TABLE VII

PREDICTED AND OBSERVED RELATIVE RATES

Reaction	Conditions	Ref.	$k_{C_6H_5}/k_H$ Obsd.	Predicted
$RCO_2C_2H_5 + H_2O \rightarrow RCO_2H + C_2H_5OH$	Acid cat. hydrolysis, 60% (vol.) aq. acetone, 25°	[a]	8.3×10^3	2.5×10^4
$RCO_2C_{10}H_{19} + CH_3OH \rightarrow RCO_2CH_3 + C_{10}H_{19}OH$	Methoxide ion catalysis CH_3OH, 30°	[b,c]	7.6×10^3	2.0×10^4
$R(CH_3)C{=}O + H_2NNHCONH_2 \rightarrow R(CH_3)C{=}NNHCONH_2 + H_2O$	Phosphate buffer *p*H 7, 25°	[d,e]	1.5×10^4	2.5×10^4

[a] W. B. S. Newling and C. N. Hinshelwood, *J. Chem. Soc.*, 1357 (1936). [b] R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, THIS JOURNAL, **72**, 4511 (1950). [c] W. A. Pavelich and R. W. Taft, Jr., unpublished results. [d] J. B. Conant and P. D. Bartlett, THIS JOURNAL, 54, 2881 (1932). [e] F. P. Price, Jr., and L. P. Hammett, *ibid.*, **63**, 2387 (1941).

substituent constant, E_s.[22] The present results suggest, therefore, that the steric substituent constants include small but significant contributions from hyperconjugation effects. However, in accord with the basic arguments of the method,[23] these effects are not expected to alter Taft's polar substituent constants, σ^*.

Experimental

The technique for measuring acetal and ketal hydrolysis rates and the preparation of the 50% dioxane–water mixture have been previously described.[24] Propiophenone diethyl ketal,[25] b.p. 104° (14 mm.), benzophenane diethyl ketal,[26] m.p. 49–50.5°, and fluorenone diethyl ketal,[27] m.p. 78–80°, are all previously known compounds.[28] The diethyl acetal of *p*-nitrobenzaldehyde, a slightly yellow liquid with b.p. 162–163° (14 mm.), is not a previously reported compound.

Anal. Calcd. for $C_{11}H_{15}O_4N$: C, 58.67; H, 6.67; N, 6.22. Found[29]: C, 58.31; H, 6.56; N, 6.47.

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[22] R. W. Taft, Jr., THIS JOURNAL, **74**, 3120 (1952).

[23] *Cf.*, ref. 18, p. 588.

[24] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 3146 (1955).

[25] E. L. Beals and F. A. Gilfillan, *J. Am. Pharm. Assoc.*, **25**, 426 (1936).

[26] Mack, *J. Chem. Soc.*, **69**, 990 (1887).

[27] Smedley, *ibid.*, **87**, 4252 (1905).

[28] All boiling points are uncorrected, melting points are corrected.

[29] Microanalysis was performed by Clark Microanalytical Laboratory, Urbana, Illinois.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

The Temperature Dependence of Ion Pair Dissociation Constants. I. *o*-Dichlorobenzene[1]

BY H. L. CURRY AND W. R. GILKERSON

RECEIVED MARCH 18, 1957

The conductances of tetraethylammonium, tetra-*n*-propylammonium and tetra-*n*-butylammonium picrates in *o*-dichlorobenzene have been determined as a function of concentration at 25, 35, 45, 55 and 65°. The ion pair dissociation constants and limiting equivalent conductances have been calculated at each temperature. The variation of the dissociation constant with temperature is discussed with reference to Bjerrum's theory and also a recent one proposed by one of the authors.

As has been pointed out in a recent critical review of the ion pair concept,[2] Bjerrum's[3] theory of ion pair dissociation qualitatively but not quantitatively describes experimental results that have been obtained. His theory gives

$$K^{-1} = \frac{4\pi N}{1000} (\epsilon^2/DkT)^3\, Q(b) \qquad (1)$$

where $b = \epsilon^2/aDkt$. Here, N is Avogadro's number, ϵ is the unit of charge and a is the distance of closest approach, being an empirical parameter. While a, as determined experimentally, is generally larger than the charge separation as determined from dipole moment measurements, it may also be much smaller.

The dependence of K upon the dielectric constant at constant temperature has been investigated in solvent mixtures and while the agreement is quite good for the water–dioxane system,[4] a discrepancy has been observed[5] in nitrobenzene–carbon tetrachloride mixtures. Further, specific solvent effects have been shown when results in ethylene chloride ($D = 10.23$), ethylidene chloride ($D = 9.90$) and *o*-dichlorobenzene ($D = 9.93$) are compared at 25°.[6] The ratio of the dissociation constant of Et_4NPi in ethylene chloride to that in *o*-dichlorobenzene is 13.9, far too large to be accounted for on the basis of the difference in dielectric constant alone. There are very few data available concerning K as a function of temperature. An early study in anisole,[7] while in qualitative agreement with Bjerrum's equation, is of doubtful validity due to approximations that were necessary to evaluate the K values. Studies in ethylene chloride, ethylidene chloride and propylene chloride have been reported.[8] It seemed, in view of the scarcity of information, of interest to extend such studies to other solvents, using salts which have been the subject of previous examina-

[1] Presented at the Southwide Chemical Conference, Memphis, December 6, 1956.

[2] C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

[3] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[4] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933).

[5] H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).

[6] F. Accascina, E. L. Swarts, P. L. Mercier and C. A. Kraus, *Proc. Natl. Acad. Sci.*, **39**, 917 (1953).

[7] G. S. Bien, R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **56**, 1860 (1934).

[8] (a) K. H. Stern and A. E. Martell, *ibid.*, **77**, 1983 (1955); (b) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

tion. The choice of solvent, *o*-dichlorobenzene, was made on the basis of its dielectric constant and the previously noted abnormally low K values found at 25°. The salts chosen were tetraethylammonium, tetra-*n*-propylammonium and tetra-*n*-butylammonium picrate.

Experimental Solvent.—*o*-Dichlorobenzene (Eastman red label) was run through a column packed with silica gel and then fractionally distilled on a three-foot column packed with glass helices. Only the middle fraction was retained. This was received in a two-liter flask protected from moisture by a calcium chloride tube. The purified solvent was stored in a dry-box under an atmosphere of nitrogen. The specific conductivity of the solvent was 3×10^{-10}/ohm cm. at 25°.

Salts.—The hydroxide corresponding to each salt was prepared from the available halide (Eastman) by metathesis with freshly prepared silver oxide in alcoholic suspension. The alcoholic hydroxide was then neutralized with picric acid. The resulting picrates were recrystallized from ethanol three times and dried *in vacuo*. The melting points were: Et_4NPi, 259-261°; Pr_4NPi, 117.0-117.4°; Bu_4NPi, 89.8°.

Conductance Measurements.—The bridge used was similar to that of Eisenberg and Fuoss.[9] Several cells were used, all similar to those of Kraus and co-workers. Cell constants were determined by intercomparison, using a 0.01 *D* KCl solution[10] as standard. The solutions were made up by weight in an atmosphere of nitrogen, and dilutions of stock solutions were made similarly. The solutions in the cells were stirred continuously, using a Teflon-covered magnet as agitator. The oil-filled thermostat was maintained at the stated temperature within 0.005°. Temperatures were determined with a resistance thermometer calibrated by the National Bureau of Standards. Two series of conductance measurements were run for each salt at each temperature. These agreed within 0.2%.

Physical Constants.—The solvent density and viscosity were determined at each temperature. The latter was measured in a Cannon–Fenske viscometer. The values obtained are listed in Table I.

TABLE I

PHYSICAL CONSTANTS OF *o*-DICHLOROBENZENE

t, °C.	d, g./cc.	$\eta \times 10^2$	D
25.00	1.3007	1.2778	9.939
35.00	1.2885	1.1036	9.571
45.00	1.2784	0.9701	9.202
55.00	1.2674	.8669	8.836
65.00	1.2558	.7720	8.515

The dielectric constant, D, of the solvent was measured, using a General Radio type 716-C capacitance bridge, with a type 716-P4 guard circuit. All measurements were made at 100 kc. The dielectric cell was similar in design to that of Sadek and Fuoss.[5]

Results

The equivalent conductances found for each concentration are given for Et_4NPi at 35° in Table II.

TABLE II

EQUIVALENT CONDUCTANCE OF Et_4NPi AT 35° IN *o*-DICHLOROBENZENE

$C \times 10^4$, M	Λ	$C \times 10^4$, M	Λ
2.419	12.30	0.4998	22.22
2.030	13.22	.4490	22.95
1.453	15.07	.3251	25.37
0.9683	17.50	.2605	27.30
.8246	18.58	.1873	29.69

The conductance–concentration data were treated by the method of Shedlovsky[11] both graphically, to determine any inconsistencies, and by least squares to get the best values of Λ_0 and K. The latter are shown in Table III. The values at 25° agree well with those determined elsewhere.[6] However, the K values found in this work are somewhat higher. A close comparison of the data shows that our Λ are slightly larger than those of Accascina. This may be due to some discrepancy in cell constants. Of more intrinsic interest is the variation of K with temperature. In the cases cited previously[8] for ethylene chloride and ethylidene chloride, the K values decreased with rising temperature. Here, however, they are seen to increase to a maximum at 45° and then decrease.

TABLE III

VALUES OF Λ_0 AND K IN *o*-DICHLOROBENZENE

			Λ_0		
Salt	25°	35°	45°	55°	65°
Et_4NPi	47.8	51.56	55.91	65.40	71.38
Pr_4NPi	40.3		50.31	58.33	66.14
Bu_4NPi	36.8	41.45	46.26	53.88	60.53
			$K \times 10^5$		
	25°	35°	45°	55°	65°
Et_4NPi	1.23	1.389	1.511	1.343	1.362
Pr_4NPi	1.64		1.710	1.568	1.467
Bu_4NPi	1.92	1.983	2.021	1.820	1.715

Values of Bjerrum's parameter, a, have been calculated from eq. 1 and appear in Table IV. It may be seen that these show a definite increase with temperature, except for the last two temperatures, where they remain constant. In ethylene chloride (ref. 8a), a for Bu_4NPi may be calculated at 5.69, 25 and 35° to be 5.83, 5.77 and 5.85 Å., respectively.

TABLE IV

VALUES OF BJERRUM'S PARAMETER, $a \times 10^8$ CM., IN *o*-DICHLOROBENZENE

t, °C.	Et_4NPi	Pr_4NPi	Bu_4NPi
25	3.92	4.03	4.10
35	4.01		4.18
45	4.05	4.11	4.19
55	4.05	4.12	4.20
65	4.09	4.13	4.19

If one is to allow a to vary with temperature, then it would be expected to increase as the temperature increases. However, there seems to be a closer correlation between a and the product DT. In *o*-dichlorobenzene, DT decreases with T; in ethylene chloride, DT increases; in ethylidene chloride, DT again decreases. The a values vary in an inverse manner. A recent study of Et_4NPi in a series of phthlate esters as solvents[12] shows the same trend. Kraus has shown[13] that a values calculated from Bjerrum's are much larger than the separation of charge as determined from the dipole moments of salts in benzene.

An expression for K which takes into account specific ion–solvent interaction has been derived

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(9) H. Eisenberg and R. M. Fuoss, THIS JOURNAL, **75**, 2914 (1953).

(10) G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

(11) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(12) C. M. French and N. Singer, *J. Chem. Soc.*, 1424 (1956).

(13) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936); C. S. Hooper and C. A. Kraus, THIS JOURNAL, **56**, 2265 (1934).

recently[14] on the basis of Kirkwood's free-volume theory of solutions. This theory gives

$$K = \left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} (gv\sigma) \exp\left(-\frac{E_s}{RT} - \frac{N\epsilon^2}{aRDT}\right) \quad (2)$$

where $\mu = m_+m_-/(m_- + m_+)$, m_i being the mass of the ith ion, $E_s = E_- + E_+ - E_\pm$, E_i being the interaction energy between the ith ion and surrounding solvent, $E_\pm$ being the energy of interaction between solvent and the ion pair, the factor $(gv\sigma) = (g_+g_-v_+v_- \quad \sigma_+\sigma_-)/(g_\pm v_\pm \sigma_\pm)$, g_i being the rotational and vibrational contribution to the partition function of the ith particle, v_i being the free volume available to the ith particle and σ being a factor varying between unity for solids and e for gases. If values of K as a function of T are available, the parameters $(gv\sigma)$ and E_s, characteristic of the solvent and salt, can be chosen so as to give a value of a, the distance of closest approach, which is independent of the temperature and solvent. Using the data obtained in this study, such calculations have been made. The results are shown in Fig. 1, where values of $F = \log K - 3/2 \log T + E_s/T$ are plotted *vs.* $1/DT$. The values of a, E_s and $(gv\sigma)$ for each salt are given in Table V. At this point, no generalizations can be made concerning the variations in E_s and $(gv\sigma)$, due to their complex nature and the lack of more extensive data. It may be said that the free-volume theory accounts for the observed facts as well as Bjerrum's theory. Certainly a constant value of a is more satisfying than one which varies in an unpredictable manner. It may be noted that the a value for Bu_4NPi in this solvent is the same as that found[14] in the solvents ethylene chloride, ethylidene chloride, propylene chloride and anisole. This work is being extended to other solvent systems in an effort to accumulate data which may lead to some correlation for the values of E_s and $(gv\sigma)$ thus obtained.

TABLE V

SALT PARAMETERS IN *o*-DICHLOROBENZENE

Salt	$a \times 10^8$, cm.	E_s, cal./mole	$(gv\sigma)$, cm.^{3}
Et_4NPi	1.59	4800	1.2×10^{-13}
Pt_4NPi	1.88	2880	2.4×10^{-17}
Bu_4NPi	2.51	1903	2.2×10^{-19}

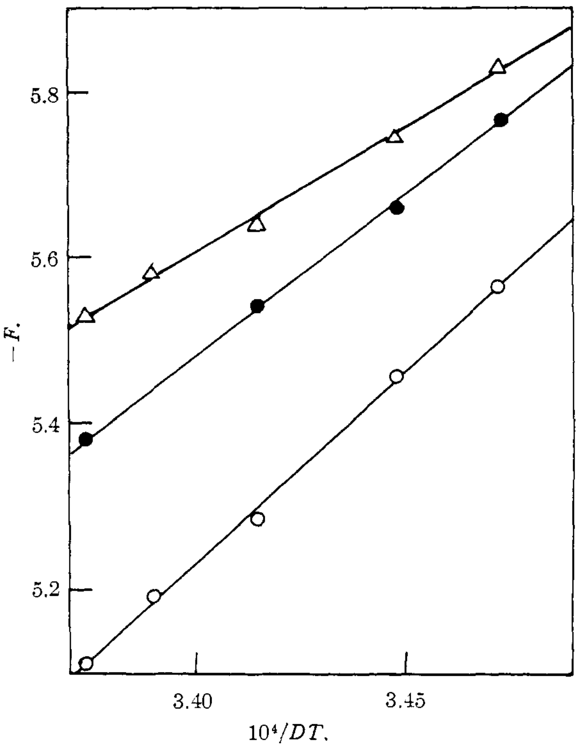

Fig. 1.—Values of the function F are plotted *vs.* $1/DT$ for the salts Et_4NPi (open circle), Pr_4NPi (closed circle, $F + 1.00$) and Bu_4NPi (triangle, $F + 1.500$) in *o*-dichlorobenzene.

Acknowledgment.—We wish to acknowledge the support of this work by contract with the United States Army, Office of Ordnance Research.

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[14] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF HOUSTON]

Further Studies of the Boron Bases: $CaHB(CH_3)_2$[1]

BY GEORGE W. CAMPBELL, JR.[2]

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The reaction of tetramethyldiborane with calcium in liquid ammonia has produced the new compound $CaHB(CH_3)_2 \cdot NH_3$. The Lewis base activity of this salt is lower than that of the comparable sodium salt, as indicated by its inactivity toward $B(CH_3)_3$ in liquid ammonia. $CaHB(CH_3)_2 \cdot NH_3$ reacted with tetramethyldiborane, to produce NH_3-soluble $Ca[H_2B(CH_3)_2]_2 \cdot XNH_3$ and a second product, formulated in speculation as "$Ca[B(CH_3)_2]_2$." In methyl ether solution, $CaHB(CH_3)_2 \cdot NH_3$ reacted with SiH_3Cl to product SiH_4 in equal molal quantity. Cryoscopic and tensiometric measurements of $CaHB(CH_3)_2$ in NH_3 indicate the monomer state of the salt in solution. The identity of $CaHB(CH_3)_2 \cdot NH_3$ as a salt of the $HB(CH_3)_2^=$ anion is argued on the basis of chemical evidence. Attempts to prepare the lithium and potassium salts of the $HB(CH_3)_2^=$ have suggested that the lithium salt can be prepared, but only hinted that the potassium salt can exist. Neither salt was obtained in a state approaching purity. However, these studies have provided a possible explanation for the contamination of the sodium salt with $B(CH_3)_3$, and the formation of $B(CH_3)_3$ in the reactions of tetramethyldiborane with potassium and with sodium in liquid ammonia.

The discovery of the boron base $Na_2HB(CH_3)_2$ and its ability to establish a firm B–B bond by reacting with trimethylboron in liquid ammonia[3] implies the possibility of forming previously unknown bonds by an electron-donor action of boron

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[1] Presented in part at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 12, 1956.

[2] Now at United States Borax and Chemical Corp., Research Laboratories, Anaheim, California.

[3] A. B. Burg and G. W. Campbell, Jr., THIS JOURNAL, **74**, 3744 (1952).