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Dissociation Constants of Several Protonated Amines in Propylene Carbonate

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Synopsis. The dissociation constants pK(BH$^+$) of five protonated monoamines in propylene carbonate have been determined potentiometrically using a glass electrode which was calibrated in a picric acid–picrate buffer solution. The pK(BH$^+$) values found at 25 °C were 10.1 for aniline, 11.9 for pyridine, 15.9 for ammonia, 17.0 for 1,3-diphenylguanidine, and 17.9 for triethylamine.

The dissociation and homoconjugation constants of several acids (HA) have been determined in propylene carbonate,[1] the results of which showed that propylene carbonate is a somewhat stronger base than acetonitrile, being of the same order of strength as acetone. In the present paper, the dissociation constants, pK(BH$^+$), of five protonated monoamines (BH$^+$) in propylene carbonate are presented. The pK(BH$^+$) values were obtained potentiometrically using a glass electrode which had been shown to respond with a Nernstian slope to paH in propylene carbonate. In each measurement, the electrode was calibrated in a picric acid–tetraethylammonium picrate buffer solution, the paH of which was calculated from the pK(HA) of picric acid of 9.30.[1]

Experimental

Materials. Propylene carbonate was a synthetic grade Merck product and purified as described in a previous report.[1] The water content of the purified solvent was less than 0.005%. Aniline, pyridine, 1,3-diphenylguanidine, and triethylamine were analytical reagent grade products (Wako Chemicals Co.), and purified by the method of Coetzee and Padmanabhan.[2] Pyridine was distilled from potassium hydroxide and then from barium oxide.[3] Ammonia was drawn into the propylene carbonate and the concentration of the resulting solution was determined by titration with perchloric acid.

The perchlorates of aniline, pyridine, 1,3-diphenylguanidine, triethylamine, and ammonia were prepared by neutralizing the bases with 70% perchloric acid, followed by recrystallization and careful drying *in vacuo*.[2] In the neutralization of triethylamine and the recrystallizations of the perchlorates of pyridine, 1,3-diphenylguanidine, and triethylamine, ethanol was used as the solvent.

Potentiometric Measurements. Potentiometric measurements were conducted at 25.0±0.5 °C as previously reported.[1] In the paH measurement of mixtures of a base and its perchlorate, 50 ml of the perchlorate solution was placed in the cell and appropriate volumes of the stock solution of the base were titrated to change the value of $\log(C_{BH^+}/C_B)$ from +1.0 to −1.0. Before and after each titration, the glass electrode was checked in the standard buffer solution (4×10^{-3} mol dm^{-3} picric acid and 4×10^{-3} mol dm^{-3} tetraethylammonium picrate) of paH 9.3_3. The potentials obtained in the standard buffer solution before and after each titration agreed within ±1 mV.

Results and Discussion

Typical results of the potentiometric measurements are shown in Table 1. In this case, 50 ml of 3.0×10^{-3} mol dm^{-3} pyridinium perchlorate in propylene carbonate was titrated with 3.0 mol dm^{-3} pyridine in the same solvent. The pK(BH$^+$) value was calculated according to Eq. 1,

$$pK(BH^+) = paH + \log\frac{C_{BH^+}f_{BH^+}}{C_B} \quad (1)$$

where $\log f_{BH^+} = -0.69C_{BH^+}^{1/2}$.[1] In Table 1, the p$K$(BH$^+$) values for $\log(C_{BH^+}/C_B)$ between +1.0 and −1.0 are constant within ±0.02. The titrations were conducted three or four times for each of the five protonated monoamines. In all cases, the values of pK(BH$^+$) in each titration were nearly constant (the largest standard deviation, 0.06). This indicates that under the experimental conditions the reaction BH$^+$= B+H$^+$ predominates in solution.

In Table 2, the pK(BH$^+$) values obtained are summarized. The standard deviations of the pK(BH$^+$) values in Table 2 are equal to or less than 0.1. But since the Nernstian response of the glass electrode was verified only at the paH range between 5 and 10,[1] it seems better to consider that the uncertainties of the pK(BH$^+$) values are about ±0.15 pK units.[4]

The values of pK(BH$^+$) in propylene carbonate are smaller than those in acetonitrile by approximately 0.5 pK units (except in the case of 1,3-diphenylguanidine where the difference is 0.9 pK units). As reported,[1] propylene carbonate is a 10 to 40 times stronger

Table 1. Potentiometric determination of pK(BH$^+$) of the pyridinium ion in propylene carbonate[a]

$\log(C_{BH^+}/C_B)$	E/mV	paH[b]	pK(BH$^+$)
+1.00	$-334._0$	11.03	11.99
+0.70	$-351._5$	11.32	11.98
+0.40	$-368._5$	11.61	11.97
+0.22	$-378._5$	11.78	11.96
+0.10	$-386._0$	11.91	11.97
0.00	$-391._0$	11.99	11.95
−0.30	$-407._0$	12.26	11.92
−0.60	$-426._0$	12.58	11.94
−0.78	$-437._0$	12.77	11.95
−0.90	$-445._5$	12.91	11.97
−1.00	$-453._0$	13.04	12.00
			Av 11.96±0.02

a) 50 ml of 3.0×10^{-3} mol dm^{-3} pyridinium perchlorate in propylene carbonate was titrated with up to 0.50 ml of 3.0 mol dm^{-3} pyridine in propylene carbonate. b) paH was obtained by paH=9.33−(E+233.5)/59.2.

Table 2. $pK(BH^+)$ of protonated monoamines in propylene carbonate and acetonitrile

Monoamine	$pK(BH^+)$ in PC[a)]	$pK(BH^+)$ in AN[a,b)]	ΔpK
Aniline	10.09±0.10	10.56	0.47
Pyridine	11.92±0.07	12.33	0.41
Ammonia	15.90±0.04	16.46	0.56
1,3-Diphenylguanidine	16.98±0.04	17.90	0.92
Triethylamine	17.94±0.06	18.46	0.52

a) PC=propylene carbonate, and AN=acetonitrile.
b) Values from Ref. 2.

base towards protons than acetonitrile. The solvation of protonated amines would also be stronger in propylene carbonate than in acetonitrile, though the difference between the two solvents appears to be smaller than in the case of the proton. On the basis of these considerations, the above differences in $pK(BH^+)$ values between the two solvents are reasonable.[5)]

References

1) K. Izutsu, I. M. Kolthoff, T. Fujinaga, M. Hattori, and M. K. Chantooni, Jr., *Anal. Chem.*, **49**, 503 (1977).
2) J. F. Coetzee and G. R. Padmanabhan, *J. Am. Chem. Soc.*, **87**, 5005 (1965).
3) E. K. Ralph and W. A. Gilkerson, *J. Am. Chem. Soc.*, **86**, 4783 (1964).
4) The approximate values of $\{dpK(BH^+)/dT\}/K$ at 25 °C, as determined from the measurement of the heat of the reaction of $BH^+=B+H^+$, are -0.01_2 for aniline, -0.01_3 for pyridine, -0.02_5 for 1,3-diphenylguanidine, and -0.03_3 for triethylamine. K. Izutsu, T. Nakamura, and T. Hizawa, unpublished results.
5) Talarmin *et al.* reported $pK(HA)$ of 11.3 for picric acid, $pK(BH^+)$ of 12.4 for aniline and 19.4 for 1,3-diphenylguanidine. These values were determined using both hydrogen and glass electrodes, which were standardized in a solution of trifluoromethanesulfonic acid ($pK(HA)=2.2$), and by assuming the Nernstian response of these electrodes. The large discrepancies in pK values between the results of Talarmin *et al.* and this study require further study. J. Talarmin, M. L'Her, and J. Courtot-Coupez, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **287**, 105 (1978).