[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Relative Reactivities of Organic Halides in Displacement Reactions. II. Reaction of Mercuric Nitrate with Some Normal Chain Alkyl and Aralkyl Bromides[1]

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Rate constants, heats of activation and entropies of activation have been determined for a series of bromoalkanes and of (ω-bromoalkyl)-benzenes in their reaction with mercuric nitrate in aqueous dioxane. No alternation effects were observed; the results are explainable simply on the basis of hyperconjugation and inductive effects.

Introduction

Conant and co-workers[3] have shown that for a series of normal chain alkyl and aralkyl chlorides, the reactivity in the typical S_N2 reaction with potassium iodide in acetone solution shows a definite alternation effect as the number of methylene groups between the functional group, such as a phenyl or ketone group, and the chlorine atom is increased. In the (ω-chloroalkyl)-benzene chlorides, for example, the alternation in rate is appreciable up to (7-chloroheptyl)-benzene with benzyl chloride the most, and (2-chloroethyl)-benzene the least, reactive compound in the series. A similar phenomenon was observed in esters and ethers, and the general concept of "alternate polarity" has become quite firmly established in the literature.[4] Dewar[5] has more recently offered an explanation of the alternation effect, as observed in Conant's work, based on second-order hyperconjugation.

Since, however, the effect has been reported only for S_N2 reactions, there is still doubt as to whether or not it is merely electronic in nature. If the effect were entirely electronic, a similar alternation in reaction rates in a homologous series of alkyl halides might be expected in reactions of the ionization mechanism or S_N1 type, as well.

The present paper deals with the reaction of mercuric nitrate with benzyl bromide and (2-bromoethyl)-, (3-bromopropyl)-, (4-bromobutyl)-, (5-bromopentyl)- and (6-bromohexyl)-benzene, as well as ethyl bromide, 1-bromopropane, 1-bromobutane and 1-bromopentane. Roberts and Hammett[6] have presented convincing evidence in the case of benzyl chloride that the reaction proceeds by way of a rate-determining formation of a carbonium ion

$$Hg^{++} + R\text{-}Cl \longrightarrow HgCl^{+} + R^{+}$$

followed by a fast step to form the alcohol or alkyl nitrate. The rate of reaction of alkyl halides in ionizing solvents is accelerated by a factor of several hundred on addition of small concentrations of mercuric nitrate. This acceleration is attributed to the driving force derived from the energy of formation of a mercury–halogen bond.

Later Benfey[7] used this reaction in his study on ethyl bromide, 1-bromopropane, 1-bromo-2-methylpropane and bromocyclohexane and found that the reaction occurred by the rate-determining attack of mercuric ion on halogen, with an equilibrium governing the relative concentrations of mercuric ion, mercuric monobromide ion and mercuric dibromide. Of the three mercuric species involved, only the first contributed perceptibly to the rate. Benfey explained the experimentally determined rate sequence ethyl > *n*-propyl > isobutyl on the basis of a hyperconjugation effect.

In the present studies on bromoalkanes and (ω-bromoalkyl)-benzenes we have calculated the heats of activations and have confirmed the results and explanation offered by Benfey. No alternation effect was observed in the (ω-bromoalkyl)-benzene series.

Experimental

Materials.—Eastman Kodak Co. C.P. 1,4-dioxane was purified in 2-l. quantities by the method of Beste and Hammett.[8] The simple bromoalkanes as well as benzyl bromide, (2-bromoethyl)-benzene and (3-bromopropyl)-benzene were all Eastman Kodak white label products. All the bromides were washed with concentrated sulfuric acid, water, 10% sodium carbonate solution, again with water, then dried over calcium chloride and finally fractionally distilled just before use. 1-Bromopropane was prepared from 1-propanol by treatment with sodium bromide and sulfuric acid.

(4-Bromobutyl)-benzene.—To the Grignard reagent prepared by reaction of 18.5 g. (1 mole) of (2-bromoethyl)-benzene with 25 g. of magnesium in 500 ml. of anhydrous ether, 60 g. (1.4 moles) of well-cooled ethylene oxide was added dropwise over one hour at −10–0°. Then half of the ether was removed by distillation, the same volume of benzene was added, and the mixture was distilled until the temperature of the distillate reached 60°. The reaction mixture was decomposed with ice-water, neutralized with dilute sulfuric acid, and the product extracted several times with ether. The combined extracts were neutralized with sodium carbonate, washed and dried over Drierite. Fractional distillation of the residue after removal of solvent yielded 106 g. of 4-phenyl-1-butanol, b.p. 124–125° (14 mm.).

A mixture of 76 g. of the alcohol, 102 g. of freshly prepared thionyl bromide[9] and 100 ml. of chloroform was heated on a steam-bath for 2 hours. The chloroform and excess thionyl bromide were removed at the water-pump, and the residue was washed with 10% sodium carbonate solution, then with water, and dried over calcium chloride. Fractional distillation gave 60 g. of crude (4-bromobutyl)-benzene, b.p. 98° (2.5 mm.). The crude product was washed three times with concentrated sulfuric acid to remove unreacted alcohol, then with water, 10% sodium carbonate solution, and again with water, then dried over calcium chloride and finally distilled. The fraction which distilled

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[1] First paper in this series, S. Oae and C. A. VanderWerf, THIS JOURNAL **75**, 2724 (1953).

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[3] J. B. Conant and W. R. Kirner, THIS JOURNAL, **46**, 232 (1924); J. B. Conant, W. R. Kinner and R. E. Hussey, *ibid.*, **47**, 488 (1925).

[4] See, for example, (a) G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **123**, 532 (1923); (b) Lapworth, *Mem. Proc. Manchester Lit. and Phil. Soc.*, **64**, No. 3 (1920); (c) E. Müller, "Neuere Anschauungen der Organischen Chemie," Julius Springer, Berlin, 1940, pp. 66–73.

[5] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp. 157–159.

[6] I. Roberts and L. P. Hammett, THIS JOURNAL, **59**, 1063 (1937).

[7] O. T. Benfey, *ibid.*, **70**, 2163 (1948).

[8] G. W. Beste and L. P. Hammett, *ibid.*, **62**, 2481 (1940).

[9] R. C. Elderfield, *et al.*, *ibid.*, **68**, 1516 (1946).

TABLE I

1-BROMOBUTANE–MERCURIC NITRATE REACTION IN 70% DIOXANE AT 25°

$[\mathrm{Hg(NO_3)_2}] = 0.02471\ N$; $[\mathrm{CH_3CH_2CH_2CH_2Br}] = 0.0250\ N$; $[\mathrm{HNO_3}] = 0.0245\ N$; $N = -\mathrm{d}x/[\mathrm{RBr}]x\mathrm{d}t$, x, [RBr] and dx all expressed in N; $K = 4$; $[\mathrm{Hg^{++}}]/x$ calculated by eq. 2. By extrapolation $k_1 = 0.0665$ mole^{-1} min.$^{-1}$ l.

t_1, min.	0	60	116	230	442	647
t_2, min.	60	116	230	442	647	1393
Δx	0.001201	0.000921	0.001573	0.002296	0.001598	0.003869
x^a	.02411	.02305	.02190	.01987	.01792	.01519
[RBr](mole/l.)^a	.02440	.02334	.02209	.02016	.01821	.01548
N	.0340	.0306	.0287	.0270	.0239	.0220
N_{cor}	.0324	.0310	.0295	.0270	.0245	.0210
$\mathrm{Hg^{++}}/x$	.488	.466	.441	.402	.363	.317
$k_1 = N_{\mathrm{cor}}/\mathrm{Hg^{++}}/x$	.0665	.0665	.0669	.0672	.0675	.0662

^{a} Mean value of the concentrations at t_1 and t_2.

at 107–107.5° (6 mm.) was collected and used for the kinetic experiments.

Anal. Calcd. for $C_{10}H_{13}Br$: C, 56.4; H, 6.2; Br, 37.5. Found: C, 56.6; H, 6.0; Br, 37.6.

(5-Bromopentyl)-benzene.—To the Grignard reagent prepared from 200 g. of (3-bromopropyl)-benzene and 25 g. of magnesium in 500 ml. of anhydrous ether, 60 g. of ethylene oxide was added and the product treated as described for (4-bromobutyl)-benzene to yield 86 g. of 5-phenyl-1-pentanol. Reaction of the alcohol with an equivalent quantity of thionyl bromide gave the crude bromide, b.p. 123–125° (7 mm.) in 70% yield. After the usual sulfuric acid treatment, the fraction of pure (5-bromopentyl)-benzene distilling at 123–125° (7 mm.) was collected.

Anal. Calcd. for $C_{11}H_{15}Br$: C, 58.2; H, 6.6; Br, 35.3. Found: C, 58.2; H, 6.8; Br, 35.3.

(6-Bromohexyl)-benzene.—6-Phenyl-1-hexanol, b.p. 128–130° (2.5 mm.), was obtained in 57% yield by treatment of the Grignard reagent of (4-bromobutyl)-benzene with ethylene oxide by the general method previously described. Conversion of the alcohol to the bromide, b.p. 113–114° (2 mm.), was accomplished in 64% yield.

Anal. Calcd. for $C_{12}H_{17}Br$: C, 59.8; H, 7.1; Br, 33.1. Found: C, 60.1; H, 7.2; Br, 32.9.

The refractive indices, $n^{20}\mathrm{D}$, of the (ω-bromoalkyl)-benzenes were as follows: (2-bromoethyl)-benzene, 1.5560; (3-bromopropyl)-benzene, 1.5438; (4-bromobutyl)-benzene, 1.5382; (5-bromopentyl)-benzene, 1.5318; and (6-bromohexyl)-benzene, 1.5295.

Kinetic Determinations and Calculation of Rates.—The kinetic measurements were made by following the production of bromide ion according to the method described in detail by Roberts.[10] Dioxane (70% by volume) was used throughout as solvent. Mercuric nitrate and nitric acid were added to bring the concentration of each to approximately 0.025 N; the exact concentrations were determined by titration. Exactly 100 ml. of the freshly prepared solution was placed in a 250-ml. stoppered flask and was kept immersed in a thermostat until the temperature of the solution was identical with that of the bath. Then an amount of organic bromide required to make the solution approximately 0.025 N in that reagent was weighed into a 1-ml. weighing bottle and was added with vigorous shaking to the reaction flask. At measured intervals, after this initial time, 10-ml. samples were pipetted into 5 ml. of 0.1 N potassium chloride solution. The excess chloride ion was titrated against 0.025 N mercuric nitrate solution with diphenyl carbazide as indicator in a solution made sufficiently acidic with nitric acid.

Rate calculations were made by the method of Benfey.[7] Values for N were calculated from his equation

$$-\mathrm{d}x/[\mathrm{RBr}]x\mathrm{d}t = k_1[\mathrm{Hg^{++}}]/x + k_2[\mathrm{HgBr^+}]/x = N \quad (1)$$

in which k_1 and k_2 are the velocity constants for the possible reactions, respectively, and x is the concentration of total mercuric ion at time t.

$$\mathrm{RBr} + \mathrm{Hg^{++}} \xrightarrow{k_1} \mathrm{R^+} + \mathrm{HgBr^+}$$

$$\mathrm{RBr} + \mathrm{HgBr^+} \xrightarrow{k_2} \mathrm{R^+} + \mathrm{HgBr_2}$$

The equilibrium controlling the concentrations of the two mercuric ion species is

$$\mathrm{Hg^{++}} + \mathrm{HgBr_2} \rightleftarrows 2\mathrm{HgBr^+}$$

$$K = [\mathrm{HgBr^+}]^2/[\mathrm{Hg^{++}}][\mathrm{HgBr_2}]$$

Following the method of Benfey,[7] in the special case where $K = 4$

$$[\mathrm{HgBr^+}]/x = 1 - x/x_0,\ [\mathrm{Hg^{++}}]/x = {}^1/_2 x/x_0 \quad (2)$$

where x_0 is the initial concentration of mercuric ion in equivalents. Values of N, calculated from equation 1, were plotted against the mean x/x_0, and a smooth curve drawn through the points to give the corrected values of N. The rate constant k_1 was calculated from the ratio

$$N_{\mathrm{cor}}/[\mathrm{Hg^{++}}]/x = k_1$$

Data for a typical run in the study of the reaction of 1-bromobutane with mercuric nitrate are shown in Table I.

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 Table II.

TABLE II

RATE CONSTANTS OF REACTION OF ALKYL AND ARALKYL BROMIDES WITH MERCURIC NITRATE

Compound	Temp., °C.	k (mole^{-1} sec.$^{-1}$ l.)	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
Ethyl bromide	25.23	2.47×10^{-2}		
	37.12	7.93×10^{-3}	15.3	0.21
1-Bromopropane	25.23	1.35×10^{-3}		
	40.60	5.03×10^{-3}	15.8	.36
1-Bromobutane	25.23	1.12×10^{-3}		
	40.60	4.22×10^{-3}	15.9	.39
1-Bromopentane	25.23	1.11×10^{-3}		
	40.60	4.17×10^{-3}	15.9	.39
Benzyl bromide	Too fast to be measured, even at 0°			
(2-Bromethyl)-	25.23	5.02×10^{-4}		
benzene	40.60	2.07×10^{-3}	17.0	.64
(3-Bromopropyl)-	25.23	4.48×10^{-4}		
benzene	40.60	1.75×10^{-3}	16.7	.60
(4-Bromobutyl)-	25.23	7.53×10^{-4}		
benzene	40.60	2.90×10^{-3}	16.2	.48
(5-Bromopentyl)-	25.23	7.87×10^{-4}		
benzene	40.60	3.03×10^{-3}	16.2	.47
(6-Bromohexyl)- benzene	25.23	7.80×10^{-4}		

No hint of an alternation effect was observed in the reaction of either the 1-bromoalkane or the (ω-bromoalkyl)-benzene series with mercuric nitrate. The rate sequence ethyl bromide > 1-bromopropane, as well as the lower heat of activation

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[10] I. Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).

for the reaction of the former, may be explained by the increase in hyperconjugative resonance stabilization of the transition state with an increase in the number of available β-hydrogen atoms.[7] Differences in the rate constants for 1-bromopropane, 1-bromobutane, and 1-bromopentane, all of which have two β-hydrogen atoms, are very slight.

The rapid reaction of benzyl bromide is of course, explained by resonance stabilization of the transition state through participation of the phenyl group. In (2-bromoethyl)-benzene, the tendency of phenyl group to destabilize the transition state, presumably because of its electron-withdrawing inductive effect, is apparently not overcome significantly by the possible neighboring group interaction of the β-phenyl group.[11] From the heat of activation sequence, (2-bromoethyl)-benzene > (3-bromopropyl)-benzene > (4-bromobutyl)-benzene, it is seen that the electron-withdrawal effect of the phenyl group is diminished with an increase in the number of carbon atoms through which it must act, apparently disappearing altogether in the last-named compound. Even here, however, the phenyl-substituted bromide reacts more slowly than 1-bromobutane, indicating that the phenyl group inhibits the reaction through another mechanism, as well. It may be that mercuric ion, as was observed for silver ion, forms a loose complex[12] with the phenyl group in which its electrophilic character, and therefore the rate of its reaction with the bromides, is considerably decreased.

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[11] See D. J. Cram, This Journal, **71**, 3863 (1949); S. Winstein and co-workers, *ibid.*, **74**, 1113, 1140 (1952).

[12] L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 3113, 5034 (1950).

[Contribution from the Chemical Laboratories of The University of Texas and the University of Virginia]

The *cis*- and *trans*-β-Aroyl-α- and β-methylacrylic Acids and β-Aroyl-α-methylenepropionic Acids

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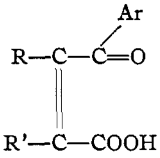
Ultraviolet absorption studies on the *cis*-β-aroyl-α- and β-methylacrylic acids and related compounds show that the *cis* compounds in solution are cyclic but are open-chain in the form of the anions. The *cis*-β-benzoyl-α- and β-methyl compounds and both β-aroyl-α-methylenepropionic acids have been made, respectively, from citraconic and itaconic anhydrides by Friedel–Crafts reactions. The structures and configurations have been demonstrated. The *trans* isomers are the stable forms; the *cis* isomers are labile; and the β-aroyl-α-methylenepropionic acids also are labile and the least stable of the three types. Interconversions of the various isomers are described.

This paper deals with the extension of earlier work and represents a joint effort which is basic to three fields of interest, the study of ring-chain tautomerism of compounds containing groups capable of interacting when sterically favorable circumstances are involved,[2] the influence of configuration and substitution on the effectiveness of the whole or parts of conjugated systems,[3] and the reactions and 1,3-hydrogen shifts during reactions of systems of the type —COCH=C(CH<)CO—.[4]

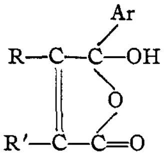
cis-β-Aroylacrylic acids (I) show no tendency to form cyclic derivatives.[2j] On the other hand, the *cis*-α[2b,f] and β[2b]-methyl, α,β[2c,g,h]-dimethyl and α,β-dibromo[2a] derivatives (II or III) give cyclic esters under acid-catalyzed esterification or methanolysis of the acid chloride, although they react with diazomethane and through the silver salts with methyl iodide to give open-chain esters.

ArCOCH=CHCOOH

I



II



III

The *cis*-acid of the β-(4-bromobenzoyl)-α-methylacrylic series (XIVb) was believed to be open-chained II because of its ready solubility in sodium bicarbonate and facile acid- or base-catalyzed rearrangement to the more stable *trans* isomer, whereas the structurally isomeric *cis*-β-methyl acid Vb which was not so easily rearranged and which was slow to dissolve in sodium bicarbonate, was presumed to be cyclic. Polarographic studies by Wawzonek, *et al.*,[2l] indicate that the latter compound Vb is cyclic to a considerable degree but open-chain in the form of the anion.

It has now become possible through determination of the ultraviolet absorption characteristics of the various compounds involved in both the α-

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[1] (a) University of Virginia. (b) University of Texas. This work was supported in part by a grant-in-aid from the Research Corporation (to P.S.B.). (c) E. C. A. Scholarship from the State Department, University of Texas, 1952–1953. (d) Graduate Assistant, University of Virginia, 1952–1953. (e) Experimental contributions will be described in greater detail in doctoral dissertations to be completed shortly at the Universities of Texas and Virginia.

[2] (a) R. E. Lutz, This Journal, **52**, 3405 (1930); (b) R. E. Lutz and R. J. Taylor, *ibid.*, **55**, 1168 (1933); (c) **55**, 1593 (1933); (d) R. E. Lutz and A. W. Winne, *ibid.*, **56**, 445 (1934); (e) R. E. Lutz, *ibid.*, **56**, 1378 (1934); (f) R. E. Lutz, D. T. Merritt and M. Couper, *J. Org. Chem.*, **4**, 95 (1939); (g) R. E. Lutz and M. Couper, *ibid.*, **6**, 77; (h) 91 (1941); (i) R. E. Lutz and F. B. Hill, *ibid.*, **6**, 175 (1941), (j) R. E. Lutz and G. W. Scott, *ibid.*, **13**, 284 (1948); (k) C. L. Browne and R. E. Lutz, *ibid.*, in press; (l) S. Wawzonek, H. W. Vaught, Jr., and J. W. Fan, This Journal, **67**, 1300 (1945).

[3] (a) L. P. Kuhn, R. E. Lutz and C. R. Bauer, *ibid.*, **72**, 5058 (1950); (b) R. E. Lutz and C. R. Bauer, *ibid.*, **73**, 3456 (1951.

[4] (a) R. E. Lutz and P. S. Bailey, *ibid.*, **67**, 2229 (1945); (b) P. S. Bailey, G. Nowlin, S. H. Pomerantz, J. V. Waggoner and E. E. Kawas, *ibid.*, **73**, 5560 (1951); (c) P. S. Bailey and S. H. Pomerantz, *ibid.*, **75**, 281 (1952); (c) P. S. Bailey, Thomsen and Bath, a paper to be published shortly.