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THE KINETICS OF THE REACTION OF ACYL PEROXIDES WITH ALKALI IODIDES—II

THE EFFECT OF THE CATIONS ON THE REACTION RATE OF BENZOYL PEROXIDE

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Abstract—The reactions of benzoyl peroxide with various alkali and onium iodides were studied in both 95·1% and absolute ethanol. The nature of the cation exerts a remarkable effect on the rate, and, in a series of alkali iodides, the rate constant increases in the order: $Li^+ < Na^+ < K^+ < Cs^+ < Rb^+$. This order coincides with the order of their limiting conductance values, which reflect the size of solvated ions. It is concluded that the cation participates in the rate determining step of the reaction and stabilizes the negative charge which is developing on the oxygen atom of benzoyl peroxide in consequence of the electron-transfer from an iodide ion; with the cation of smaller size, this stabilization will be stronger, resulting in enhanced rate. The reaction with triethylsulphonium iodide is faster than with tetraethylammonium iodide; this fact is explained in terms of the structure of the sulphonium cation.

A KINETIC study of the reaction between benzoyl peroxide and potassium iodide in ethanol to give potassium benzoate and iodine showed that it follows the rate law: rate $= k_2[Bz_2O_2][KI]$.[1] Potassium iodide was used throughout as the iodide because of its ease in purification. Recourse was had to more soluble sodium iodide, however, when it was necessary to work with a much higher concentration of the iodide and this iodide was found to react much more slowly than with the same concentration of potassium iodide. This observation suggested a possible effect of the nature of the cation on the reaction rate. This paper reports the kinetics of the reaction between benzoyl peroxide and various alkali and onium iodides.

EXPERIMENTAL

The apparatus with which the production of I_2 was followed colorimetrically and the general procedure was the same as described in Part I.[1]

Materials

Lithium iodide trihydrate. A slight exess of the azeotropic mixture of HI with water (b.p. 124°, 58%) was added to Li_2CO_3. The solution was evaporated to dryness under a stream of N_2 and the residue recrystallized from aqueous EtOH. (Found: I, 68·01. Calc. for $LiI·3H_2O$: I, 67·54%.)

Sodium iodide. Commercial NaI was used without further purification. (Found: I, 83·64. Calc. for NaI: I, 84·66%.)

Rubidium iodide. The double salt of rubidium oxalate and rubidium hydrogen oxalate was heated in a Pt crucible. The resulting Rb_2CO_3 was treated with an equiv amount of the azeotropic mixture of HI and water. The solution was evaporated to dryness under continuous bubbling of N_2. The resulting crystals of RuI were pale-yellow owing to contamination with trace of I_2. In order to remove the contaminating I_2, the crystals were dissolved in distilled water, and the solution passed through a column of anion-exchange resin (Dia-ion, S.A.-100), which had been converted into an iodide

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[1] G. Tsuchihashi, S. Miyajima, T. Otsu and O. Simamura, *Tetrahedron* 21, 1039 (1965).

type resin (R-I) by treatment with NaIaq. The I_2 could be eliminated by the following exchange reaction: $RbI_3 + R\text{-}I \rightarrow RbI + R\text{-}I_3$. The eluted solution was vacuum-distilled with bubbling of N_2 and the remaining crystals were dried in a vacuum desiccator (Found: I, 60·05. Calc. for RbI: I, 59·75%).

Caesium iodide. CsCl was heated until red hot with oxalic acid in a Pt crucible to give Cs_2CO_3. The subsequent procedure to change the carbonate to the pure iodide was the same as that for RbI. (Found: I, 49·97. Calc. for CsI: I, 48·85%).

Tetraethylammonium iodide. Et_4NI was purified by recrystallization from aqueous EtOH (1:1). The crystals were dried in a vacuum desiccator over conc. H_2SO_4. (Found: I, 49·73. Calc. for $C_8H_{20}NI$: I, 49·34%).

Trimethylphenylammonium iodide. Me_3PhNI was prepared from N,N-dimethylaniline (b.p. 121°) and MeI (b.p. 42·5°). The resulting white crystals were recrystallized from MeOH and dried in a vacuum desiccator, m.p. 212°. (Found: I, 47·60. Calc. for $C_9H_{14}NI$: I, 48·23%).

Triethylsulphonium iodide. Et_2S (b.p. 92°) was refluxed with the equiv amount of EtI (b.p. 72°) for 5 hr on a water bath. The resulting material was dissolved in hot EtOH and the solution filtered through a hot-water funnel into cold ether. The resulting crystals were filtered off and dried in a vacuum desiccator. (Found: I, 50·46. Calc. for $C_6H_{15}SI$: I, 51·54%).

TABLE 1. PSEUDO FIRST-ORDER RATE CONSTANTS k FOR THE REACTION OF BENZOYL PEROXIDE WITH SODIUM IODIDE

Solvent	Temp °C	[NaI] × 10^3 mole/l.	$k \times 10^3$ sec^{-1}
Ethanol	40·0	9·883	5·60 ± 0·14*
Ethanol	29·5	4·988	0·83 ± 0·01
Ethanol	29·5	7·373	1·42 ± 0·02
Ethanol	29·5	9·836	1·98 ± 0·03
Ethanol	20·5	9·973	0·79 ± 0·02
95·1% Ethanol	40·0	9·818	3·30 ± 0·02
95·1% Ethanol	29·5	5·014	0·57 ± 0·02
95·1% Ethanol	29·5	9·909	1·18 ± 0·06
95·1% Ethanol	20·5	9·968	0·56 ± 0·03

* Standard deviation.

Initial concentration of benzoyl peroxide: 1·5 × 10^{-5} mole/l.

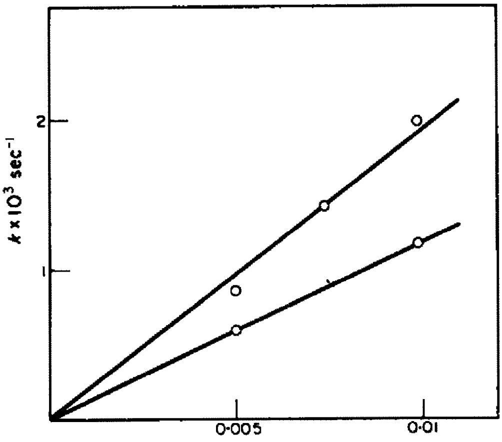

FIG. 1. Observed first-order rate constants at various concentrations of sodium iodide at 29·5°.

I: in ethanol; II: in 95% ethanol

Ammonium iodide. NH_4I was purified by recrystallization from aqueous EtOH (1:1) and dried over H_2SO_4 in a vacuum desiccator. (Found: I, 86·56. Calc. for NH_4I: I, 87·52%).

TABLE 2. THE REACTIONS OF BENZOYL PEROXIDE WITH VARIOUS IODIDES IN ABSOLUTE ETHANOL

Iodide	Temp °C	k_2 l. mole^{-1} sec^{-1}	$\Delta H^{\ddagger}_{\text{kcal/mole}}$	$\Delta S^{\ddagger}_{\text{E.U.}}$
Lithium	49·0	0·326 ± 0·001	17·0 ± 0·5	−8·1 ± 1·7
(trihydrate)	40·0	0·149 ± 0·001		
	29·5	0·055 ± 0·003		
Sodium	40·0	0·566 ± 0·006	17·8 ± 0·3	−2·9 ± 1·1
	29·5	0·202 ± 0·004		
	20·5	0·080 ± 0·003		
Potassium	29·5	0·444 ± 0·004	12·0 ± 0·4	−20·4 ± 1·4
	20·5	0·248 ± 0·004		
	11·0	0·112 ± 0·006		
Rubidium	40·0	1·38 ± 0·04	14·5 ± 0·3	−11·7 ± 1·0
	29·5	0·568 ± 0·006		
	20·5	0·275 ± 0·005		
Caesium	40·0	1·14 ± 0·02	13·6 ± 0·6	−14·9 ± 2·0
	29·5	0·506 ± 0·005		
	20·5	0·252 ± 0·017		
Ammonium	40·0	0·336 ± 0·003	16·9 ± 0·1	−7·0 ± 0·6
	29·5	0·118 ± 0·004		
	20·5	0·0527 ± 0·0004		
Tetraethyl-ammonium	40·0	0·237 ± 0·002	14·1 ± 0·5	−15·4 ± 1·9
	29·5	0·105 ± 0·007		
	20·5	0·049 ± 0·002		
Trimethyl-phenylammonium	40·0	0·281 ± 0·001	15·5 ± 0·7	−11·7 ± 2·3
	29·5	0·098 ± 0·002		
	20·5	0·050 ± 0·003		
Triethyl-sulphonium	40·0	0·306 ± 0·001	13·4 ± 0·5	−18·1 ± 1·8
	29·5	0·139 ± 0·008		
	20·5	0·069 ± 0·002		

RESULTS AND DISCUSSION

The results of the investigation with sodium iodide are summarized in Table 1. Since the initial concentration of sodium iodide was always in considerable excess over benzoyl peroxide, the rate of production of iodine turned out to be of the first order with respect to the concentration of benzoyl peroxide. The pseudo-first order rate constants, k, were calculated as described in Part I and plotted against the initial concentration of the iodide, giving a straight line as shown in Fig. 1. The slope of the line gave the bimolecular rate constant, k_2, establishing the rate law:

$$\text{Rate} = k_2[\text{Bz}_2\text{O}_2][\text{NaI}].$$

Similarly rates were measured with various iodides, and the bimolecular rate constants and activation parameters calculated are listed in Tables 2 and 3.

It is readily seen that the nature of the cation exerts a remarkable effect on rate; in a series of alkali iodides, the rate constant increases in the order: $Li^+ < Na^+ < K^+ < Cs^+ < Rb^+$. More than a ten-fold difference in rate was found between the reactions with lithium and with rubidium iodide in absolute ethanol solution. Addition

Table 3. The reactions of benzoyl peroxide with various iodides in 95·1% ethanol

Iodide	Temp °C	k_2 l. mole^{-1} sec^{-1}	$\Delta H^{\ddagger}_{\text{kcal/mole}}$	$\Delta S^{\ddagger}_{\text{e.u.}}$
Lithium (trihydrate)	49·0	0·403 ± 0·004	15·5 ± 1·0	−12·4 ± 3·5
	40·0	0·178 ± 0·006		
	29·5	0·079 ± 0·005		
Sodium	40·0	0·336 ± 0·002	16·4 ± 0·7	−8·6 ± 2·5
	29·5	0·119 ± 0·006		
	20·5	0·056 ± 0·003		
Potassium	29·5	0·213 ± 0·002	10·1 ± 0·7	−28·4 ± 2·6
	20·5	0·128 ± 0·004		
	11·0	0·0659 ± 0·0013		
Rubidium	40·0	0·788 ± 0·002	13·9 ± 0·4	−14·7 ± 1·7
	29·5	0·337 ± 0·003		
	20·5	0·167 ± 0·006		
Caesium	40·0	0·590 ± 0·001	14·9 ± 0·9	−12·1 ± 3·3
	29·5	0·249 ± 0·016		
	20·5	0·115 ± 0·020		
Ammonium	40·0	0·268 ± 0·006	14·8 ± 0·2	−14·0 ± 0·8
	29·5	0·114 ± 0·001		
	20·5	0·0517 ± 0·0005		
Tetraethyl-ammonium	40·0	0·267 ± 0·003	15·0 ± 0·4	−13·2 ± 1·3
	29·5	0·111 ± 0·002		
	20·5	0·0504 ± 0·0009		
Trimethyl-phenylammonium	40·0	0·284 ± 0·003	15·8 ± 0·6	−10·4 ± 1·9
	29·5	0·133 ± 0·002		
	20·5	0·049 ± 0·001		
Triethyl-sulphonium	40·0	0·262 ± 0·002	11·2 ± 0·3	−25·7 ± 1·1
	29·5	0·127 ± 0·002		
	20·5	0·075 ± 0·001		

Table 4. Limiting equivalent conductances λ° for alkali cations in solution at 25°C and rates of reactions k_2 of benzoyl peroxide with alkali iodides at 29·5°

	λ° (ohm^{-1} cm^2 (g equiv.)$^{-1}$)		k_2 (l. mol^{-1} sec^{-1})	
Cation	in water	in ethanol	in absolute ethanol	in 95% ethanol
Li$^+$	38·66	17·05	0·055	0·079
Na$^+$	50·11	20·31	0·202	0·119
K$^+$	73·52	23·55	0·444	0·213
Rb$^+$	77·8		0·568	0·337
Cs$^+$	77·3		0·506	0·249

of water to the solution diminished the rate of reaction with alkali iodides by about half except the case with lithium iodide, whereas no significant effect of added water was observed with quaternary ammonium iodides.

The foregoing order of the effect of alkali cations seems to be related with the order of the size of the ions. In fact, as Table 4 shows, a parallelism exists between the effect of alkali cations and their limiting equivalent conductance values which reflect the size of a solvated ion;[2] the larger the limiting conductance value, that is,

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[2] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* Chap. 6. Butterworths, London (1955).

the smaller the radius of a solvated cation, the more strongly it accelerates the reaction.

According to Bjerrum's theory the degree of ionic association of an alkali iodide is greater when the radius of the alkali cation is smaller.[3] Therefore, if free iodide ions should react faster than associated ones as is observed by Winstein in a substitution reaction,[4] the alkali iodide with a cation of larger size would react faster than the iodide of a smaller cation, contrary to the experimental findings.

It is therefore concluded that the cation participates in the transition state by coordination and stabilizes by its electrostatic effect the negative charge developing on the oxygen atom of benzoyl peroxide in consequence of the electron-transfer from an iodide ion. With the cation of smaller size, this stabilization will be stronger, resulting in the enhanced rate in accordance with the experimental results.

The rates of reactions with tetraethylammonium and trimethylphenylammonium iodide are slower than with caesium iodide and even with sodium iodide; this is understandable since the quaternary ammonium cations are much larger.[5]

It is worth noting that the rates with the quaternary ammonium iodides are hardly changed by change of the solvent, i.e., in going from absolute ethanol to 95% ethanol, whereas this change of the solvent causes appreciable lowering of the rates for alkali iodides. These facts suggest that the quaternary ammonium cations are too large either to play a significant role in the transition state or to be affected, with respect to solvation, by the change of the solvent, in order to show an appreciable change in the behaviour in the transition state. The reaction with triethylsulphonium iodide is somewhat faster than with tetraethylammonium or trimethylphenylammonium iodide. This is explained in terms of the structure of the sulphonium cation, which is of a pyramidal type[6] with one side of the sulphur atom exposed.

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[3] H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions* p. 70. Reinhold, New York (1958).

[4] S. Winstein, L. G. Savedoff, S. G. Smith, I. D. R. Stevens and J. S. Gall, *Tetrahedron Letters* No. 9, 24 (1960).

[5] Ref. 2, p. 119.

[6] W. J. Pope and S. J. Peachey, *J. Chem. Soc.* 77, 1072 (1900).