REACTIVITY OF ION PAIR AGGREGATES

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Abstract-The kinetics of n-propyl iodide with tetrabutylammonium bromide
exhibits that the ion pair aggregates are active nucleophiles and the
reactivity may increase with increase in aggregation number.

Brandstrom et al.[1] suggested that the active nucleophile in phase transfer catalyzed
reaction is the ion pair but not the free ion. This idea is generally accepted. However,
the ion pair associates into aggregates, especially in nonpolar solvents. Are these aggre-
gates active nucleophiles and what are their reactivity compared to the ion pair?

The average number of aggregation, Agg, increases with increase in concentration[2]. Thus
if only the ion pair is active, but their aggregates are not, the observed rate constant,
k_{obs} should drop rapidly as the concentration of ion pair increases (case 1). If the aggre-
gates do react but with activity less than that of the unaggregated ion pair, the k_{obs}
should decrease slowly with increase in concentration (case 2). If the reactivity of each
anion in the aggregates are the same as the ion pair, k_{obs} should remain constant (case 3).
If the reactivity even increases with increase in Agg, the rate constant should also inc-
rease with concentration (case 4).

Landini et al. reported slow decrease of k_{obs} with increase in concentration[3]. This is
in consistence with case 2. The data of Brandstrom seems to be the case 3. Horner and Ger-
hard[4] found both rate constant and Agg are larger in benzene than those in chloroform and
claimed the reactivity increases with the number of aggregation. Nevertheless, their con-
clusion implies that the aggregates with the same Agg would have same reactivity, that
means no solvent effect. This is unreasonable and therefore, their conclusion is question-
able.

In order to study the reactivity of ion pair aggregates, n-propyl iodide is reacted
with tetrabutylammonium bromide of various concentrations in benzene. In benzene the Agg
changes rapidly with concentration[2] and the solubility of one of the products, tetrabutyl-
ammonium iodide is so small that it separates soon after mixing of the reactants and the
reaction may be treated as irreversible reaction.

$$\frac{1}{c_1^0 - c_2^0} \ln \frac{(c_1^0 - X)c_2^0}{(c_2^0 - X)c_1^0} = k_{obs}$$

Here c_1^0 and c_2^0 are initial concentrations of n-propyl iodide and tetrabutylammonium bro-
mide respectively, and X is the concentration of n-propyl bromide formed (determined by gas
chromatography). The plot shown in Figure 1 exhibits at first a straight line and bent down-
ward greadually. The rate constants listed in Table 1 are calculated from the straight por-

Table 1. Observed rate constants for the reaction of n-propyl iodide with tetrabutylammonium bromide in benzene at $20^{\circ}C$

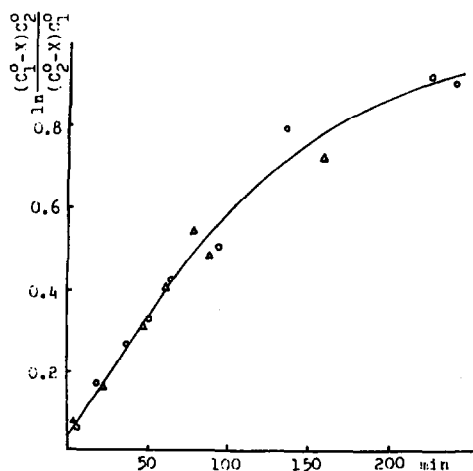| No.	C_1^0 (M)	C_2^0 (M)	Agg.[a]	k_{obs} ($M^{-1}min^{-1}$)
1	.0352	.0102	----	.116
2	.0320	.0183	4.9	.151
3	.0352	.0402	6.6	.189
4	.0352	.0603	8.1	.206
5	.0354	.0804	10.0	.205

a. From ref. 2

Figure 1 Second Order Kinetic Plot
$C_2^0 = .0603$ M

tion of the curve.

It is evident from Table 1 that the Agg increases with increase in concentration, but the observed rate constant increases only in low concentrations and approaches constant. This result is in consistence with the convex curve in Figure 1. The increase in observed rate constant with concentration and therefore, with the number of aggregation, is just the case 4. Actually, this is the first case in which the activity of each anion in aggregates increases with the aggregation number.

From data of this paper and those in the literature it is evident that the ion pair aggregates are reactive nucleophile and the reactivity of each anion in the aggregates may be higher than (this paper), the same as[1], or lower than[3] that of the unaggregated ion pair.

References
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