constants of second-row elements in π radicals. The unrestricted SCFMO method was used to calculate σ–π parameters for a number of molecular fragments. The parameters derived for ^{17}O in the C–O fragment were $Q_{OO}{}^{O} = 55.6$, $Q_{CC}{}^{O} = -16.9$, $Q_{cross}{}^{O} = -13.7$ G (where we have used the sign convention of this paper). These values are close to those derived in the present work. On the other hand a semiempirical estimation of ^{17}O σ–π parameters by Yonezawa, Kawamura, and Kato gives the completely unacceptable values $Q_{OO}{}^{O} = 22$, $Q_{CC}{}^{O} = -75$, $Q_{cross}{}^{O} = -72$ G. As the authors point, out the values calculated by fitting calculated spin densities to observed splitting constants are extremely sensitive to the calculated spin densities. In general it can be concluded that semiempirical correlations of this kind are unreliable except for the comparatively simple case of proton hyperfine splitting constants.

Acknowledgment. We wish to thank Dr. M. T. Melchior for sending us a preprint of his paper on the isotropic hyperfine interaction, and for his constructive criticism of our work. Many of his suggestions as to the content and presentation of our results have been incorporated in this paper.

A Critical Test of the Acree Hypothesis in Nucleophilic Displacement Reactions

Per Beronius and Laszlo Pataki[1]

Contribution from the Division of Physical Chemistry, University of Umeå, Umeå, Sweden. *Received February 10, 1970*

Abstract: In applying kinetic data for bimolecular reactions involving neutral molecules and ionizable species to the Acree equation, $k = k_i\alpha + k_m(1 - \alpha)$, where k is the observed second-order rate constant, k_i and k_m are rate constants for the reactions of ions and ion pairs, respectively, and α is the degree of dissociation, it is generally assumed that k_i and k_m are independent of the ionic strength. Second-order specific rates, k, for the exchange of ^{131}I between methyl iodide and alkali iodides (NaI, KI, RbI, and CsI, respectively) in methanol at 25°, where these salts are associated to only a few per cent, decrease with increasing ionic strength. It is shown that this change is due to kinetic salt effects (changes in activity coefficients of reactants and transition-state complex with ionic strength) as well as changes in ionic association and different reactivities of free and paired ions. For the range of concentration of ionic halide investigated, 2×10^{-4}–8×10^{-3} *M*, the reaction of free halide ions is subject to a negative salt effect of between 3 and 4%. A necessary consequence of the Acree hypothesis is that k_i should be independent of the nature of the cation. It is verified that this is so; the rate constants, k_i, for those exchanges in which NaI, KI, RbI, and CsI, respectively, are involved are in the ratios, 1.001:1.005:0.998:0.995. The degree of association is too insignificant to permit quantitative conclusions concerning the reactivity of paired ions, though the data do not exclude a contribution of ion pairs to the reaction rate.

The Acree hypothesis[2] that the specific rate of certain bimolecular reactions between neutral molecules and ionizable reagents varies with dilution because of different reactivities of free and paired ions has been extensively studied (see ref 3 for reviews on this subject). According to Acree, the observed second-order rate constant, k, may be expressed

$$k = k_i\alpha + k_m(1 - \alpha) \qquad (1)$$

where k_i and k_m are specific rates of reactions of free and paired ions, respectively, and α is the degree of dissociation of the ionic reactant.

Reaction rate data for several isotopic exchange reactions of the type $RY + A^+Y^{*-} \rightleftarrows RY^* + A^+Y^-$, where RY is a neutral molecule and A^+Y^- an ionic reactant, have previously[3b] been treated by means of eq 1 in order to obtain information concerning the reactivities of free and paired ions. In these studies, k_i and k_m have been regarded as independent of the ionic strength. However, it cannot be excluded that especially k_i, the second-order specific rate for exchange between RY and Y^{*-}, may be subject to a nonnegligible dependence on the ionic strength (kinetic salt effect). The main objective of the present research was to examine the possible existence of an effect of this kind. A secondary aim was to investigate whether k_i is independent of the nature of the counterion to Y^- in the ionic reactant, A^+Y^-.

The reactions studied in the present work, *viz.* the exchange of radioiodine between methyl iodide and alkali iodides in dry methanol at 25°, were selected because alkali iodides are only slightly associated in this medium, a fact which facilitates separation of the effect of ionic strength on the reaction rate from the effect of ion-pair formation.

Experimental Section

Reagents. Sodium, potassium, rubidium, and cesium iodides (Merck, Suprapur) were dried at 110° for 2 hr and allowed to cool in a vacuum desiccator.

Carrier-free $^{131}I^-$ was used to label these salts. The radioactive iodine was obtained as sodium iodide in a dilute aqueous sodium thiosulfate solution from the Atomic Energy Establishment, Kjeller, Norway. Potassium, rubidium, and cesium radioiodides were pre-

---

[1] Division of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary.

[2] S. F. Acree, *Amer. Chem. J.*, 48, 352 (1912).

[3] (a) A. Brändström, *Ark. Kemi*, 11, 567 (1957); (b) P. Beronius, *Acta Chem. Scand.*, 23, 1175 (1969).

pared by passing portions of this solution through ion exchangers (Dowex 50W-X8) saturated with the cations in question. Approximately 10 μCi of $^{131}I^-$ was used in each kinetic run.

Methyl iodide was purified by distillation in a column filled with copper pellets to remove hydrogen iodide and elementary iodine. It was stored over mercury in the dark.

Methanol (Merck, Pro analysi) was dried with magnesium methoxide, according to Lund and Bjerrum,[4] and fractionally distilled.

Kinetic Procedure. The exchange reactions, $CH_3I + NaI^* \rightleftarrows CH_3I^* + NaI$, etc., were followed electroanalytically at 25.00 ± 0.02° as described in ref 5, with the exception that the reaction was started by adding methyl iodide to a solution of the ionic radioiodide in the electrolytic cell using a gas-tight microsyringe. Differential weighing of the latter using a microgram balance made it possible to determine the quantity added, approximately 0.4 g, with an estimated uncertainty of less than ±0.1 mg. Determinations of the specific activity of the ionic iodide were made at six different reaction times. The reaction was allowed to proceed for 1.5 half-times of the exchange.

The rate of exchange, R, was calculated from activity–time data[6] as previously described.[5]

Results

A summary of kinetic data for the different alkali iodides investigated is given in Table I, where b and c are the concentrations of methyl iodide and inorganic iodide, respectively, α is the degree of dissociation of the latter, μ is the ionic strength ($c\alpha$), and k is the second-order rate constant defined by the expression $k = R/bc$.

Table I. Kinetic Data for the Exchange of ^{131}I between Methyl Iodide and Alkali Iodides in Methanol at 25°

$b \times 10^2$, M	$c \times 10^4$, M	α	$\mu \times 10^4$	$R \times 10^8$, M sec^{-1}	$k \times 10^3$, M^{-1} sec^{-1}
			NaI		
5.285	79.92	0.991	79.20	136.60	3.234
5.351	39.95	0.995	39.75	69.262	3.240
5.298	19.95	0.997	19.89	34.583	3.272
5.357	9.974	0.998	9.954	17.456	3.267
5.285	5.000	0.999	4.995	8.7705	3.319
5.888	1.997	0.9996	1.996	3.9390	3.350
			KI		
5.344	80.26	0.991	79.54	137.04	3.195
5.238	40.15	0.994	39.91	67.971	3.232
5.287	20.02	0.997	19.96	34.294	3.240
5.328	10.03	0.998	10.01	17.448	3.265
5.353	5.014	0.999	5.009	8.8491	3.297
5.364	2.002	0.9996	2.001	3.6555	3.404
			RbI		
5.334	80.34	0.976	78.41	137.52	3.209
5.346	40.28	0.986	39.72	69.532	3.229
5.328	20.05	0.992	19.89	34.494	3.229
5.360	10.03	0.995	9.980	17.714	3.295
5.328	5.043	0.998	5.033	8.9179	3.319
5.390	2.007	0.999	2.005	3.5785	3.308
			CsI		
5.347	80.04	0.964	77.16	136.99	3.201
5.310	40.01	0.978	39.13	68.431	3.221
5.446	19.97	0.987	19.71	35.041	3.222
5.332	10.02	0.993	9.950	17.369	3.251
5.362	4.999	0.996	4.979	8.9099	3.324
5.392	1.996	0.998	1.992	3.5677	3.315

To be able to calculate activity coefficients with sufficient accuracy by means of the Debye–Hückel theory, a maximum salt concentration of 8×10^{-3} M was used, whereas the lowest concentration, 2×10^{-4} M, was selected to prevent any significant disturbance of the exchange reaction by alcoholysis, *cf.* ref 7. For lower alkali iodide concentrations, the amounts of free iodide ions produced by this side reaction may cause a nonnegligible isotopic dilution of the ionic iodide.

The degree of dissociation in the third column of Table I was calculated by successive approximations in the usual manner using the ion-pair association constants, K_A, and ion-size parameters, $\mathring{a}$, quoted in Table II. These data had been obtained by application of the Fuoss–Onsager equation[8] to electrical conductance data.[9] Mean molar activity coefficients, $\gamma_\pm$, were obtained from the Debye–Hückel equation

Table II. Association Constants and Ion-Size Parameters Used in Calculating the Degree of Dissociation of Alkali Iodides in Methanol at 25°

Salt	K_A, M^{-1}	$\mathring{a} \times 10^8$, cm
NaI	2.2	4.3
KI	2.3	4.0
RbI	6.0	4.0
CsI	9.4	3.8

$$\log \gamma_\pm \simeq \log f = -\frac{1.8246 \times 10^6 (c\alpha)^{1/2} (\epsilon T)^{-3/2}}{1 + 50.29 \times 10^8 \mathring{a} (c\alpha)^{1/2} (\epsilon T)^{-1/2}} \tag{2}$$

using $\epsilon = 32.63$ for the dielectric constant of the solvent at 25°.

Analysis of the data in Table I according to a method in ref 10 does not indicate any S$_N$1 contribution to the reaction rate (graphs of R/b *vs.* $c\alpha$ yield straight lines through the origin).

Discussion

Qualitative Aspects. According to eq 1, the observed second-order specific rate, k, is a function of k_i, k_m, and α. Experimentally it is observed that k decreases with increasing ionic strength, see Table I and several examples reported in the literature, *e.g.*, ref 11–14. *A priori* it is not possible to decide if this change is a salt effect (changes in activity coefficients of reactants and transition-state complex) or if it is a consequence of an increase in ionic association with increasing concentration and different reactivities of free and paired ions. However, if we can study the displacement reaction using two or more different salts, A^+Y^-, B^+Y^-, etc., with different association constants, K_A, the distinction can be made.

For a given ionic strength, when k_i for the displacement of unpaired Y^- between RY and A^+Y^-, RY and B^+Y^-, etc., should be equal, we may distinguish among three different cases.

---

[4] H. Lund and J. Bjerrum, *Chem. Ber.*, **64**, 210 (1931).

[5] P. Beronius, *Z. Phys. Chem.* (Frankfurt am Main), **40**, 33 (1964).

[6] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," Wiley, New York, N. Y., 1951, pp 7–11.

[7] P. Beronius, *Z. Physik. Chem.* (Frankfurt am Main), **42**, 45 (1964).

[8] R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

[9] P. Beronius, G. Wikander, and A.-M. Nilsson, *Z. Physik. Chem.* (Frankfurt am Main), **70**, 52 (1970).

[10] P. Beronius and H. Johansson, *J. Phys. Chem.*, **72**, 713 (1968).

[11] C. C. Evans and S. Sugden, *J. Chem. Soc., London*, 270 (1949).

[12] S. D. Bowers and J. M. Sturtevant, *J. Amer. Chem. Soc.*, **77**, 4903 (1955).

[13] N. N. Lichtin and K. N. Rao, *ibid.*, **83**, 2417 (1961).

[14] W. Bruce, M. Kahn, and J. A. Leary, *ibid.*, **87**, 2800 (1965).

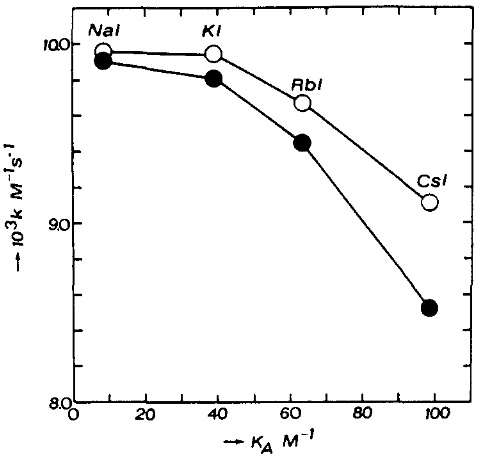

Figure 1. Second-order specific rates, k, as a function of the association constant, K_A, of alkali iodides for the exchange of ^{131}I between these salts and methyl iodide in ethanol at 25° and two different ionic strengths, μ: ○, $\mu = 2 \times 10^{-3}$; ●, $\mu = 3 \times 10^{-3}$.

(i) If $k_m > k_i$, it is obvious from eq 1, conveniently written in the form $k = k_m - \alpha(k_m - k_i)$, that k should increase with decrease in α, *i.e.*, with increase in K_A.

(ii) If $k_m = k_i$, eq 1 yields $k = k_i$; *i.e.*, k should be independent of α and hence of K_A.

(iii) If $k_m < k_i$, we find that k should decrease with increasing K_A.

Lichtin and Rao[13] studied the exchange of ^{82}Br between p-nitrobenzyl bromide and a number of ionic bromides in liquid sulfur dioxide as solvent. For a given ionic strength their data indicate that k decreases with increasing K_A, corresponding to case iii above; *i.e.*, the reactivity of paired ions is less than the reactivity of free ions. A further example,[15] from which the same conclusion can be drawn, is shown in Figure 1, where the second-order specific rate, k, for the exchange of ^{131}I between methyl iodide and sodium, potassium, rubidium, and cesium iodides, respectively, in dry ethanol at 25° has been plotted against the association constant[9] of the salt for two different ionic strengths. From the present discussion it is thus clear that the specific rate of reaction of paired ions is limited to the range $0 \leqslant k_m < k_i$.

Next, we have to try to make a quantitative estimate of the magnitude of the kinetic salt effect. The ideal system for study of this effect would be a reaction in which the ionic reactant is unassociated. In this case the kinetic salt effect is obtained directly from the variation of k with the ionic strength. The systems studied in the present investigation are not far from this ideal case, especially the exchange reaction in which sodium iodide constitutes the ionic reactant.

Quantitative Treatment of Salt Effect. To obtain a quantitative estimate of the kinetic salt effect, we shall use the kinetic data for the exchange reaction in which sodium iodide is involved, because this salt is the least associated of the alkali iodides studied. At the highest concentration used it is associated to only 0.9%. The problem thus consists of determining the dependence of k_i in eq 1 on the ionic strength. We do not know the exact magnitude of k_m, but as concluded above k_m must be less then k_i. We then have to deal with two extreme cases.

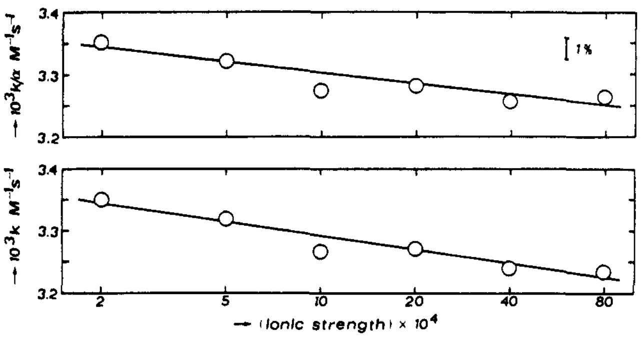

Figure 2. Graphs of k/α and of k, respectively, as a function of log (ionic strength) for the exchange of ^{131}I between sodium iodide and methyl iodide in methanol at 25°.

Case 1. If paired ions are nonreactive, *i.e.*, k_m = zero, it follows from eq 1 that

$$k_i = k/\alpha \qquad (3)$$

In this case the change in k/α with ionic strength yields the minimum possible salt effect.

Case 2. The other extreme occurs when paired ions have nearly the same reactivity as free ions, which corresponds to $k_i \simeq k_m$. If k_i is set equal to k_m in eq 1, we obtain

$$k_i = k \qquad (4)$$

and it follows that the entire change in k with concentration corresponds to the salt effect.

It is empirically found that k/α, as well as k, varies linearly with log μ, as can be seen from the upper and lower parts, respectively, of Figure 2, in which highly magnified y scales are used. The equations of the least-squares fitted straight lines, which are valid in the range $2 \times 10^{-4} \leqslant \mu \leqslant 8 \times 10^{-3}$, are

$$10^3k/\alpha = (3.13 \pm 0.037) - (0.058 \pm 0.0127) \log \mu \qquad (5)$$

and

$$10^3k = (3.07 \pm 0.031) - (0.074 \pm 0.0108) \log \mu \qquad (6)$$

respectively, where uncertainties quoted are standard deviations.

The change in k/α with the ionic strength, μ, according to eq 5 corresponds to case 1 discussed above, and yields thus the minimum possible salt effect, whereas the change in k with μ according to eq 6, which corresponds to case 2, yields the maximum salt effect.

From eq 5 a negative salt effect (decrease in specific reaction rate with increasing ionic strength) of 2.9% is evaluated for the actual concentration range of 2×10^{-4}–8×10^{-3} M. The corresponding figure according to eq 6 is 3.7%.

It has thus been established that the specific rate of the reaction between free iodide ion and methyl iodide, the latter constituting a dipole, decreases with increasing ionic strength. Qualitatively this is what may be expected, as pointed out by Benson,[16] when

---

[15] P. Beronius and L. Pataki, unpublished data.

[16] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, pp 536–537.

the orientation of the ion and the dipole in the transition-state complex is −(+ −).

Table III. Specific Rates, k_i and k_m, for the Exchange of Iodine between Methyl Iodide and Alkali Iodides in Methanol at 25°, Evaluated from k Values Corrected for Kinetic Salt Effect

Salt	$k_i \times 10^3$, M^{-1} sec^{-1}	k_i, rel units	$k_m \times 10^3$, M^{-1} sec^{-1}	Salt effect correction
NaI	3.335 ± 0.010	1.001 ± 0.003	Assumed = 0	Eq 5
KI	3.348 ± 0.023	1.005 ± 0.007	−4.5 ± 4.9	Eq 5
RbI	3.324 ± 0.013	0.998 ± 0.004	2.1 ± 1.1	Eq 5
CsI	3.316 ± 0.015	0.995 ± 0.005	2.4 ± 0.8	Eq 5
Av	3.331			
NaI	3.339 ± 0.009	1.001 ± 0.003	Assumed = k_i	Eq 6
KI	3.351 ± 0.021	1.005 ± 0.006	−1.8 ± 4.5	Eq 6
RbI	3.328 ± 0.013	0.998 ± 0.004	3.1 ± 1.1	Eq 6
CsI	3.319 ± 0.014	0.996 ± 0.004	3.1 ± 0.7	Eq 6
Av	3.334			

Specific Rate of Reaction of Free Ions. That k_i should be independent of the nature of the cation is a necessary consequence of the Acree hypothesis. Table I provides us with data to test if this is so.

To evaluate k_i, eq 1 was written in the form

$$\frac{k'}{\alpha} = k_i + k_m\frac{1-\alpha}{\alpha} \tag{7}$$

where k' is the observed second-order specific rate, k, corrected for the kinetic salt effect to a common ionic strength of 2×10^{-4}, which corresponds to the lower limit of the concentration interval studied. Equations 5 and 6, giving minimum and maximum salt effect corrections, respectively, were used. Straight lines were fitted by the method of least squares to values of k'/α *vs.* $(1 - \alpha)/\alpha$. The results are given in Table III, in which errors quoted are standard deviations.

Inspection of this table reveals that the results differ insignificantly when eq 5 and 6, respectively, are used to correct for the kinetic salt effect.

The specific rate of reaction of unpaired iodide ions is independent of the alkali metal counterion. The values of k_i for NaI, KI, RbI, and CsI differ from the average by +0.1, +0.5, −0.2, and −0.5%, respectively. These deviations fall within the limits of experimental errors.

Values of k_m have also been quoted, though we cannot expect to obtain these constants with any degree of certainty because of the slight association of ions into pairs. For rubidium and cesium iodides the values of k_m are positive and larger than their standard deviations, and we cannot exclude a contribution from the ion pairs to the reaction rate.

Consequence of Neglect of Kinetic Salt Effect. As mentioned above, the kinetic salt effect is generally neglected in evaluating the constants in the Acree equation. For those reactions in which the salt effect is negative, as in the present investigation, the increasing contribution of the ion pairs to the reaction rate with increasing concentration of the ionic reactant is counteracted by the salt effect. Neglect of the latter therefore results in an underestimate of the specific rate of reaction of the paired ions.

Acknowledgments. The authors thank Dr. Michael Sharp for linguistic revision of the manuscript and the Swedish Natural Science Research Council for financial support.

Photolysis of Stannic Iodide in *n*-Heptane

T. N. Bell, M. Boonstra, and P. A. Dobud

Contribution from the Department of Chemistry, Simon Fraser University, Burnaby 2, British Columbia, Canada. *Received October 1, 1969*

Abstract: Stannic iodide decomposes when irradiated in its first absorption band (λ_{max} 3550 Å). The decomposition is accounted for by a molecular split of iodine molecules, from an excited state of SnI_4 ($SnI_4 + h\nu \rightarrow Sn + 2I_2$). The quantum yield for this reaction is 0.19.

There is a considerable literature on photochemical decompositions, and a number of reviews have recently appeared on the photochemistry of inorganic compounds, particularly on the coordination compounds of the transition elements.[1–4] The interpretation of the mechanism of the primary photochemical process is, in many cases, not clearly understood. The absorption spectra of inorganic compounds, particularly in the ultraviolet region, are often associated with charge-transfer transitions,[5] and any interpretation of photodecompositions resulting from such absorption is intimately bound to an understanding of the electronic transitions occurring. This work was undertaken to observe the photochemical behavior of some main-group element halides in the charge-transfer region. We suggest the photodecomposition proceeds through a molecular elimination mechanism, and have attempted to interpret the decomposition through molecular orbital considerations and also the characteristics of a particular vibrational mode.

---

(1) D. V. Valentine, *Advan. Photochem.*, **6**, 123 (1968).

(2) E. L. Wehry, *Quart. Rev. Chem. Soc.*, **21**, 213 (1967).

(3) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

(4) A. W. Adamson, *Rec. Chem. Progr.*, **29**, 191 (1968).

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley, New York, N. Y., 1967.