole moment and molecular radius of the indicated species. The variable $y = (D - 1)/(2D + 1)$ determines the magnitude of the solvent effect, but it becomes quite insensitive to D when D is large. For $1 \leqslant D \leqslant 30$, y increases from zero to 0.476; further increase of D beyond 30 to "infinity" only causes y to increase to 0.500. Hence the continuum term in the rate equation above is substantially the same in all solvents of high dielectric constant, and the observed differences in rate must be due to specific structural details.

The carbonate group appears to be considerably more effective than the sulfone group in promoting the Menschutkin reaction: at 50°, the values of 10^3k_2 are 8.9 and 3.9 for ethylene and propylene carbonates, as compared with 6.6 and 2.4 for tetramethylene sulfone and dimethylsulfolane. Another contrast points up the greater importance of specific effects over those described in terms of macroscopic properties: the rate in tetramethylene sulfone (D = 42) is nearly twice that in propylene carbonate (D = 65). Here the sequence of rates is exactly reversed from the generalization that quaternization is more rapid in solvents of high dielectric constant. The marked decelerating effect of methyl substitution in these solvents also is out of all proportion to the corresponding decrease in dielectric constant.

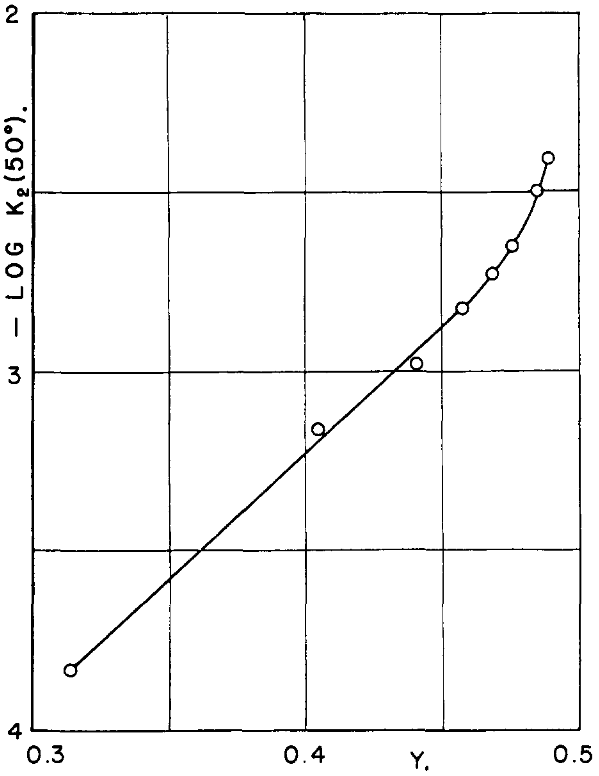

Fig. 2.—Dependence of rate on dielectric constant of mixtures.

In order to isolate the effect of dielectric constant, the reaction between picoline and butyl bromide was studied in mixtures of diphenyl ether and propylene carbonate. In the 10% mixture, the molar concentration of propylene carbonate is about the same as that of the base and the alkyl halide; in all the other mixtures, the carbonate is in excess. Consequently, solvation must be about the same in the various mixtures, and any change in rate must be due to electrostatic effects. As is shown in Fig. 2, where log k_2 (50°) is plotted against y, eq. 3 describes the dependence of rate on dielectric constant fairly well up to about 50% propylene carbonate; beyond this, the rate increases faster than corresponds to the dielectric constant. The fact that the curve of Fig. 2 has a positive slope, however, is direct evidence for the existence of a partially ionized transition state, because such a structure would have a much larger dipole moment than the reagents. In such cases, the μ^* term in eq. 3 controls and d log k_2/d$y > 0$.

The system exhibits the correlation between ΔE and log A which has been described by Hinshelwood[8] and others. The solid circles in Fig. 3 show that high values of ΔE are associated with large values of A. The open circles of Fig. 3 give the values of $\Delta H^* = \Delta E + RT$ (T = 323°K.) and $T\Delta S^*$; they naturally show the same correlation. The value of $\Delta G^* = \Delta H^* - T\Delta S^*$ decreases from 27.25 in diphenyl ether to 25.15 in propylene carbonate.

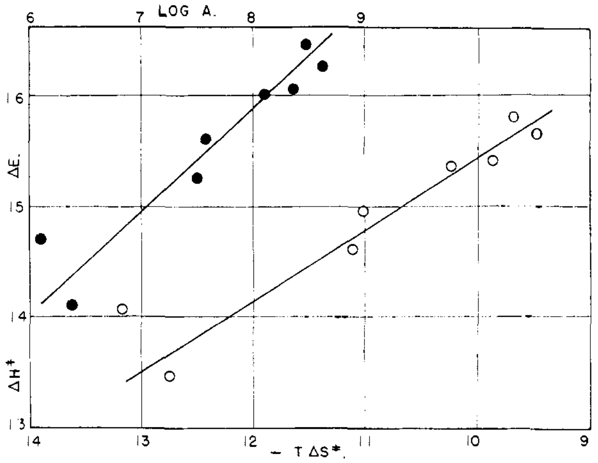

Fig. 3.—Correlation of energy and entropy terms.

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[7] Ref. 6, pp. 419–423.

[8] H. C. Raine and C. N. Hinshelwood, *J. Chem. Soc.*, **141**, 1378 (1939).