

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright 1973 by the American Chemical Society

VOLUME 95, NUMBER 14

JULY 11, 1973

## Second-Order Rate Constants and Ion Association in Aprotic Solvents by High-Precision Conductance

Eric P. Grimsrud and Byron Kratochvil\*

*Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. Received November 18, 1972*

**Abstract:** Rate constants for nucleophilic displacement reactions and ion association constants of the reactant salts can be measured simultaneously by high-precision conductance. Reactions studied involved chloride, bromide, and thiocyanate salts as nucleophiles and *n*-butyl iodide as the substrate in acetonitrile at  $24.900 \pm 0.002^\circ$ . The degree of ion association of the nucleophile salt could be measured at the same time, enabling correction of the observed rate to yield the rate constant of the displacement reaction. Ion association and rate constants thus obtained are highly reproducible, and the method is suggested as an accurate means of their determination at low concentrations. The association constants of slightly soluble salts can be determined by this method; for example, for KBr and NaBr in acetonitrile at  $24.9^\circ$  they were found to be 40 and 62.

Measurement of electrolyte conductance, one of the most sensitive physical methods available for the determination of reaction rates in solutions, has been applied mainly to reactions in which the total number of ions in solution changes as the reaction proceeds. It has been used but little to study reactions in which an anionic nucleophile displaces an anion from a substrate molecule, because in many such displacement reactions the single-ion conductivities of the nucleophile and leaving group are similar, and the net change in conductance with time is relatively small. Also, kinetic studies traditionally have been carried out in protic solvents, in which simultaneous solvolysis of the substrate can contribute to the net conductance change, further obscuring the measurement of interest.

With the rising interest in chemical kinetics in aprotic solvents, a second look at the use of conductance for investigating these types of reactions is warranted. One reason is that solvolysis reactions are usually slight. Another is that conductance also should be expected to reflect the degree of association of the nucleophile anion with the corresponding cation of the salt used. Ion association in aprotic solvents often is sufficient to have a pronounced effect on reaction rates, and therefore the extent of association should be corrected for. In addition, ion association can sometimes enhance the net conductance change occurring throughout the course of a reaction and thus increase the precision of the observed rate. We report here an investigation of these effects using high-precision con-

ductance to measure the rate constants of several selected reactions.

The reactions studied involved salts of chloride, bromide, and thiocyanate as nucleophiles and *n*-butyl iodide as substrate in acetonitrile at  $24.9^\circ$ . The reactions involving chloride and bromide are stringent tests of the method, since the single-ion conductivities of chloride and bromide differ only slightly from that of iodide. Reactions involving thiocyanate salts are of particular interest because of appreciable ion association of these salts in acetonitrile.

### Experimental Section

**Apparatus.** A 1-l. Pyrex conductance cell of the erlenmeyer type was used for measuring both rates and conventional conductance. The cell, procedure, and method of data analysis for the conventional conductance measurements have been described previously.<sup>1</sup> For kinetic measurements the salt-cup dispenser was replaced with a ground-glass stopper. Resistance measurements were made with a Leeds and Northrup Dike-Jones conductance bridge in conjunction with a General Radio Model 1310-A signal generator and a Model 1232-A tuned-amplifier null detector. An oscillator frequency of 1 kHz was used for all except the third NaSCN reaction where 2 kHz was used. A Tronac Model PCT-1000A constant-temperature oil bath was set at  $24.900 \pm 0.002^\circ$  for kinetic measurements and at  $25.000 \pm 0.002^\circ$  for conductance measurements by a calibrated platinum-resistance thermometer and Mueller bridge. The short- and long-term drift of the oil bath was judged to be within  $\pm 0.002^\circ$  of the set value.

**Chemicals.** Acetonitrile for measurements of the limiting conductance and ion association of tetraethylammonium chloride was

(1) H. L. Yeager and B. Kratochvil, *J. Phys. Chem.*, **73**, 1963 (1969).

purified by the method described in ref 1. For the kinetic measurements by conductance, acetonitrile purified by procedure one of Coetzee<sup>2</sup> was used because it resulted in less "background" reaction with *n*-butyl iodide. *n*-Butyl iodide (Eastman Organic Chemicals) was distilled under vacuum. Tetraethylammonium chloride (Eastman Organic Chemicals) and tetraethylammonium bromide (Eastman Organic Chemicals) were recrystallized from 70% methyl acetate-acetonitrile. The purified  $\text{NEt}_4\text{Cl}$  was analyzed by precipitation of  $\text{AgCl}$  in water (100.1, 100.0%). Sodium bromide (Shawinigan Reagent Grade) was recrystallized from 95% ethanol, potassium bromide (Baker Analyzed Reagent) from 80% methanol-water, and sodium thiocyanate (Baker and Adamson Reagent Grade) and potassium thiocyanate (Fisher) from acetonitrile. Analysis of the purified sodium thiocyanate by titration with standard silver nitrate solution gave a purity of 99.9%.

**Procedure for Kinetic Measurements by Conductance.** About 800 ml of acetonitrile was weighed into the conductance flask and brought to thermal equilibrium in the bath. The salt for the reaction, weighed to  $\pm 0.01$  mg in a small glass cup, was dropped into the flask, and the solution resistance was monitored until a stable value was obtained (typically 2000 to 7000  $\Omega$ ). *n*-Butyl iodide was added with a calibrated 2- or 5-ml pipet and the time of addition recorded. The solution resistance was measured frequently for the first few half-lives of reaction, then, after ten half-lives, occasionally for a few days to obtain the rate of the small background reaction that always occurred. The initial *n*-butyl iodide concentration was typically at least ten times greater than the initial salt concentration so the reaction was approximately pseudo-first order. Care was taken throughout to minimize exposure of solvent and reagents to air.

**Procedure for Kinetic Measurements by Titration.** Rate constants for several reactions were also measured at concentrations from 0.02 to 0.2 *M* by a conventional titration method. Weighed quantities of the salt and *n*-butyl iodide (delivered with a 1-ml syringe) were added to a flask containing a weighed quantity ( $\sim 100$  ml) of acetonitrile in a water bath at  $24.90 \pm 0.01^\circ$ . The reactions were allowed to proceed until only about 10% of the nucleophile had reacted so that the rate constant would reflect the degree of ion association of the nucleophile salt. The mixture was poured into 200 ml of cold deionized water to quench the reaction and immediately washed twice with 200 ml of toluene to remove organic material.

For the reactions involving thiocyanate, the iodide concentration of the quenched mixture was measured by potentiometric titration with silver nitrate solution using a silver wire indicating electrode. The aqueous mixture was saturated with  $\text{Ba}(\text{NO}_3)_2$  before titration to minimize coprecipitation of  $\text{AgSCN}$ .

For the reactions involving chloride as the nucleophile where the effect of association is less, a more accurate chloride measurement after quenching was desired. For this reason the aqueous mixture of chloride and iodide salts was evaporated to about 20 ml and separated on a 25-cm column of Dowex-1 ion-exchange resin with first 0.4 *M* then 2.0 *M*  $\text{NaNO}_3$ . The separated iodide was collected and titrated with standard silver nitrate.

The rate constants for all reactions were calculated according to eq 1.

## Calculations

**Rate Constants from Conductance Data.** The general rate equation for a second-order irreversible reaction is

$$\frac{2.303}{b_0 - a_0} \log \frac{a_0(b_0 - x)}{b_0(a_0 - x)} = kt \quad (1)$$

where  $a_0$  and  $b_0$  are initial concentrations,  $x$  is the product concentration at time  $t$ , and  $b_0 > a_0$ . For our application *n*-butyl iodide is represented by  $b$ , the nucleophile by  $a$ , and iodide by  $x$ .

Since conductance is a linear physical property of the solution over small concentration ranges

$$f_x = (L - L_0)/(L_\infty - L_0)$$

where  $f_x$  is the fraction of reaction relative to the reactant of lowest concentration and  $L$  is the conductance at time  $t$ .  $L_0$  and  $L_\infty$  are the initial and final solution

(2) J. F. Coetzee, *Pure Appl. Chem.*, **13**, 429 (1966).

conductances. Because  $f_x = x/a_0$ ,  $x = a_0[(L - L_0)/(L_\infty - L_0)]$ . Substitution for  $x$  in eq 1 then gives eq 2,

$$\frac{2.303}{b_0 - a_0} \log \left[ \frac{1 - \frac{L - L_0}{L_\infty - L_0} \frac{a_0}{b_0}}{1 - \frac{L - L_0}{L_\infty - L_0}} \right] = k_2't \quad (2)$$

where the rate constant is symbolized by  $k_2'$  to signify an observed rate.

Equation 2 assumes that the observed conductance change is due entirely to the second-order reaction of interest. In the systems studied, however, a small but measurable background conductance change always occurred. This change corresponded to a reaction that was first order with respect to *n*-butyl iodide concentration, very slow relative to the reactions of interest, independent of water concentration in the acetonitrile, and relatively constant for different batches of acetonitrile. The background reaction undoubtedly involves production of ions from neutral molecules, so although it occurs at a negligible rate compared with the second-order reaction under study, a correction must be applied because the solution conductance is highly sensitive to it. The correction is made by subtracting the background conductance change from the measured conductance change

$$L' - L_0' = (L - L_0) - (L'' - L_0'') \quad (3)$$

where  $L - L_0$  is the measured conductance change,  $L'' - L_0''$  is the contribution of background reaction to conductance change, and  $L' - L_0'$  is the conductance change reflecting the reaction of interest. The  $L' - L_0'$  values obtained are substituted for the  $L - L_0$  values in eq 2.

From the knowledge that the background rate is first order in *n*-butyl iodide and very slow relative to the second-order reaction, an evaluation of  $L'' - L_0''$  for each conductance-time measurement was made as follows. For the background reaction

$$dL''/dt = Bk_1(b) = Bk_1(b_0 - x) \quad (4)$$

where  $Bk_1$  is the product of a sensitivity factor of the background reaction to conductance and its rate constant. With the assumption that the displacement reaction under study is pseudo-first order, the relation

$$x = a_0(1 - e^{-b_0k_2't})$$

holds. Substituting this value for  $x$  in eq 4, integrating, and evaluating between the limits for  $L''$  from  $L_0''$  to  $L''$ , and for  $t$  from 0 to  $t$ , gives

$$L'' - L_0'' = Bk_1 \left[ (b_0 - a_0)t + \frac{a_0}{b_0k_2'} (1 - e^{-b_0k_2't}) \right] \quad (5)$$

For evaluation of  $L'' - L_0''$  at any time  $t$ , first the rate of conductance change must be measured after ten half-lives of the main reaction. At this point, from eq 4,  $dL/dt = dL''/dt = Bk_1(b_0 - a_0)$ . From this the product  $Bk_1$  is calculated and used in all subsequent calculations. For any conductance value at any time  $t$ ,  $Bk_1$  and an estimated value of  $k_2'$  are substituted in eq 5 to yield a value for  $L'' - L_0''$  that in turn is substituted in eq 3. The resulting  $L' - L_0'$  value is then used in eq 2. The least-squares slope of the line ( $y = k_2't$ ) formed by these points is taken to be the observed

rate,  $k_2'$ . Unless otherwise indicated, all points from 10 to 70% reaction were used for measurement of the least-squares slope. If the original approximation of  $k_2'$  used in eq 5 differs from the value thus determined, the process is repeated with the new  $k_2$  value substituted in eq 5. A value of  $L_\infty$  was obtained from measurements made after ten half-lives of the reactions and then corrected for the contribution from the background reaction by the method just described. All calculations described above were carried out by computer.

A special method is required to obtain a value for  $L_0'$  because the solution requires time to equilibrate after the addition of *n*-butyl iodide. Also, for about the first 15 min the conductance increases comparatively rapidly, owing apparently to a trace impurity in the reaction mixture. To circumvent this interference, an extrapolation procedure was generally used to obtain  $L_0'$ . Since the reactions especially in the initial stages are pseudo-first order

$$\log(L_\infty' - L') = \log(L_\infty' - L_0') - \frac{b_0 k_2 t}{2.303} \quad (6)$$

A plot of  $\log L_\infty' - L'$  vs.  $t$  gives a straight line for data taken after the initial 15 min. Extrapolation of this line to  $t = 0$  yields an intercept equal to  $\log(L_\infty' - L_0')$ , from which  $L_0'$  can be calculated.

Another method of determining  $L_0$  is useful in some circumstances. Equation 2, expressed in the form  $y = k_2' t$ , has an intercept of zero. Consequently, the correct  $L_0'$  can be found by successive approximations of  $L_0'$  in eq 2 until a least-squares intercept of zero results from the rate data. This method was used to find  $L_0'$  for reactions involving NaSCN, where interference was more pronounced during the first portions of the reactions, and points between 40 and 80% reaction were used to determine  $L_0'$  and  $k_2'$ .

**Ion Association from Conductance Data.** Since ion association influences the magnitude of an observed rate, it is desirable to know the extent of association of the reactant nucleophile. Equation 7 shows how to obtain this information from the initial and final solution conductivities

$$\frac{L_0'}{L_\infty'} = \frac{\Lambda_{MA} \alpha_{A^-}}{\Lambda_{MI} \alpha_{I^-}} \quad (7)$$

where  $\Lambda$  is the salt conductivity expected,  $\alpha_{A^-}$  is the fraction of nucleophilic anion that is unassociated at the beginning of the reaction, and  $\alpha_{I^-}$  is the fraction of the displaced anion that is unassociated at the end of the reaction. In this study the displaced ion was always iodide, and the association constants for the iodide salts used were known from conventional conductance measurements: for NaI<sup>3</sup> and KI,<sup>4</sup>  $K_A = 0$ ; and for Et<sub>4</sub>NI,<sup>5</sup>  $K_A = 5$ . After adjustment of these values for activity-coefficient effects at the concentrations used,  $\alpha_{I^-}$  was calculated for each reaction. Limiting ion conductivities were used in eq 7 for the  $\Lambda$  values of the salts, except for the NaSCN reactions. These were calculated from the following single-ion conductivities:

(3) R. P. T. Tompkins, E. Andalafit, and G. J. Janz, *Trans. Faraday Soc.*, **65**, 1906 (1969).

(4) G. J. Janz, A. E. Marcinkowsky, and I. Ahmad, *Electrochim. Acta*, **9**, 1687 (1964).

(5) G. Kortum, S. D. Hokhale, and H. Wilski, *Z. Phys. Chem.*, (Frankfurt am Main), **4**, 86 (1955).

84.8,<sup>6</sup> 76.9,<sup>6</sup> and 83.6<sup>6</sup> for NEt<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>; and 100.7, 100.7,<sup>6</sup> 102.4,<sup>6</sup> and 113.4<sup>7</sup> for Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and SCN<sup>-</sup>. The value for chloride was determined in this work from conventional high-precision conductance measurements of NEt<sub>4</sub>Cl. The use of limiting ion conductivities in eq 7 was considered justifiable for most of the reactions studied here. The magnitude of the error introduced by this approximation is discussed later. A more precise value of  $\Lambda$  was calculated when necessary from the Fuoss-Onsager equation<sup>8</sup> in the form

$$\Lambda = \Lambda_0 - S(C\alpha)^{1/2} + EC\alpha \ln C\alpha + JC\alpha$$

where  $S$ ,  $E$ , and  $J$  are constants determined by high-precision conductance measurements and  $C$  is the total salt concentration. Since  $\alpha_{A^-}$  is the value ultimately sought in eq 7, the calculation requires an iteration procedure. The  $\alpha_{A^-}$  values for the NaSCN reactions were calculated using this procedure.

With  $\alpha_{A^-}$  from eq 7 and only the unassociated nucleophile assumed to be reactive,<sup>9</sup> the observed rate was corrected for the effect of ion association by

$$k_2 = k_2' / \alpha_{A^-} \quad (8)$$

where  $k_2$  is the actual rate constant of the displacement reaction of interest.

The ion association constant of the nucleophile salt can also be calculated from  $\alpha_{A^-}$ . The conditional association constant for the process  $M^+ + A^- \rightleftharpoons M^+A^-$  is found from

$$K_A' = \frac{[M^+A^-]}{[M^+][A^-]} = \frac{1 - \alpha_{A^-}}{a_0 \alpha_{A^-}^2} \quad (9)$$

The value of  $K_A'$  is dependent on ionic strength. The thermodynamic association constant  $K_A$  is given by

$$K_A = \frac{[M^+A^-]}{[M^+][A^-]} \frac{1}{(\gamma_{\pm})^2}$$

where  $\gamma_{\pm}$  is the concentration-dependent activity coefficient and the activity coefficient of the neutral ion pair is assumed to be unity. The concentration dependence of  $K_A'$  is then given by

$$K_A' = (\gamma_{\pm})^2 K_A \quad (10)$$

Values for  $\gamma_{\pm}$ , and therefore of  $K_A'$ , are more concentration dependent in most nonaqueous solvents than in water. For evaluation of thermodynamic association constants, activity coefficients were calculated from the extended Debye-Hückel<sup>10</sup> expression, with  $z_i = 1$ ,

$$\log \gamma_i = \frac{-353 z_i^2 \mu^{1/2}}{D^{3/2} + 2.91 \times 10^8 \mu^{1/2} D a} \quad (11)$$

$D = 36$ ,  $a = 4 \times 10^{-8}$  cm, and  $\mu = C_{MA} \alpha_{A^-}$ .

## Results and Discussion

Results of the reactions as measured by conductance are listed in Table I. The estimated accuracies of the measurement of rate constant  $k_2$ , included with each

(6) C. H. Springer, J. F. Coetzee, and R. L. Kay, *J. Phys. Chem.*, **73**, 471 (1969).

(7) H. L. Yeager and B. Kratochvil, *J. Phys. Chem.*, **74**, 963 (1970).

(8) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, New York, N. Y., 1959.

(9) W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, **86**, 261 (1964).

(10) J. F. Coetzee, *Progr. Phys. Org. Chem.*, **4**, 45 (1967).

Table I. Results of Nucleophilic Displacement Reactions in Acetonitrile at 24.9° by High-Precision Conductance

Nucleophile	Initial concn [MX] <sub>0</sub> × 10 <sup>4</sup> [RI] <sub>0</sub> × 10 <sup>2</sup>	L <sub>0</sub> ' × 10 <sup>4</sup> , Ω <sup>-1</sup>	L <sub>∞</sub> × 10 <sup>4</sup> , Ω <sup>-1</sup>	t <sub>∞</sub> × 10 <sup>-4</sup> , sec	Bk <sub>1</sub> × 10 <sup>11</sup>	% ΔL <sub>RX</sub> <sup>a</sup>	% ΔL <sub>BG</sub> <sup>b</sup>	k <sub>2</sub> ' <sup>c</sup>	α <sub>A</sub> <sup>-</sup>	k <sub>2</sub> <sup>d</sup>	K <sub>A</sub> '	K <sub>A</sub>
NEt <sub>4</sub> Cl	4.920 2.366	1.231532	1.248943 10.835	2.3	1.367	0.047	3.935 ±0.003 × 10 <sup>-3</sup>	0.994	3.96 ±0.08 × 10 <sup>-3</sup>	12	14	
NEt <sub>4</sub> Cl	5.870 1.882	1.460300	1.480575 9.0250	2.4	1.361	0.027	3.996 ±0.001 × 10 <sup>-3</sup>	0.993	4.02 ±0.06 × 10 <sup>-3</sup>	12	14	
NEt <sub>4</sub> Cl	16.88 2.063	4.017000	4.083399 9.0360	2.7	1.641	0.012	3.930 ±0.005 × 10 <sup>-3</sup>	0.987	3.98 ±0.03 × 10 <sup>-3</sup>	8	11	
NEt <sub>4</sub> Br	10.16 1.936	2.478726	2.509504 17.10	2.7	1.207	0.035	3.422 ±0.007 × 10 <sup>-3</sup>	0.993	3.45 ±0.06 × 10 <sup>-3</sup>	7	9	
KBr	8.674 2.200	2.068553	2.145674 9.628	2.0	3.708	0.020	3.312 ±0.002 × 10 <sup>-3</sup>	0.973	3.40 ±0.02 × 10 <sup>-3</sup>	33	40	
NaBr	6.302 1.988	1.459193	1.521384 10.353	1.9	4.236	0.025	3.281 ±0.001 × 10 <sup>-3</sup>	0.969	3.38 ±0.02 × 10 <sup>-3</sup>	53	64	
NaBr	9.147 2.119	2.066380	2.177577 11.120	2.0	5.359	0.022	3.224 ±0.002 × 10 <sup>-3</sup>	0.958	3.37 ±0.02 × 10 <sup>-3</sup>	50	61	
KSCN	5.831 5.520	1.525436	1.459865 18.7995	2.2	-4.447	0.148	5.642 ±0.001 × 10 <sup>-4</sup>	0.988	5.71 ±0.12 × 10 <sup>-4</sup>	20	24	
KSCN	7.883 5.280	2.032800	1.948854 19.356	2.6	-4.258	0.129	5.664 ±0.002 × 10 <sup>-4</sup>	0.986	5.74 ±0.10 × 10 <sup>-4</sup>	18	22	
NaSCN	11.72 5.970	2.708907	2.740116 19.500	2.0	1.067	0.084	5.45 ±0.07 × 10 <sup>-4</sup>	0.928	5.87 ±0.30 × 10 <sup>-4</sup>	71	92	
NaSCN	17.03 2.031	3.795590	3.929635 43.3148	2.2	3.484	0.048	5.17 ±0.02 × 10 <sup>-4</sup>	0.903	5.73 ±0.07 × 10 <sup>-4</sup>	70	92	
NaSCN	27.28 5.528	5.650000	6.098698 25.3600	2.6	7.880	0.062	4.95 ±0.01 × 10 <sup>-4</sup>	0.864	5.73 ±0.04 × 10 <sup>-4</sup>	67	93	

<sup>a</sup> The relative conductance change caused by the reaction of interest. % ΔL<sub>RX</sub> = [(L<sub>∞</sub>' - L<sub>0</sub>')/L<sub>0</sub>'] × 100. <sup>b</sup> The relative conductance change caused by the background reaction. % ΔL<sub>BG</sub> = [(L<sub>∞</sub>'' - L<sub>0</sub>'')/L<sub>0</sub>'] × 100. <sup>c</sup> The uncertainties indicated with the observed rates are the standard deviations of the least-squares slopes of the data applied to eq 2. <sup>d</sup> The uncertainties in the corrected rate constants are estimates taking into account the background reaction. See discussion of sources of errors in text.

value, were determined from the relative magnitudes of %ΔL<sub>RX</sub> and %ΔL<sub>BG</sub> as described below.

The reaction between tetraethylammonium chloride and *n*-butyl iodide illustrates the sensitivity of the technique, as the single-ion conductivities of Cl<sup>-</sup> and I<sup>-</sup> in acetonitrile, 100.7 and 102.4, differ by only 1.7%, and the limiting-ion conductivities of the corresponding tetraethylammonium salts differ by less than 1%. Nevertheless, values for k<sub>2</sub>' of high precision were obtained for these reactions. In addition to differences in values of λ<sup>0</sup> for Cl<sup>-</sup> and I<sup>-</sup>, differences in the association constants of NEt<sub>4</sub>Cl and NEt<sub>4</sub>I increase the sensitivity of the method somewhat. This point is illustrated by the third NEt<sub>4</sub>Cl run in Table I, in which the nucleophile concentration was three times greater than in the first two. The greater ion association of NEt<sub>4</sub>Cl at higher concentration increased %ΔL<sub>RX</sub>. This, along with a decrease in %ΔL<sub>BG</sub>, improves the estimated accuracy of this rate determination. The rate constants for the three NEt<sub>4</sub>Cl reactions corrected for ion association agree closely. All values differ from each other by less than the estimated uncertainty and are within 1% of the mean value of 3.99 × 10<sup>-3</sup> M<sup>-1</sup> sec<sup>-1</sup>.

The K<sub>A</sub> values obtained for NEt<sub>4</sub>Cl are 14, 14, and 11.

Since the salt concentration in the third reaction was greater than in the first two, ion association was greater, and for this reason the K<sub>A</sub> value from this run is probably the most accurate. Values of K<sub>A</sub> for NEt<sub>4</sub>Cl determined by conventional high-precision conductance are 8 ± 2 and 3 ± 2 (Table II). The salt concentrations were higher in the first of these two runs, and this K<sub>A</sub> agrees closely with that calculated from the third NEt<sub>4</sub>Cl rate measurement.

The bromide reactions illustrate how changing the cation of the nucleophile salt, and thereby the amount of ion association, can induce a greater conductance change for a given reaction. Although the single-ion conductivities of chloride and bromide are the same in acetonitrile, a smaller %ΔL<sub>RX</sub> resulted from the NEt<sub>4</sub>Br reaction than from the NEt<sub>4</sub>Cl reactions owing to fewer ion pairs in the bromide case. Changing the cation of the nucleophile salt from Et<sub>4</sub>N<sup>+</sup> to K<sup>+</sup> to Na<sup>+</sup> caused %ΔL<sub>RX</sub> to increase appreciably. Values of k<sub>2</sub> for the bromide reactions agree with each other within their estimated uncertainties. The background contributions to the KBr and NaBr reactions are sufficiently small to assign an estimated uncertainty of less than 1% to these rate constants. Each of the k<sub>2</sub> values for

**Table II.** Conductance Data for  $\text{NEt}_4\text{Cl}$  in Acetonitrile at 25 $^\circ\text{a}$ 

Run 1			Run 2		
10 $^4$ C	$\Lambda$ 10 $^8$ $k_0 = 5.30$	$\Delta\Lambda$	10 $^4$ C	$\Lambda$ 10 $^8$ $k_0 = 1.55$	$\Delta\Lambda$
7.523	174.17	-0.02	5.001	176.43	0.01
10.423	172.08	0.01	8.323	173.63	-0.01
14.423	169.85	0.04	12.172	171.01	-0.02
18.835	167.22	-0.03	15.079	169.32	-0.01
22.411	165.56	0.00	17.877	167.85	0.01
26.654	163.75	-0.02	20.703	166.48	0.02
31.956	161.77	0.04	23.926	165.02	0.03
35.612	160.44	-0.02	26.990	163.66	-0.03

  

Conductance Parameters and Averaged Conductance Values				
	$\Lambda_0$	$\bar{a}$	$K_A$	$\sigma\Lambda$
Run 1	185.63 $\pm$ 0.09	3.2 $\pm$ 0.4	8 $\pm$ 2	0.03
Run 2	185.51 $\pm$ 0.06	2.2 $\pm$ 0.4	3 $\pm$ 2	0.03

<sup>a</sup> Procedure and data treatment described in ref 1. The conductance equation used is the Fuoss-Onsager equation<sup>8</sup> of the form  $\Lambda = \Lambda_0 - S(C\alpha)^{1/2} + EC\alpha \log C\alpha + JC\alpha - K_A C\alpha \Lambda f^2$ .

bromide attack are within 0.6% of the mean value of  $3.38 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ . Again, an increase in NaBr concentration can be seen to increase  $\% \Delta L_{\text{RX}}$  as a result of increased ion association.

The association constant of 9 for  $\text{NEt}_4\text{Br}$  is in line with the trend for tetramethylammonium salts of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  in acetonitrile.<sup>11</sup> From the KBr and NaBr reactions,  $K_A = 40$  for KBr in acetonitrile and 64 and 61 for NaBr. These association constants cannot be measured by conventional conductance techniques because of limited solubility and slow rates of dissolution of KBr and NaBr in this solvent. Thus conductance-rate techniques provide a unique means of measuring association of some salts.

The thiocyanate reaction with *n*-butyl iodide represents a different case in that the  $\text{SCN}^-$  nucleophile has a higher single-ion conductivity (113.4) than iodide (102.4) in acetonitrile at 25 $^\circ$ . Accordingly the solution conductance would be expected to decrease with time for an unassociated thiocyanate salt, though slight association would tend to diminish the net conductance change. Association was minimized by running the KSCN reactions at low salt concentrations; the conductance of the solution did decrease with time (Table I). For the first KSCN run  $\% \Delta L_{\text{RX}}$  was larger than that for the second, as predicted on the basis of effects of concentration on association. The  $k_2$  values agree within the estimated uncertainty of about 2%. The ion association constants, 24 and 22, compare reasonably with the value of  $26 \pm 2$  obtained by the conventional conductance method.<sup>7</sup>

The NaSCN reactions illustrate convincingly the striking effect ion association can have on net conductance changes throughout a reaction. Ion association of NaSCN is sufficiently large to cause the solution conductance to increase while completely dissociated NaI is being formed, even though the more mobile  $\text{SCN}^-$  ion is being replaced by  $\text{I}^-$ . Thus the direction of conductance change observed for the KSCN reaction is reversed, notwithstanding that the displacement reaction under study is the same. For the first NaSCN reaction in Table I, 8% of the total conductance change is caused by background reaction, giving a

relatively high uncertainty in  $k_2$ . Thus the precision of the method suffers when single-ion conductivity differences in the nucleophile and leaving anion are nearly cancelled by differences in ion association. (An earlier NaSCN reaction, not shown in Table I, with a NaSCN concentration of  $1.026 \times 10^{-3} \text{ M}$ , resulted in essentially no conductance change throughout most of the reaction.) Higher salt concentrations result in greater ion association and a several-fold increase in  $\% \Delta L_{\text{RX}}$ . The  $k_2$  values for these runs have estimated uncertainties of about  $\pm 1\%$  and agree extremely well with each other as well as with those calculated from the KSCN reactions. Although the absolute magnitude of the background was the same for the NaSCN and KSCN reactions, for the NaSCN reactions the values of  $\% \Delta L_{\text{BG}}$  are smaller because higher salt concentrations, and therefore higher  $L_0$  values, were used in their calculations. This illustrates, as did the third  $\text{NEt}_4\text{Cl}$  reaction, an advantage of higher salt concentrations in decreasing the rate uncertainty.

The average of the association constants obtained from the three NaSCN reactions, 92, compares favorably with the value of  $87 \pm 4$  measured by conventional conductance.<sup>12</sup> Although the rate constant from the first NaSCN reaction is subject to relatively large error, the corresponding association constant should not be, because the accuracy of the calculation of  $K_A$  does not depend on the magnitude of  $\% \Delta L_{\text{RX}}$ .

**Sources of Error.** The largest source of uncertainty in rate constants determined by the above method is related to measurement of the background reaction. This reaction is very slow, it is not affected by the addition of water, and its rate is relatively constant for more than 3 weeks. It could be reduced in magnitude by varying the method of solvent purification, but never was eliminated. Improved accuracy in rate measurements would be expected for reactions where  $\% \Delta L_{\text{BG}}$  is small with respect to  $\% \Delta L_{\text{RX}}$ . With the accuracy of  $Bk_1$  (eq 5) conservatively assumed to be  $\pm 50\%$ , specific estimations of the error in the  $k_2$  values listed in Table I can be made. On this basis, for example, a reaction in which the ratio  $\% \Delta L_{\text{BG}} / \% \Delta L_{\text{RX}}$  is 0.03 should give a precision in  $k_2$  on the order of  $\pm 2.0\%$ , while one in which the ratio is 0.005 should be accurate to within  $\pm 0.5\%$ .

This uncertainty in  $Bk_1$  does not have a significant effect on the association constants. Although it is difficult to assign magnitudes to the errors in the  $K_A'$  and  $K_A$  values, the main sources of error are apparent. Conditions of small association ( $\alpha$  close to 1) lead to greater uncertainty in  $K_A'$  values calculated from eq 9. Values of  $K_A$  also will contain an error contribution from uncertainties in the activity coefficients used in eq 10. Since, however, the salt concentrations used for the conductance method are relatively low,  $\gamma$  values calculated from eq 11 are probably comparatively accurate and add only a small error to the  $K_A$  values. Another possible source of error in the association constants arises from uncertainties in the limiting-ion conductivities used in eq 7. The single-ion conductivities used in this study were judged accurate to within about  $\pm 0.1$  conductance unit ( $\pm 1$  ppt). This uncertainty would have a significant effect on the resulting  $K_A$  only if ion association was slight ( $\alpha$  close to 1). The esti-

(11) B. Kratochvil and H. L. Yeager, *Top. Curr. Chem.*, **27**, 24 (1972).(12) J. K. Senne and B. Kratochvil, *Anal. Chem.*, **43**, 79 (1971).

mated uncertainty in the  $L_0'$  values used here had no significant effect on either association constants or observed rates since (from eq 2) the observed rate is taken from the slope of the line, not the individual points.

Except for the NaSCN reactions, ratios of  $\Lambda_0$  values of the salts were taken in eq 7 as approximations of the true conductance ratios at the concentrations used. The validity of this assumption was tested for several reactions by comparing the  $\alpha_{A^-}$  values determined in this way with those obtained from  $\Lambda$  values calculated *via* the Fuoss–Onsager equation. It was found that the magnitude of the error in  $\alpha_{A^-}$  using the  $\Lambda_0$  approximation increases with increased salt concentrations, with increased ion association of one salt, and as the difference in the two  $\Lambda_0$ 's increases. However, only for the NaSCN reactions would the resulting error in  $\alpha_{A^-}$  be of any significance. For the reaction involving  $9.147 \times 10^{-4} M$  NaBr, the use of  $\Lambda_0$  values in place of  $\Lambda$  in eq 7 would result in less than a 0.2% error. Except for the NaSCN reactions, this source of error in  $\alpha_{A^-}$  is even less in the other reactions. For the NaSCN reactions,  $\Lambda$  values calculated by the Fuoss–Onsager expression were used because the expected errors from use of  $\Lambda_0$ 's became significant: 0.6, 0.9, and 1.2% expected error at  $1.172 \times 10^{-3}$ ,  $1.703 \times 10^{-3}$ , and  $2.728 \times 10^{-3} M$  NaSCN concentrations.

If reaction conditions are not properly adjusted another source of error is possible. It has been assumed that  $\alpha_{A^-}$  remains constant throughout the reaction. If  $\alpha_{A^-}$  changes the instantaneous rate will change in proportion. It can be shown that at any point during reaction,  $\alpha_{A^-} = 1/(K_A[M^+] + 1)$ . For the reactions studied,  $[M^+]$  changed little during reaction and, therefore,  $\alpha_{A^-}$  remained almost constant; the worst case was one NaSCN reaction where  $\alpha_{A^-}$  decreased by 1.7% from start to reaction completion. However, for other salts or solvents where ion association is greater, extra care must be taken in the selection of reaction conditions. For example, in a reaction of the type studied, but with a salt having a  $K_A$  of 500 and a concentration of  $2.7 \times 10^{-3} M$ , a decrease in  $\alpha_{A^-}$  of about 25% from start to finish would result if the product salt was completely dissociated. This would be reflected as curvature of the line formed upon application of the data to eq 2. Two ways of circumventing this problem are possible. In the above example, lowering the salt concentration to  $5 \times 10^{-4} M$  would reduce the change in  $\alpha_{A^-}$  to 2.5%, making possible a satisfactory  $k_2'$  measurement. Alternatively,  $k_2'$  values could be obtained by using data taken at the initial fraction of reaction only, because in this region  $\alpha_{A^-}$  will be known or determined from eq 7. With these precautions it should be possible to extend the method to reaction systems involving much greater ion association than was experienced here.

Another possible source of error would occur if the reaction stopped at some equilibrium position short of completion. Such an occurrence might have only a small effect on the resulting  $k_2'$  value if the data points used were in the early stage of the reaction, but could lead to large errors in the  $\alpha_{A^-}$  value and the association constant if eq 7 were applied directly to the data. Equation 7 applied to this situation should be modified to

$$\frac{L_0'}{L_\infty'} = \frac{\Lambda_{MA} \alpha_{A^-}}{\Lambda_{MI} \alpha_{I^-}} f_{\text{equil}} \quad (12)$$

where  $f_{\text{equil}}$  is the fraction of complete reaction at which equilibrium is attained. This, of course, means that another variable in addition to  $\alpha_{A^-}$  is introduced. Nevertheless, if all other variables in eq 12 are known or can be measured independently, it is possible to evaluate  $f_{\text{equil}}$ , which would be useful kinetic information. From it an equilibrium constant could be calculated that, divided by the forward rate, would yield the rate of the reverse reaction. This would provide a means of determining rates of reactions otherwise difficult or impossible to measure.

For the reactions studied use of eq 7 is valid, as all the reactions were estimated on the basis of rate data to go to at least 99.9% completion.

**Use of the Method at Other Temperatures.** Obviously eq 2, 3, and 5 apply equally well to measurement of a rate  $k_2'$  at any temperature. However, for determining  $\alpha_{A^-}$  and then  $k_2$ , the application of eq 7 to data taken at temperatures other than 25° warrants careful consideration. When the  $\Lambda$ 's or  $\lambda$ 's of the ions involved are known at the temperatures of interest, the calculation of  $\alpha_{A^-}$  from eq 7 is straightforward. However, the temperature dependence of these constants in many nonaqueous solvents has not yet been studied. For water<sup>13</sup>

$$\lambda^\circ = \lambda^\circ_{25^\circ} [1 + z(T - 25)] \quad (13)$$

where  $T$  is expressed in °C and  $z$  is a constant for each ion, ranging from 0.019 to 0.021 for most ions except  $H^+$  and  $OH^-$ . This temperature dependence results mainly from a decrease in viscosity of the solvent with increasing temperature, the slight variation of the  $z$  values with various ions being due to specific interactions of the solvent with ions.

For some aprotic solvents unknown values of  $z$  may be assumed to be nearly equal for the ions involved. This approximation obviously cannot be used in protic solvents such as water, where specific interaction of solvent with ions through hydrogen bonding is important. Solvent–ion interactions, especially solvent–anion interactions, in aprotic solvents of moderate dielectric constant such as acetonitrile are less specific, however, and the assumption that the  $z$  values of anions in these solvents are equal is probably more valid. With this assumption, from eq 13

$$\frac{\Lambda^\circ_{T,MA}}{\Lambda^\circ_{T,MI}} = \frac{\Lambda^\circ_{25^\circ,MA}}{\Lambda^\circ_{25^\circ,MI}}$$

Consequently, eq 7 might sometimes be applied to the calculation of  $\alpha_{A^-}$  at any temperature by use of  $\Lambda^\circ$  or  $\lambda^\circ$  obtained at 25°. As small inequalities for  $z$  values of anions likely do exist, even in dipolar aprotic solvents, the assumption just described would be more valid for reactions run at temperatures closer to the temperature at which the single-ion conductivities were measured.

**Effect of Ion Association on Observed Rates.** With accurate values of  $k_2$  it is now possible to quantitatively assess the effect of ion association on rates at higher nucleophile concentrations and thereby test the assumption that only the free nucleophile anion is reactive. This assessment was accomplished by measuring the rates of several  $NEt_4Cl$ ,  $KSCN$ , and  $NaSCN$  reactions with *n*-butyl iodide in acetonitrile at 24.9° by con-

(13) S. Glasstone, "Textbook of Physical Chemistry," Van Nostrand, New York, N. Y., 2nd ed, 1946, p 895.

ventional titration methods at salt concentrations from 0.02 to 0.2 *M*. The observed rates are shown in Table III. All were lower than the corresponding  $k_2$  values

**Table III.** Rates of Displacement Reactions with *n*-Butyl Iodide at Higher Nucleophile Concentrations in Acetonitrile at 24.9°

Nucleophile	Concn	$k_2'$	$\alpha_{A^-}$ <sup>a</sup>	$K_A$ <sup>b</sup>	$K_A$ <sup>c</sup>
NEt <sub>3</sub> Cl	0.2196	$3.10 \times 10^{-3}$	0.777	1.7	9
	0.1015	$3.30 \times 10^{-3}$	0.827	2.4	10
	0.0516	$3.45 \times 10^{-3}$	0.865	3.5	11
	0.0208	$3.66 \times 10^{-3}$	0.917	4.7	11
KSCN	0.1123	$3.57 \times 10^{-4}$	0.623	8.6	32
	0.0313	$4.53 \times 10^{-4}$	0.791	10.7	27
NaSCN	0.1100	$2.42 \times 10^{-4}$	0.422	29	92
	0.0296	$3.41 \times 10^{-4}$	0.595	39	86

<sup>a</sup>  $\alpha = k_2'/k_2$ , where  $k_2$  ( $3.99 \times 10^{-3} M^{-1} sec^{-1}$  for the chloride reaction and  $5.73 \times 10^{-4} M^{-1} sec^{-1}$  for the thiocyanate reaction) was determined by the conductance method. <sup>b</sup> Calculated from  $\alpha$  by eq 9. <sup>c</sup> Calculated by eq 10, with activity coefficients calculated by eq 11.

determined by the conductance method. The assumption that only the free anion is reactive can be tested by setting  $\alpha_{A^-} = k_2'/k_2$  and calculating an association constant from this value. An additional assumption made in this treatment is that the rate of the displacement reaction is not affected significantly by a change in ionic strength. This assumption probably is valid for reactions of the type studied here.<sup>14</sup> These association constants are shown in Table III along with the calculated thermodynamic association constant  $K_A$ , where

(14) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965, p 221.

the activity coefficients were again calculated by the extended Debye-Hückel equation. The resulting  $K_A$  values agree closely with those previously determined by both the reaction conductance method described here and by normal conductance. These results are consistent with the premise that only the free ion is reactive. Also,  $K_A$  values thus determined support the validity of those determined by reaction conductance and conventional high-precision conductance methods.

### Conclusions

Accurate rate constants corrected for ion-pairing effects can be obtained by high-precision conductance. To maximize the accuracy of the rate measurement, it may be advantageous to select nucleophile salts that are associated. For the reactions studied, uncertainties in rates on the order of  $\pm 1\%$  were obtained through selection of cation and salt concentration. The limit of accuracy in each case is the presence of a small background reaction. Other systems, perhaps less likely to exhibit this complication, may have much smaller uncertainties in the  $k_2$  values obtained.

Also, accurate association constants can be obtained from the conductance-rate data. This feature is particularly valuable for the determination of association constants of slightly soluble salts.

The method should be useful also for the study of systems where the reactivity of the ion pair is in question. The data allow simultaneous measurement of a reaction rate and the degree of association, the interrelation of which indicates the relative reactivity of free and associated anions.

**Acknowledgment.** Financial support by the National Research Council of Canada is gratefully acknowledged.

## Reversible Reactions of Gaseous Ions. VIII. The $t\text{-C}_4\text{H}_9^+$ ( $i\text{-C}_5\text{H}_{12}$ , $i\text{-C}_4\text{H}_{10}$ ) $t\text{-C}_5\text{H}_{11}^+$ System

J. J. Solomon and F. H. Field\*

Contribution from The Rockefeller University,  
New York, New York 10021. Received March 3, 1973

**Abstract:** The equilibrium  $t\text{-C}_4\text{H}_9^+ + i\text{-C}_5\text{H}_{12} \rightleftharpoons t\text{-C}_5\text{H}_{11}^+ + i\text{-C}_4\text{H}_{10}$  has been investigated using the chemical ionization technique at source pressures up to 5 Torr. The existence of equilibrium in the mass spectrometer source was established by extensive pressure and repeller studies and by variation of the partial pressures of  $i\text{-C}_4\text{H}_{10}$  and  $i\text{-C}_5\text{H}_{12}$ . Thermodynamic quantities have been determined from the temperature variation of the equilibrium constant over the temperature range 323–548°K. The following thermodynamic values were obtained:  $\Delta G^\circ_{300} = -2.9$  kcal/mol,  $\Delta H^\circ = -3.6$  kcal/mol, and  $\Delta S^\circ = -2.3$  eu. The heat of formation of the *tert*-pentyl ion was found to be 161 kcal/mol. This value is referred to  $\Delta H_f^\circ(t\text{-C}_4\text{H}_9^+) = 169$  kcal/mol.

Reversible association reactions of gaseous ions have been studied extensively using mass spectrometric techniques by Kebarle,<sup>1</sup> DePaz, Leventhal, and Fried-

(1) (a) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967); (b) A. Good, D. A. Durden, and P. Kebarle, *J. Chem. Phys.*, **52**, 212 (1970); (c) A. J. Cunningham, J. D. Payzant, and P. Kebarle, *J. Amer. Chem. Soc.*, **94**, 7627 (1972).

man,<sup>2</sup> and Field and coworkers.<sup>3</sup> Other workers

(2) M. DePaz, J. J. Leventhal, and L. Friedman, *J. Chem. Phys.*, **51**, 3748 (1969).

(3) (a) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969); (b) D. P. Beggs and F. H. Field, *ibid.*, **93**, 1567 (1971); (c) *ibid.*, **93**, 1576 (1971); (d) F. H. Field and D. P. Beggs, *ibid.*, **93**, 1585 (1971); (e) S. L. Bennett and F. H. Field, *ibid.*, **94**, 5186 (1972); (f) *ibid.*, **94**, 5188 (1972); (g) *ibid.*, **94**, 6305 (1972); (h) *ibid.*, **94**, 8669 (1972).