TABLE VII

PROPERTIES AND ANALYSES OF SOME *p*-BROMOBENZENESULFONATES

Compound	M.p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
m-$CH_3OC_6H_4(CH_2)_3OBs$	36–38	$C_{16}H_{17}O_4SBr$	49.88	49.72	4.44	4.27
m-$CH_3OC_6H_4(CH_2)_4OBs$	36–38	$C_{17}H_{19}O_4SBr$	51.13	51.08	4.80	4.75
3,4-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	68–71	$C_{18}H_{21}O_5SBr$	50.35	50.65	4.93	4.80
3,5-$(CH_3O)_2C_6H_3(CH_2)_4OBs$	56–57	$C_{18}H_{21}O_5SBr$	50.35	50.20	4.93	4.83
3,4-$(CH_3O)_2C_6H_3(CH_2)_5OBs$	73–73.5	$C_{19}H_{23}O_5SBr$	51.47	51.19	5.23	4.99

lithium aluminum hydride for 12 hours. The alcohol, b.p. 160–163° (2 mm.), $n^{25}D$ 1.5278, was a viscous colorless liquid weighing 5 g. A small sample was redistilled for analysis; $n^{25}D$ 1.5272.

Anal. Calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.87; H, 8.78.

2-(3,4-Dimethoxyphenyl)-ethanol.—The reduction of 3,4-dimethoxyphenylacetic acid with lithium aluminum hydride by the usual method afforded a 37% yield of alcohol, b.p. 140–143° (3 mm.), m.p. 43–45°.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.75. Found: C, 65.86; H, 7.75.

Preparation of Bromobenzenesulfonates and Kinetic Measurements.—The *p*-bromobenzenesulfonates of the various alcohols were prepared by the low temperature method described previously.[5] Physical properties and analyses of these derivatives are summarized in Table VII.

Kinetic measurements were carried out as described previously.[5]

Formolysis Products of 4-(3,5-Dimethoxyphenyl)-1-butyl *p*-Bromobenzenesulfonate.—A solution of 1.95 g. of the *p*-bromobenzenesulfonate was solvolyzed for ten hours at 75° in a solution of 0.35 g. of sodium formate in 100 ml. of anhydrous formic acid. The resulting solution was diluted with 700 ml. of water and extracted with 500 ml. of petroleum ether in three portions. The extracts were washed with water and a sodium bicarbonate solution. The solvent was carefully distilled off, and the residue was reduced with 2 g. of lithium aluminum hydride.

The reduced product was chromatographed on 50 g. of alumina. The first fraction was eluted with 500 ml. of pentane. This solution contained 0.67 g. of 5,7-dimethoxytetralin, b.p. 100° (1.55 mm.), $n^{25}D$ 1.5452. This material was dehydrogenated with 2 g. of chloranil in boiling xylene as described previously.[3,7] The 1,3-dimethoxynaphthalene formed gave 0.35 g. of pure picrate, m.p. 140–141°, mixed m.p. with the picrate obtained from the corresponding solvolysis product from 4-(2,4-dimethoxyphenyl)-1-butyl *p*-bromobenzenesulfonate,[3] 140–141°.

A second fraction from the chromatography was eluted with 700 ml. of ether. There was obtained from this fraction 0.10 g. of alcohol, $n^{25}D$ 1.5310, which formed 0.11 g. of a nitrobenzoate, m.p. 64.5–66°, mixed m.p. with 4-(3,5-dimethoxyphenyl)-1-butyl nitrobenzoate, 65–66°.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE INSTITUTE OF SCIENTIFIC AND INDUSTRIAL RESEARCH, OSAKA UNIVERSITY]

Reactivities of Several ω-Substituted Primary Alkyl Bromides with Tertiary Amines[1,2]

BY KATSUHIKO AKAGI, SHIGERU OAE[3,4] AND MASUO MURAKAMI

RECEIVED AUGUST 29, 1956

Rate constants, heats of activation and entropies of activation have been determined for a series of reactions between ω-substituted primary alkyl bromides and tertiary amines in two different solvents, *i.e.*, nitrobenzene and 50% ethanol. Alternation of reactivities was observed when nitrobenzene was used as a solvent, but no such phenomenon was observed when the solvent was 50% ethanol. The phenyl group showed little polar influence on the reactivities.

Our previous investigations[5] have been extended to the quaternization reactions of ω-substituted primary alkyl bromides with tertiary amines in two different solvents, *i.e.*, nitrobenzene and 50% ethanol, with the thought that these quaternization reactions might give a different trend from those of the reactions of the same bromides with thiosulfate ion, since it has been suggested[6] that the polar characteristic of the quaternization reaction is quite different.

Many studies of the quaternization reaction of alkyl halides with tertiary amines have been reported and our present experiments were carried out following the typical procedure used by Laidler and Hinshelwood[7] and later by Brown and Eldred.[8]

Experimental

The methods of preparations and purifications of all the organic halides have been described elsewhere.[5] The nitrobenzene was purified by partially freezing the fractionated material, which melted around 5.0–5.7°. The portions which melted from 5.5–5.7° were collected for use. Ethanol 50%, was made as reported in the previous paper.[5]

Investigation of Products.—It is known that primary alkyl halides gives quaternary ammonium salts in quantitative yield[9] and also that β-haloalkyl alcohols give quaternary ammonium chlorides in the reaction with trimethylamine.[10] No report has indicated any formation of olefin in the reaction of primary halide with tertiary amine.

In this study, the reaction products were investigated only in the case of β-bromoethyl ether in both 50% ethanol and in nitrobenzene, because among those studied kinetically this compound would be the most likely to give elimination products. The mixture of 1.53 g. of β-bromoethyl ethyl ether and 1.01 g. of triethylamine was placed in a 25-ml.

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[1] Paper VI on "Relative Reactivities of Organic Halides in Displacement Reactions," Paper V, THIS JOURNAL, **78**, 4034 (1956).

[2] Presented at the 9th General Meeting of the Japanese Chemical Society, Kyoto, April, 1956.

[3] John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa.

[4] To whom requests for reprint may be addressed.

[5] K. Akagi, S. Oae and M. Murakami, THIS JOURNAL, **78**, 4034 (1956).

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 346.

[7] K. J. Laidler and C. N. Hinshelwood, *J. Chem. Soc.*, 858 (1938).

[8] H. C. Brown and N. R. Eldred, THIS JOURNAL, **71**, 445 (1949).

[9] O. Westphal and D. Jerchel, *Ber.*, **73B**, 1002 (1940).

[10] J. W. LeHeus, *Arch. Pharm.*, **262**, 570 (1924).

ampoule and was diluted either by 15 ml. of 50% ethanol or by 15 ml. of nitrobenzene and sealed. The sealed ampoules were heated at 80° for 144 hr. continuously to complete the reactions. Then the tubes were broken and the solvents were distilled very carefully in order to collect vinyl ethyl ether, but no trace of vinyl ethyl ether was obtained. Then the solvents were removed to complete dryness *in vacuo*, and from the 50% alcohol solution 2.45 g. of colorless crystalline solid (m.p. 87–90°) and from the nitrobenzene solution 2.48 g. of pale brown crystalline solid (m.p. 90–93°) were obtained in yields of 96.5 and 97.6%, respectively. After recrystallization from either ethanol–petroleum ether mixture or acetone–petroleum ether mixture the m.p. was 97–98°.

Anal. Calcd. for $C_{10}H_{24}ONBr$: Br, 31.5. Found: Br, 31.3.

Kinetic Studies.—Kinetic measurements and rate calculations were made by the procedure used by previous workers.[7,8] In this case, however, reaction was carried out in sealed tubes. Usually the concentration of the stock solutions was 0.20 *N*, so that on mixing equal volumes of the stock solutions the concentration would be 0.10 *N* with respect to both amine and alkyl bromide. After mixing, each 5-ml. of the well-cooled mixed sample was pipeted into a 10-ml. ampoule and sealed. The first tube was taken out for the initial concentration 15 minutes after all the sealed tubes were immersed in a well-controlled thermostat. At suitable time intervals, ampoules were taken out and placed in an ice–water mixture. Each ampoule was broken in standard 0.025 *N* hydrochloric acid and the excess acid was back-titrated with 0.025 *N* barium hydroxide using methyl red as the indicator. Calibration was made at each temperature in order to avoid large errors due to the expansion of the solutions at different temperatures. The rate constants were calculated using the second-order rate equation. Typical runs are given in Tables I, II and III.

TABLE I

REACTION RATE DATA FOR TRIETHYLAMINE AND ω-BROMOPROPYLBENZENE IN NITROBENZENE AT 80.0°

Time, sec.	$(a - x) \times 10^{-2}$, mole/l.	$10^4 k$, l. mole^{-1} sec.$^{-1}$
0	9.3805	
5460	8.7755	1.30
5460	8.6814	1.36
8820	8.3985	1.30
11640	8.1149	1.35
14940	7.8533	1.34
18540	7.6026	1.35
22020	7.3655	1.35
24600	7.1327	1.36
	Mean	1.34 ± 0.02

TABLE II

REACTION RATE DATA FOR TRIETHYLAMINE AND γ-BROMOPROPYL ETHYL ETHER IN NITROBENZENE AT 104.8°

Time, sec.	$(a - x) \times 10^{-2}$, mole/l.	$10^4 k$, l. mole^{-1} sec.$^{-1}$
0	9.1033	
2370	7.8657	7.23
5040	6.8305	7.25
2440	6.1084	7.24
9840	5.5236	7.24
12180	5.0540	7.23
	Mean	7.24 ± 0.01

TABLE III

REACTION RATE DATA FOR TRIMETHYLAMINE AND β-BROMOETHYL ETHYL ETHER IN 50% ETHANOL AT 49.8°

Time, sec.	$(a - x) \times 10^{-2}$, mole/l.	$10^4 k_2$, l. mole^{-1} sec.$^{-1}$
0	9.0316	
2400	8.2058	4.65
4200	7.6837	4.63
5880	7.2542	4.61
7560	6.8666	4.62
9960	6.3825	4.62
11400	6.1068	4.65
13200	5.8190	4.63
	Mean	4.63 ± 0.01

Results and Discussion

The rate-constants, calculated as described, together with the heats of activation, $\Delta H^{\ddagger}$, and entropies of activation, $\Delta S^{\ddagger}$, for the reactions studied are listed in Tables IV, V and VI. The individual points used to calculate the rate constants result in an average deviation of approximately 1% or less throughout the experiments.

TABLE IV

RATE CONSTANTS FOR THE REACTION OF ω-SUBSTITUTED PRIMARY ALKYL BROMIDES WITH TRIETHYLAMINE IN NITROBENZENE

Benzene	$10^3 k_2$, l. mole^{-1} sec. ^{1} 60.0°	70.0°	80.0°	$\Delta H^{\ddagger}$ at 70°, kcal./mole	$\Delta S^{\ddagger}$ at 70°, e.u.
β-Bromoethyl-	0.0532	0.106	0.185	13.9	−36.6
γ-Bromopropyl-	.0400	.0748	.134	13.4	−38.6
δ-Bromobutyl-	.0438	.0836	.149	13.6	−37.8

Ethyl ether	$10^3 k_2$, l. mole^{-1} sec.$^{-1}$ 75.3°	90.3°	104.8°	$\Delta H^{\ddagger}$ at 90.3°, kcal./mole	$\Delta S^{\ddagger}$ at 90.3°, e.u.
β-Bromoethyl-	0.0628	0.145	0.322	13.6	−37.1
γ-Bromopropyl-	.156	.352	.724	13.0	−36.9
δ-Bromobutyl-	.134	.302	.633	13.0	−37.4

TABLE V

RATE CONSTANTS FOR THE REACTION OF ω-BROMOALKYL ETHYL ETHER WITH TRIMETHYLAMINE IN NITROBENZENE

Ethyl ether	$10^3 k_2$, l. mole^{-1} sec.$^{-1}$ 24.9°	37.3°	49.8°	$\Delta H^{\ddagger}$ at 37.3°, kcal./mole	$\Delta S^{\ddagger}$ at 37.3°, e.u.
β-Bromoethyl-	0.110	0.255	0.570	12.0	−34.3
γ-Bromopropyl-	.422	.926	1.97	11.8	−34.4
δ-Bromobutyl-	.405	.856	1.73	10.5	−36.8

TABLE VI

RATE CONSTANTS FOR THE REACTION OF ω-BROMOALKYL ETHYL ETHER WITH TRIMETHYLAMINE IN 50% ETHANOL

Ethyl ether	$10^3 k_2$, l. mole^{-1} sec.$^{-1}$ 24.9°	37.3°	49.8°	$\Delta H^{\ddagger}$ at 37.8°, kcal./mole	$\Delta S^{\ddagger}$ at 37.3°, e.u.
β-Bromoethyl	0.0415	0.148	0.463	17.9	−16.6
γ-Bromopropyl	.116	.401	1.22	17.4	−16.1
δ-Bromobutyl	.316	1.01	3.19	16.9	−15.7

When nitrobenzene was used as the solvent, alternation of reactivities was observed with the increase of methylene linkage in the reaction of these ω-substituted primary alkyl bromides with both triethylamine and trimethylamine. With ω-phenyl-substituted primary alkyl bromides the phenyl group showed little polar influence on reactivities and the reactivities were affected only by the change in the entropy changes. It is particularly interesting that even in the reaction of ω-ethoxy-substituted alkyl bromides with triethylamine, the changes in the heat of activation were found to be rather small compared to that in the reaction with thiosulfate ion.[5] This seems to indicate that the transition stage is nearer to the ideal symmetrical transition step, where the bond-fission requirements are equal to bond-forming requirements,[11]

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[11] Probably such a reaction as those between alkyl halides and the same halide ion would pass though such a symmetrical transition stage.

when the concept of Hammond[12] on the transition state is applied in our case. Thus, the bond-fission requirements in this case are less than those in the case of the reaction with thiosulfate ion. But in the reactions of ω-ethoxy-substituted alkyl bromides, the heat of activation decreased with the increase of the connecting methylene group as in the previous reactions with thiosulfate ion, although alternation of rates was observed in this case. The relatively small values of the heat of activations in spite of rather lower rates of reaction would probably be due to large contribution of solvation in the transition states. Solvation seems also to be responsible for the relatively large values of activation entropies.

However, in 50% ethanol solution, the rate sequence and other kinetic values of ω-ethoxyalkyl bromides were quite different from those in nitrobenzene. No alternation of rates was observed; instead, reactivity increased while heat of activation decreased with the increase of connecting methylene group between ethoxy group and halogen, as in the previous reactions with thiosulfate ion. It is known that in quaternization reactions both the heat and entropy of activation varies a great deal depending upon the solvent used.[13] For example, in the reaction of *p*-methylbenzyl bromide with pyridine the heat and entropy of activation in absolute acetone were 11.3 kcal. and −37.15 e.u., while those values in 90% ethanol were 15.4 kcal. and −22.5 e.u., respectively. Here also we found large differences of temperature coefficient values in two different solvents, *i.e.*, nitrobenzene and 50% ethanol. The differences in solvating power and in nature of solvation would be the responsible factor for these large changes from one solvent to another.[14]

Acknowledgment.—We wish to express our sincere thanks to the Ministry of Education for a Grant as well as the Grant-in-Aid for the Scientific Research and particularly to the Society of the Sigma Xi for the Grant-in-Aid which enabled us to purchase some chemicals from the United States. Our thanks are due both to Mr. Takuzo Fujino who kindly calibrated all our measuring apparatus and to Mr. Tsunehei Oki who carried out a part of the kinetic measurements.

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[12] G. S. Hammond, THIS JOURNAL, 77, 334 (1955).

[13] J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 519, 1840 (1935).

[14] Both nitrobenzene and acetone have a rather highly negatively polarized oxygen atom in carbonyl and nitro group, which would easily solvate with positively charged quaternary nitrogen at the transition state, thus probably lowering the heat of activation; this strong solvation would also give relatively large negative values of entropy of activation. However, the oxygen atom in water or alcohol would not play such a large role.

OSAKA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Ozonolyses of 1,2-Dibenzoylpropene and 1,2-Dibenzoylethylene. Markownikoff's Rule and the Initial Attack of Ozone on an Unsaturated System[1]

BY PHILIP S. BAILEY AND SHEAFFERS S. BATH

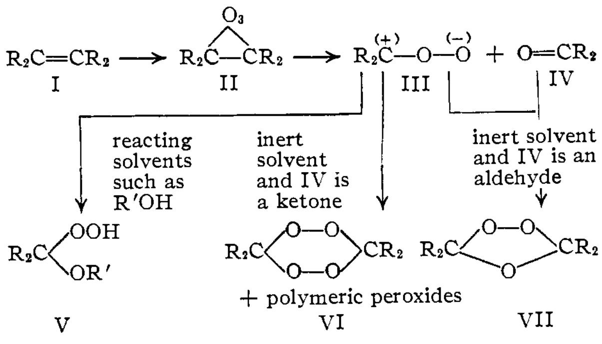
RECEIVED DECEMBER 8, 1956

The ozonolysis of 1,2-dibenzoylpropene in methanol furnishes direct evidence for the specificity previously noted in the attack of ozone on unsymmetrical olefins. The products were phenylglyoxal and α-hydroperoxy-α-methoxypropiophenone. The results are correlated with Markownikoff's rule and a mechanism is proposed which rationalizes the known facts concerning the initial attack of ozone on an unsaturated system Decompositions of α-hydroperoxy-α-methoxypropiophenone and the corresponding hydroperoxide from the ozonolysis of 1,2-dibenzoylethylene in methanol are described.

The Criegee[2] mechanism for ozonolysis has been of tremendous importance in giving a better understanding of the course of the ozonolysis reaction, in particular, the character and fate of the most important intermediate in the reaction, the zwitterion III. It leaves in doubt, however, the nature of the initial attack of ozone on an unsaturated system and of the intermediates leading to the formation of the zwitterion III and the aldehyde or ketone IV.

Recent studies have shown that ozone, like hydrogen chloride and other unsymmetrical reagents, attacks unsymmetrical olefins in a specific manner.[3] This observation furnishes an important clue to the nature of the initial ozone attack.

Criegee Mechanism



The earlier examples of this specificity of ozone attack include isobutene (VIII), which produced an ozonide (XI) as the major product when ozonized in inert solvents, and camphene (XIV) which gave rearrangement products of zwitterion XV.[2c,3] This means, in the case of isobutene, that preferential

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[1] A portion of this paper was presented at the International Ozone Conference, Chicago, Ill., November 28–30, 1956.

[2] (a) R. Criegee and G. Wenner, *Ann.*, 564, 9 (1949); (b) R. Criegee and G. Lohaus, *ibid.*, 583, 6 (1953); (c) R. Criegee, G. Blust and H. Zinke, *Chem. Ber.*, 87, 766 (1954); (d) R. Criegee, A. Kerckow and H. Zinke, *ibid.*, 88, 1878 (1955).

[3] P. S. Bailey, *ibid.*, 88, 795 (1955).