(which are for 25°). Considering the uncertainties of the calculation the agreement between observed and calculated kinetic salt effects is quite satisfactory. A similar comparison can be made in the case of dipropyl formal for the two salts, sodium and potassium chloride, utilizing the 25° kinetic and salting out data of Olson and Tong.[6] The agreement for these cases is also good. It thus appears that the conclusions reached for methylal have general validity.

In the previous paper[1] it was shown that with the strong acids, hydrochloric and perchloric, plots of log k_h *vs.* $-H_0$ gave slopes of 1.25 and 1.08, respectively, and it was tentatively concluded that these departures from a slope of unity might be due to salt effects. If for these cases one proceeds as in eq. 6 to 8 for the kinetic salt effects and assumes that the discrepancies are due to the term f_B/f_M, one arrives at the equation

$$\log k = -H_0 + (k_M - k_B)C_A + \text{const.} \qquad (9)$$

where C_A is molar concentration of acid and k_M and k_B are again the salting out parameters. For hydrochloric acid k_M has the value 0.00 (Table I) and k_B is estimated in Table II as -0.10. Equation (9) then becomes

$$\log k_h = -H_0 + 0.10C_A + \text{const.}$$

A plot of log k_h *vs.* $(-H_0 + 0.10C_A)$ for the hydrochloric acid data of Table I of the previous paper results in a straight line of slope 1.04 showing that explicit recognition of salt effects improves the strong acid data just as it does the data for salts.

From these salt and acid results for methylal we conclude that quite generally when a correlation is sought between rate data and H_0 a correction should be made for differences in the effects of electrolytes on the activity coefficients of the reacting neutral molecule and the indicator used for H_0. One then can ask why in several cases involving strong acids have correlations which ignore the correction been quite satisfactory? A partial answer is that in some cases the reacting molecule and the indicator may fortuitously be such that the term f_M/f_B remains at unity. However, a more important point is that normally the salt effects of the strong acids hydrochloric, sulfuric and perchloric are quite small,[4] varying for a wide series of neutral molecules from only slight salting in to slight salting out. Because of this, the correction term f_M/f_B tends to be relatively unimportant for these acids.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Conductances of Some Salts and Ion-Pair Equilibria in Acetic Acid at 30°[1,2]

BY MARK M. JONES[3] AND ERNEST GRISWOLD

RECEIVED JANUARY 30, 1954

The conductances in acetic acid at 30° of the bromides, acetates and formates of potassium, sodium and lithium in concentrations ranging roughly from 10^{-5} to 10^{-3} M have been determined. Values of the limiting equivalent conductance and of the ion-pair dissociation constant have been obtained. Values of the latter are of the order of 10^{-7}. It is shown that these results may be used to give an independent test of a hypothesis previously advanced to account for salt effects on the solubility of potassium bromide in this solvent. Constants calculated from the conductance data for the postulated ion-pair exchange reactions $KBr + MX \rightleftarrows MBr + KX$ agree reasonably well with those previously obtained from solubility data.

In a recently reported investigation[4] of neutral salt effects on the solubility of potassium bromide in anhydrous acetic acid at 30°, it was pointed out that the experimental results could be interpreted quantitatively by assuming (1) that potassium bromide and the other salts involved exist largely undissociated in this solvent, presumably as ion-pairs of the type proposed by Bjerrum,[5] and (2) that these undissociated salts enter into metathetical reactions of the type

$$KBr + MX \rightleftarrows MBr + KX \qquad (a)$$

which proceed until equilibrium is attained. By introducing the additional assumption that the concentrations of free ions are negligible in comparison with those of the undissociated species, and that the activity coefficients of the latter are equal and remain constant throughout, the following equilibrium equations may be written

$$\frac{[MBr][KX]}{[MX]} = \frac{(\Delta S)^2}{C - \Delta S} = K \qquad (1)$$

Here the brackets denote molal concentrations, C the initial molal concentration of added salt MX, and ΔS the increase in molal solubility of potassium bromide resulting from presence of added salt. In the solubility studies mentioned above it was indeed found that equation 1 was obeyed over a rather wide range in concentration of each of a number of heteroionic added salts.

An independent test of equation 1 is possible, based upon the following considerations. From the work of Fuoss and Kraus[6] with solvents of moderately low dielectric constant it seems probable that in acetic acid the dissociation of salts such as KBr and MX, although slight may nevertheless be described by equilibrium equations such as

$$\frac{(K^+)(Br^-)}{(KBr)}\,\frac{y_{K^+}y_{Br^-}}{y_{KBr}} = K_{KBr} \text{ and}$$

$$\frac{(M^+)(X^-)}{(MX)}\,\frac{y_{M^+}y_{X^-}}{y_{MX}} = K_{MX} \qquad (2)$$

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(1) From a thesis presented to the Graduate School of the University of Kansas by Mark M. Jones in partial fulfillment of the requirements for the Ph.D. degree, 1952.

(2) Presented at the 123rd meeting of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(3) Du Pont Fellow, 1951–1952.

(4) E. Griswold, M. M. Jones and R. K. Birdwhistell, THIS JOURNAL, **75**, 5701 (1953).

(5) N. Bjerrum, *Det Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **7**, No. 9, 1 (1926).

(6) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 476, 1019 (1933).

in which the parentheses denote molar concentrations and the y's the corresponding activity coefficients. For the postulated equilibrium in a reaction of the type represented by (a) it should then be possible to combine relations such as those in (2) to give the equilibrium equation

$$\frac{(\mathrm{MBr})(\mathrm{KX})}{(\mathrm{KBr})(\mathrm{MX})}\,\frac{y_{\mathrm{MBr}}y_{\mathrm{KX}}}{y_{\mathrm{KBr}}y_{\mathrm{MX}}} = \frac{K_{\mathrm{KBr}}K_{\mathrm{MX}}}{K_{\mathrm{MBr}}K_{\mathrm{KX}}} \equiv K' \qquad (3)$$

The molar concentrations in this expression may be replaced by molalities, and if it is again assumed that the activity coefficients of the undissociated species are equal and constant, then equation 3 may be modified to give

$$\frac{[\mathrm{MBr}][\mathrm{KX}]}{[\mathrm{MX}]} = K'S_0 \qquad (4)$$

where S_0 is the molal solubility of potassium bromide in acetic acid alone. It is apparent that $K'S_0$ from (4) should be equal to K from (1) if the basic assumptions are correct. Inasmuch as the dissociation constants represented in the quotient K' in (3) may be determined from conductance measurements[6,7] on the respective individual salts, such measurements would appear to afford an independent check of numerical values of the constant K obtained from solubility measurements.

The conductivities of several acids and a number of salts in acetic acid at 25° have been reported by other investigators.[8,9] The manner in which the equivalent conductance of these salts varies with concentration is typical of that for incompletely dissociated electrolytes, and strongly suggests the existence of ion-pair equilibria in these solutions. However, since these studies included only two of the salts involved in the solubility studies,[4] and were, moreover, carried out at a different temperature, the results could not be used for the present purpose. Therefore, in the present study the conductances in acetic acid of the bromides, formates and acetates of potassium, sodium and lithium in concentrations ranging roughly from 10^{-5} to 10^{-3} M have been determined at 30°. Values of the various dissociation constants have been obtained by the method of Fuoss and Kraus, and the results used in the manner proposed above.

Experimental

The acetic acid employed was prepared by the method previously described.[4] The product melted at 16.60 or slightly higher and had a specific conductance of 3–4 × 10^{-8} ohm^{-1}. Correction for the specific conductance of the solvent was made in each case.

The salts used were prepared from C.P. materials, recrystallized at least twice and suitably dried. Solutions were prepared by weight, the more concentrated solutions being first prepared and then one or more dilutions made. All transfers were conducted in a dry-box. In calculating the volume concentrations it was assumed that for these dilute solutions the volume of the solution was the same as that of the pure acid present.

For the conductance measurements a Campbell–Shackelton shielded ratio box, Leeds and Northrup model 1554-A-2, was employed, together with oscillator, amplifier and suitable resistance and capacitance components. The oscillator was operated at a frequency of 1000 c.p.s. Five different cells of the type recommended by Jones and Bollinger,[10] having cell constants ranging from 0.1 to 0.3 were used. They were calibrated with standard potassium chloride solutions, using the data of Li and Fang.[11] The cells were suspended in an oil-bath which in turn was suspended in a water-bath maintained at 30.00 ± 0.02°.

Results and Discussion

The results of the measurements are given in Table I.

TABLE I

EQUIVALENT CONDUCTANCES OF SALTS IN ACETIC ACID AT 30°

C, moles/l. × 10^4	Λ, ohm^{-1}	C, moles/l. × 10^4	Λ, ohm^{-1}	C, moles/l. × 10^4	Λ, ohm^{-1}
Potassium bromide		Sodium bromide		Lithium bromide	
0.914	1.281	0.1109	6.789	0.2177	4.640
2.247	1.150	.5596	2.222	0.5836	3.170
2.334	1.107	.5908	2.245	1.146	2.286
3.525	.908	1.382	1.229	1.409	2.269
3.661	.874	4.757	.7727	1.440	2.123
4.498	.6785	4.973	.6801	1.682	2.067
6.173	.6006	18.90	.5377	1.861	1.980
9.614	.4861	20.46	.5194	3.442	1.496
11.90	.4422			3.681	1.348
13.32	.4203			5.818	1.198
23.38	.3420			6.583	1.100
76.07	.1954			7.555	0.972
				21.72	.6792
				47.70	.5015
				54.93	.4777
Potassium formate		Sodium formate		Lithium formate	
0.8069	1.264	1.250	0.7534	4.010	0.3863
2.309	0.7489	2.583	.5371	4.838	.3466
3.011	.5967	3.616	.4264	5.723	.3087
9.230	.3890	5.349	.3748	5.960	.3040
15.70	.3781	13.27	.2457	6.686	.2912
17.68	.2821	16.17	.2323	6.783	.2831
19.35	.2800	17.10	.2251	8.500	.2549
52.31	.1787	19.05	.2116	43.54	.1182
56.68	.1643	98.41	.1080	57.69	.1080
112.6	.1318			107.4	.08333
437.7	.1091			211.7	.08425
Potassium acetate		Sodium acetate		Lithium acetate	
0.1558	3.640	0.1154	4.082	0.2718	3.022
.2882	2.508	.3597	1.527	.3980	2.275
.8895	1.706	.4982	1.316	.4910	1.651
1.066	1.557	.5550	1.229	2.058	0.7387
2.336	1.014	.8507	1.032	2.687	.6375
2.462	0.997	1.004	0.916	6.365	.3817
3.321	.870	2.277	.7417	7.722	.3035
3.901	.7965	10.34	.2787	14.48	.2234
10.46	.5118	11.73	.2664	17.16	.2225
25.09	.3539	16.63	.2221	33.87	.1606
34.74	.3069	21.50	.1603		
38.72	.2961	64.48	.1569		
44.60	.2816				

When the data in Table I were treated by the method of Fuoss and Kraus it was found that plots of the function $\mathrm{F}(z)/\Lambda$ against $c\Lambda f^2/\mathrm{F}(z)$, as proposed by these investigators, gave straight lines of rather steep slope over the lower concentration range. Accurate extrapolation was difficult. Nev-

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(7) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

(8) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007 (1934).

(9) B. V. Weidner, A. W. Hutchison and G. C. Chandlee, *ibid.*, **60**, 2877 (1938).

(10) G. Jones and G. M. Bollinger, *ibid.*, **53**, 411 (1931).

(11) N. C. C. Li and H. Fang, *ibid.*, **64**, 1544 (1942).

ertheless, what appeared to be best values of the limiting equivalent conductance, Λ_0, and the ion-pair dissociation constant, K, were obtained, and the results are given in Table II.

TABLE II

LIMITING EQUIVALENT CONDUCTANCE AND ION-PAIR DISSOCIATION CONSTANT OF SOME SALTS IN ACETIC ACID AT 30°

Salt	Λ_0	$K \times 10^7$
Potassium bromide	41	1.1
Sodium bromide	37	1.3
Lithium bromide	29	7.2
Potassium formate	35	1.1
Sodium formate	31	0.65
Lithium formate	23	0.87
Potassium acetate	24	3.6
Sodium acetate	20	2.1
Lithium acetate	13	6.0

In Table III is presented a comparison of the numerical values of the equilibrium constant, K, for the postulated ion-pair exchange reaction (a), as previously obtained[4] from solubility data by equation 1, with the corresponding constants, S_0K', calculated from the dissociation constants in Table II and the previously reported value of $S_0 = 0.01837$ m.

In view of the uncertainties involved in determining the individual dissociation constants from the conductance data, the agreement shown in Table III would appear to be rather surprisingly good. The fact that the constants obtained from the two very different types of measurement are of the same order of magnitude lends considerable further support to the hypothesis previously advanced that reactions of type (a) may be of major importance in accounting for salt effects on solubility in those solvents in which both the solvent salt and the solute salt exist largely as ion-pairs.

TABLE III

COMPARISON OF ION-PAIR EXCHANGE CONSTANTS OBTAINED FROM SOLUBILITIES AND FROM CONDUCTANCE MEASUREMENTS

Added salt	K eq. 1	$K'S_0$ eq. 4
Sodium acetate	0.0114	0.0090
Sodium formate	.0102	.0092
Lithium acetate	.00250	.0047
Lithium formate	.00328	.0022

Returning to the results presented in Table II, it is of interest to note that in a series of salts possessing a common anion the limiting equivalent conductances are observed to decrease in the order potassium > sodium > lithium, which, of course, corresponds to the order observed in water solutions, and may very probably be attributed to a similar cause, namely, a progressively increased degree of solvation.

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[CONTRIBUTION FROM ARTHUR D. LITTLE, INC.]

The Thermal Decomposition of Methylenedinitramine

BY MARVIN C. TOBIN, JOHN P. FOWLER, HENRY A. HOFFMAN AND CHARLES W. SAUER[1]

RECEIVED SEPTEMBER 18, 1953

Data are presented for the thermal decomposition of molten and solid methylenedinitramine and solid methylenedinitramine inhibited with picric acid. It is shown that the course of the decomposition of the solid is similar to that of other materials. A theory of the phenomena observed in the decomposition of solids is presented. Infrared spectra are presented for methylenedinitramine and its solid decomposition product.

In contrast to the tremendous amount of research carried out on the kinetics of decompositions taking place in the gas or solution phases, relatively little has been done with pure liquids or solids. Yet the decomposition of liquids or solids is often of the greatest practical interest, especially in connection with the storage of unstable materials. In addition, many phenomena appear in connection with the decomposition of solids which are absent in the gas or liquid phases, due to the mobility of the molecules of the latter. Methylenedinitramine makes a good subject for this type of study, due to its low melting point and comparative ease of decomposition.

It is well known[2] that the decomposition of methylenedinitramine is catalyzed by its products. Since it was desired to examine the primary decomposition process, the decompositions were carried out by heating the material in open tubes to allow escape of volatile products, and following the progress of weight loss with respect to time. This procedure was considered feasible in view of the lack of any sign that the compound reacted with the atmosphere. Trial tests showed that the rate of sublimation of the solid was very small.

This paper also reports the existence of a stabilizer for methylenedinitramine–picric acid. The discovery of this arose from a search for a way to inhibit the decomposition of methylenedinitramine.

Experimental

Samples.—The methylenedinitramine[3] was twice recrystallized from freshly distilled 2-nitropropane, by saturating the solvent at room temperature, and chilling in a full, stoppered bottle in a deep-freezer chest. In this way, possible decomposition during recrystallization was prevented. The pure material was dried under suction on a sintered glass filter, the crystals crushed and dried under vacuum; m.p. 105–106° dec.

To prepare the sample of methylenedinitramine–picric

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(1) This work was done under Contract DA-19-020-ORD-47 with the Office of the Chief of Ordnance and has been released by the War Department for publication.

(2) A. H. Lamberton, C. Lindley and J. C. Speakman, *J. Chem. Soc.*, 1650 (1949).

(3) This sample was from an experimental batch prepared by the Atlas Powder Co., Tamaqua, Penna.