Kinetic Salt Effect in Ion — Molecule Reactions. I. The Isotopic Exchange between Tetraethylammonium Iodide and Methyl Iodide in Ethylene Glycol at 25 °C

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Kinetic salt effect is one of the various factors that have to be considered in analyzing kinetic data for ion—molecule reactions.¹ For such reactions in organic solvent media unequivocal quantitative evaluation of the kinetic salt effect is usually rendered difficult because of association of the ionic reactant to higher aggregates such as ion pairs and triple ions, *cf.* Refs. 2–3.

The present study of the isotopic exchange reaction between a quaternary ammonium iodide and methyl iodide in ethylene glycol constitutes part of an investigation initiated to obtain quantitative information about the kinetic salt effect. Qualitatively the effect of ionic strength on reactions involving ions and dipolar molecules may be predicted.⁴

Reagents. Ethylene glycol (Merck, *p.a.*) was flushed with nitrogen to remove dissolved oxygen. Methyl iodide (Merck) was purified by distillation in a column filled with copper turnings and stored over mercury in the dark. The iodine content of the tetraethylammonium iodide used (Merck) was found to be $\geq 99\%$ according to isotope dilution analysis. The salt was labelled using carrierfree radiiodide (¹³¹I). Solutions were prepared at 25 °C.

Kinetic procedure. The electrodeposition method,⁵ was used to follow the exchange reaction,

at 25.00 ± 0.05 °C. The rate of exchange, R , was iteratively calculated⁶ from the McKay equation,⁷

$$\ln(1-F) = -Rt(a+c)/ac \quad (1)$$

where F is the fractional exchange, t is the reaction time, a is the concentration of methyl iodide, and c is the concentration of tetraethylammonium iodide.

A typical graph obtained upon plotting $\ln(1-F)$ vs. t according to eqn. (1) is shown in Fig. 1.

Discussion. A compilation of the results of the kinetic measurements is given in Table 1

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Fig. 1. Graphic representation of eqn. (1) for the exchange reaction studied at $c = 6.004$ mM.

in which the observed rate constant, k , in the last column is defined by the expression, $k = R/ac$.

The value of k shows a slight tendency to decrease with increasing concentration of tetraethylammonium iodide (column 2) but is within experimental errors independent of the concentration of methyl iodide (column 1). As briefly discussed below this effect may be given various explanations.

In a previous investigation⁸ of the exchange reaction between sodium iodide and methyl iodide in ethylene glycol using ¹³¹I as a radioactive indicator no $\text{S}_{\text{N}}1$ contribution to the reaction rate could be detected. The reaction appeared to be of purely $\text{S}_{\text{N}}2$ type. The results of the present study confirm the absence of $\text{S}_{\text{N}}1$ exchange. This may be seen from Fig. 2, where R/a has been plotted vs. c according to the equation

$$R/a = k_1 + kc \quad (2)$$

Table 1. Kinetic data for the exchange of ¹³¹I between tetraethylammonium iodide and methyl iodide in ethylene glycol at 25 °C.

$a \times 10^3$ M	$c \times 10^4$ M	$R \times 10^8$ M s ⁻¹	$k \times 10^8$ M ⁻¹ s ⁻¹
5.109	100.06	416.61	8.150
5.174	80.05	347.00	8.378
5.289	60.04	270.49	8.518
5.530	40.04	190.34	8.596
5.450	30.03	141.16	8.625
5.365	20.02	92.289	8.592
3.087	12.30	33.150	8.731
6.561	10.01	57.642	8.777
5.284	10.01	45.612	8.623
5.232	5.003	22.848	8.729

Fig. 2. Graphic representation of eqn. (2).

for a mixed S_N1-S_N2 reaction. In eqn. (2), which is applicable provided that the ionic reactant behaves like a strong electrolyte, k_1 is the rate constant for S_N1 exchange. The straight line in Fig. 2 passes within experimental errors through the origin, i.e. k_1 is zero.

In the higher concentration range investigated the points of R/a vs. c show negative deviations from the limiting tangent. These deviations might be described in terms of the extended Acree equation,⁸

$$k = \gamma k_i^\infty \alpha + k_p(1 - \alpha) \quad (3)$$

where γ is a salt effect correction factor, k_i^∞ is the rate constant at infinite dilution for the exchange reaction between free iodide ion and methyl iodide, k_p is the corresponding rate constant for the exchange reaction involving paired iodide ion, and α is the degree of dissociation of the salt.

In the case of complete dissociation, that is $\alpha = 1$, eqn. (3) reduces to, $k = \gamma k_i^\infty$, i.e. the total change in k , which amounts to about 6% for the concentration interval of the salt, would represent the kinetic salt effect.

Application⁹ of various conductance equations to electrical conductance data¹⁰ for tetraethylammonium iodide in ethylene glycol at 25°C suggests that the salt may be subject to a slight ion-pair formation though complete dissociation cannot be ruled out. Hence, the possibility that the change in the observed rate constant with concentration of the ionic reactant is due to ion-pair formation and a lower reactivity of paired ions as compared with free ions cannot be ruled out.

Let us, for the purpose of calculation, assume the extreme case that the kinetic salt effect is negligible ($\gamma = 1$) and that the exchange with the organic reactant proceeds solely via free iodide ions ($k_p = 0$). In this case the expression,

$$1/k = 1/k_i^\infty + c\gamma_\pm^2 k K_A / (k_i^\infty)^2 \quad (4)$$

can be derived.¹¹ In eqn. (4) K_A is the ion-pair association constant and $\gamma_\pm$ is the mean molar activity coefficient of free ions. The latter quantity was estimated¹¹ from the Debye-Hückel equation putting the distance parameter equal to the Bjerrum radius¹² ($q = 7.43 \text{ \AA}$ at 25°C for ethylene glycol).

A graph of $1/k$ vs. $c\gamma_\pm^2 k$ according to eqn. (4) is shown in Fig. 3. From the equation of the least squares fitted straight line we obtain $k_i^\infty = (8.80 \pm 0.04) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ and $K_A = 12 \pm 2 \text{ M}^{-1}$, where the errors are standard deviations. This value of K_A is of the same magnitude as can be derived⁸ from electrical conductance data.¹⁰

Further studies of kinetic salt effect in ethylene glycol as solvent are in progress.

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Fig. 3. Graphic representation of eqn. (4).

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Synthesis of Areneselenenyl Benzenesulfinates and Benzenethiosulfonates, and Tetraphenylarsonium Areneselenenyl Sulfites and Thiosulfates

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A large number of stable aromatic selenenyl sulfur compounds, ArSeSR , have been isolated (for a review see Ref. 1). Many of these compounds have an NO_2 -group in the *ortho* position of the areneselenenyl group.² The ability of Se(II) to achieve coordination numbers higher than two probably serves to make these compounds more stable due to an intramolecular bonding between the selenium atom and one of the oxygen atoms of the nitro group.³

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In this note we present the synthesis of some new aromatic selenenyl sulfur compounds which do not have any stabilizing groups in the *ortho* position. The various compounds are listed in Table 1.

Aromatic selenenyl benzenesulfinates were prepared from the corresponding aromatic selenenyl bromides and sodium benzenesulfinate in carbon tetrachloride, eqn. 1.

Aromatic selenenyl benzenethiosulfonates could be prepared from the corresponding aromatic selenenyl bromides and sodium benzenethiosulfonate in carbon tetrachloride, eqn. 2.

Analogous sulfur compounds, which have an NO_2 -group in the *ortho* position of the areneselenenyl group, have been isolated.⁴

Tetraphenylarsonium salts of aromatic selenenyl sulfites. A number of organic selenosulfates, seleno Bunte salts, have been prepared by the action of selenosulfate on alkyl chlorides or bromides in water or aqueous ethanol, eqn. (3) (see Ref. 1, p. 151).

However, in most cases the resultant organic selenosulfate was converted *in situ* to the corresponding diselenide. Until now, no aromatic seleno Bunte salt has been reported. We found that tetraphenylarsonium salts of aromatic selenosulfates could be prepared according to eqn. 4, from the corresponding areneselenenyl benzenesulfinates dissolved in ether, by reaction with a mixture of sodium sulfite and tetraphenylarsonium chloride dissolved in water:

The aromatic selenosulfate formed is immediately precipitated as a tetraphenylarsonium salt prior to the formation of any diaryldiselenide.

Pyridinium *S*-aryl thiosulfates have been prepared by Baumgarten.⁵