

## Apparent $S_N1$ Contribution to $S_N2$ Reaction Rate Due to Ion Association

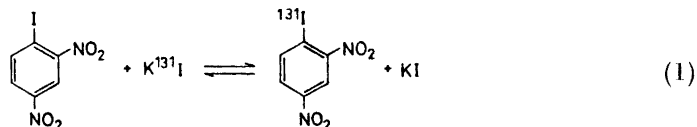
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Calculations using kinetic data for a particular system demonstrate that neglect of the effect of ion-pair formation on reaction rate may result in apparent mixed  $S_N1$ - $S_N2$  kinetics for reactions which are purely  $S_N2$  type.

Interpretation of kinetic data for reactions involving electrolytes under conditions favouring ion-pair formation is not straightforward. The purpose of the present paper is to show that neglect of ion association, or use of an incorrect ion-pair association constant in reactions where one of the reactants is an electrolyte, may apparently make a purely  $S_N2$  reaction to be partially of  $S_N1$  type.

To discuss this effect, we shall use kinetic data for the exchange reaction between potassium iodide and 1-iodo-2,4-dinitrobenzene in acetone at 44.0°C. This reaction, which has been studied at different concentrations of potassium iodide by Broadbank *et al.*,<sup>1</sup> using  $^{131}\text{I}$  as a radioactive indicator may be represented by the overall formula



The course of this reaction was observed by removing samples of the reaction mixture at different reaction times and distributing the reactants between water and toluene followed by activity measurements of the two different phases.

The specific reaction rate,  $k$ , was calculated from the McKay equation in its special form for second-order kinetics

$$\ln \left[ 1 - \frac{x(a+c)}{ab} \right] = -(a+c)kt \quad (2)$$

where  $a$  is the initial concentration of the aromatic iodide,  $b$  and  $c$  the initial concentrations of radioactive and inactive potassium iodide, respectively, and  $x$  the concentration of radioactive aromatic iodide at reaction time,  $t$ .

The rate constants thus established by Broadbank *et al.*<sup>1</sup> are reproduced in the second column of Table 1. Using these rate constants and the concentra-

Table 1. Kinetic data for exchange of iodine between potassium iodide and 1-iodo-2,4-dinitrobenzene in acetone at 44.0°C according to Ref. 1. The concentration,  $a$ , of aromatic iodide was 0.01 M.

$c \times 10^3$ M	$k \times 10^4$ M <sup>-1</sup> s <sup>-1</sup>	$R \times 10^9$ M s <sup>-1</sup>
19.6	1.23	24.11
9.8	1.48	14.50
9.8	1.51	14.80
1.96	2.72	5.33

tions of the reactants in this table we have calculated the total rate of exchange,  $R$ , by means of the expression

$$R = kac \quad (3)$$

The values of  $R$  calculated by this means are listed in the last column of the same table.

As can be seen from Table 1, the rate constant,  $k$ , according to eqn. (2) increases with decreasing electrolyte concentration. In part this might be due to the kinetic salt effect. As recently shown,<sup>2</sup> however, the kinetic salt effect in reactions between electrically neutral species and ionic species is of minor importance in the relevant range of ionic strengths and will be neglected in the following discussion.

Let us now first assume that the ionic reactant is non-associated in the solvent concerned, *cf.* Ref. 1, and that the change in  $k$  with the concentration of this reactant reflects simultaneous S<sub>N</sub>1 and S<sub>N</sub>2 exchanges. With these assumptions we may express the total rate of exchange by means of the equation

$$R = k_1 a + k_2 ac \quad (4)$$

where  $k_1$  and  $k_2$  are the rate constants for S<sub>N</sub>1 and S<sub>N</sub>2 exchange, respectively.

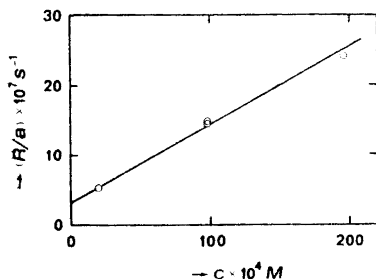


Fig. 1. Graph of  $R/a$  vs.  $c$  according to eqn. (4) for the exchange of iodine between potassium iodide and 1-iodo-2,4-dinitrobenzene in acetone at 44.0°C.

A graph of  $R/a$  vs.  $c$  according to eqn. (4) is shown in Fig. 1. The non-vanishing intercept of the line suggests that the reaction is partially first-order. The equation of the straight line in this figure, calculated using the relative deviation least squares method<sup>3</sup> to give equal weights to all the points, yielded  $k_1 = 3.2 \times 10^{-7} \text{ s}^{-1}$  with a standard deviation of  $0.3 \times 10^{-7} \text{ s}^{-1}$ . Hence, a significant first-order contribution to the reaction rate is indicated.

Let us now investigate how our conclusions concerning the reaction mechanism may change, if we regard the ionic reactant as being partially associated to ion-pairs. To that end we shall calculate the first-order rate constant,  $k_1$ , for different values\* of the association constant,  $K_A$ , of this reactant.

In case of ion-pair formation the concentration of free iodide ions is reduced from the analytical concentration,  $c$ , of potassium iodide to  $c\alpha$ , where  $\alpha$  is the degree of dissociation of the ion-pairs. If paired iodide ions do not react with the aromatic iodide, cf. Ref. 4, the total rate of exchange should be equal to

$$R = k_1 a + k_2 a c \alpha \quad (5)$$

The values of  $\alpha$  needed to determine the constants in eqn. (5) were iteratively calculated as described in a previous paper<sup>5</sup> using  $\epsilon = 18.9$  for the permittivity of acetone at 44.0°C and  $\hat{a} = 3.5 \times 10^{-8} \text{ cm}$  for the ion-size parameter in the Debye-Hückel equation. The  $\alpha$ -values obtained for three different association constants,  $K_A$ , at the concentrations of potassium iodide in the kinetic measurements (Table 1) are listed in Table 2.

Table 2. Degree of dissociation of 1:1-electrolyte in acetone at 44.0°C as a function of the electrolyte concentration for different ion-pair association constants.

$c \times 10^3$ M	$K_A = 200$	$\alpha$ $K_A = 1000$	$K_A = 5000 \text{ M}^{-1}$
19.6	0.6645	0.3423	0.1435
9.8	0.7179	0.4057	0.1832
1.96	0.8546	0.6016	0.3257

According to eqn. (5) a straight line of intercept  $k_1$  and slope  $k_2$  should be obtained upon plotting  $R/a$  as a function of  $c\alpha$ . Graphs of this kind are shown in Fig. 2. The curves *A*, *B*, and *C*, calculated as above by means of the relative deviation least squares method, refer to the association constants 200, 1000, and 5000  $\text{M}^{-1}$ , respectively.

As can be seen in Fig. 2, and also in Table 3 where values of  $k_1$  are listed, first-order contributions to the reaction rate are indicated for  $K_A$  equal to 200 and 1000  $\text{M}^{-1}$ . However, for  $K_A$  equal to 5000  $\text{M}^{-1}$  the first-order contribution vanishes. In this latter case  $k_1 = 0$  within experimental errors, see Table 3.

\* No data for calculating the association constant for potassium iodide in acetone at 44.0°C are available in the literature and it should be noted that the present discussion is no attempt to establish the mechanism of the reaction treated but merely, as pointed out in the introduction, to demonstrate how the assumptions concerning the association behaviour of the ionic reactant may affect the conclusions drawn.

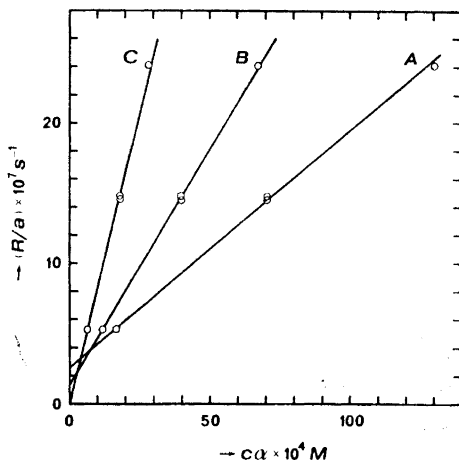


Fig. 2. Graph of  $R/a$  vs.  $c\alpha$  according to eqn. (5) for the exchange of iodine between potassium iodide and 1-iodo-2,4-dinitrobenzene in acetone at 44.0°C. The lines labelled by A, B, and C were calculated using the association constants,  $K_A$ , equal to 200, 1000, and 5000  $M^{-1}$ , respectively.

Table 3. Dependence of the apparent  $S_N1$  rate constant on the choice of ion-pair association constant,  $K_A$ , for the same reaction as in Table 1.

Curve (Fig. 2)	$K_A$ $M^{-1}$	$k_1 \times 10^7$ $s^{-1}$
A	200	$2.5 \pm 0.2$
B	1000	$1.4 \pm 0.1$
C	5000	$0.0 \pm 0.3$

In the discussion above we have made two simplifications. Any kinetic salt effect has been neglected and the ion-pairs have been assumed to be non-reactive. However, according to an earlier investigation<sup>6</sup> reactions of similar kind to the system discussed here are subject to a small but measurable kinetic salt effect in the observed range of ionic strengths. In addition it cannot be excluded that the ion-pairs exhibit certain reactivity.

Hence, the kinetic data employed to establish the reaction mechanism should refer to sufficiently low concentrations of the ionic reactant for the ion-pair and kinetic salt effects to be negligible.

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