[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Effect of Halogen Atoms on the S_N1 Reactivity of Other Halogen Atoms Attached to the Same Carbon Atom

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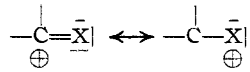
This paper reports the results of one phase of an investigation concerning the effect of halogen atoms on the reactivity of other halogen atoms attached to the same carbon atom. The data reported herein were obtained in attempting to determine the effect on S_N1 reactivity.

There are several ways in which α-halogen atoms (as compared to α-hydrogen atoms) could influence the ease of carbonium ion formation and hence the S_N1 reactivity. The inductive effect should make the central carbon atom more positive and decrease S_N1 reactivity. It might be thought that the larger halogen atoms cause "B" strain[1] and thus increased reactivity. However, from the examination of models this does not appear likely. α-Halogen atoms could also stabilize the carbonium ion by resonance



$$-\underset{\oplus}{\overset{|}{C}}=\underset{-}{\bar{X}}| \longleftrightarrow -\overset{|}{C}-\underset{\oplus}{\bar{X}}|$$

It is this consideration which is the most important according to Hughes,[2] who cites as evidence the work of Olivier and Weber.[3] These workers found that in the rate of hydrolysis in 50% aqueous acetone, $C_6H_5CCl_3 > C_6H_5CHCl_2 > C_6H_5CH_2Cl$. Olivier and Weber found the rate of hydrolysis to be independent of the concentration of hydroxide ion in the cases of benzal chloride and benzotrichloride. This, Hughes cites as proof that the hydrolysis proceeds *via* the carbonium ion mechanism. We do not agree that this is absolute proof of the mechanism, but do agree that the S_N1 mechanism seems considerably more probable. Work designed to determine the mechanism of these hydrolysis reactions is under way in this Laboratory.

It will be assumed in this paper that the reaction does proceed by the carbonium ion mechanism (in the case of the trihalides, at least). Among the other bits of evidence for this point of view is the fact that α-halogenation decreases the S_N2 reactivity in the cases where the mechanism is known to be S_N2 (methyl halides are more reactive than methylene halides),[4] yet in the case of the benzyl halides, the reactivity is found to be increased by α-halogen atoms.

In order, then, to see if α-bromination also brings about the effect noted with α-chlorination and to compare the magnitude of the effects due to bromine and to chlorine, the rates of hydrolysis of all of the α-chloro and α-bromo derivatives of toluene have been determined in 50% aqueous acetone. The data obtained are shown in Table I.

TABLE I

RATES OF HYDROLYSIS IN 50% AQUEOUS ACETONE[a]

Compound	$k \times 10^4$ (min.$^{-1}$) 20°	30°	45°	E,[b] kcal.	$k \times 10^4$ (30°) per Br	per Cl
$C_6H_5CH_2Cl$		0.2231 ± 0.0041	1.174 ± 0.028	21.2		0.2231
$C_6H_5CH_2Br$		5.684 ± 0.085	25.07 ± 0.24	19.1	5.684	
$C_6H_5CHCl_2$[c]		2.214 ± 0.037	13.66 ± 0.14	23.3		1.107
$C_6H_5CHClBr$	8.602 ± 0.063	31.08 ± 0.19	162.4 ± 1.0	21.9	31.08	
$C_6H_5CHBr_2$		6.847 ± 0.047	47.06 ± 0.44	24.6	3.423	
$C_6H_5CCl_3$	34.55 ± 0.25	110.5 ± 0.9		20.5		36.8
$C_6H_5CCl_2Br$	717.1 ± 14.1	2122 ± 41		19.2	2122	
$C_6H_5CClBr_2$	643.9 ± 11.5	1803 ± 59		18.2	901	
$C_6H_5CBr_3$	362.3 ± 12.9	1131 ± 21		20.1	377	

[a] By volume. [b] ± about 0.5 kcal. [c] Since even three fractionations did not remove the last traces of more reactive compounds from the sample, the first 5% of the reaction was ignored in calculating the rate constant.

It is assumed that in all of the reactions investigated the replacement of the first halogen atom is the rate-controlling step. In agreement with this assumption, it was found that benzoyl chloride, a possible intermediate in the hydrolysis of the chlorine-containing trihalides, hydrolyzed at a rate too fast to measure under the conditions used.

In the case of the halides containing both chlorine and bromine, it is assumed that the reaction consists very largely of the rate-controlling replacement of a bromine atom first, rather than a chlorine atom. One reason for this is that in nucleophilic displacement reactions, bromides have been invariably found to be much more reactive than the corresponding chlorides. Moreover, in the case of the chlorobromides the bromine is activated by an α-chlorine atom, while the chlorine atom has an α-bromine as a substituent. Since it is found in the current investigation that α-chlorine increases reactivity more than α-bromine, it is seen that this makes the predominant initial replacement of bromine even more likely.

In order to learn the reactivity of the individual halogen atoms in a given halide, the rate constants for the various halides have been divided by the number of the halogen atoms thought responsible for the reaction. That is, the constants for the bromides and bromochlorides are divided by the number of bromine atoms, and the constants for the chlorides by the number of chlorine atoms.

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[1] H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

[2] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[3] S. C. J. Olivier and A. P. Weber, *Rec. trav. chim.*, **53**, 869 (1934).

[4] P. Petrenko-Kritchenko and V. Opotsky, *Ber.*, **59B**, 2131 (1926).

An examination of the rate constants shows that in all cases the replacement of α-hydrogen by chlorine causes increased reactivity. This is also true of bromine, except that the bromine on benzyl bromide is more reactive than those on benzal bromide. This may be due to the fact that benzyl bromide hydrolyzes largely by the S_N2 mechanism, and hence the rate constant shown is much larger than the rate constant for S_N1 hydrolysis. The fairly small difference in rates between benzyl and benzal chloride may be due to S_N2 hydrolysis of benzyl chloride. The benzyl halides should certainly have more tendency to react by the S_N2 mechanism than any of the other halides used.

The observed order of reactivity appears attributable to the resonance stabilization of the carbonium ion by the directly attached halogen atom. When the halogen atom is chlorine, it would be expected that this stabilization would be greater than with bromine, due to the greater ease of double bond formation with chlorine, an element in an earlier period of the periodic table.

The only generalization drawn from the activation energies is that those for the benzal halides are higher than those for the benzyl- and benzotrihalides.

Experimental

Compounds Used.—Fractionated Eastman Kodak Co. benzyl chloride, b.p. 178–179° (745 mm.). Benzyl bromide from the photobromination of toluene, b.p. 76° (10 mm.). Eastman Kodak Co. benzal chloride (fractionated three times), b.p. 206–207° (740 mm.). Eastman Kodak Co. benzotrichloride (fractionated twice), b.p. 85–86° (8 mm.).

Also used were the following compounds for most of which the boiling point and analysis are the only reported data:

Benzal Chlorobromide.—Benzyl chloride was brominated at 150° in the presence of light.[5] A fraction boiling at 93–94° (7 mm.) was used.

Anal. Calcd. for $C_6H_5CHClBr$: side chain halogen, 56.14. Found: halogen, 55.66.

Benzal Bromide.—This was prepared by the photobromination of toluene. A fraction boiling at 108–109° (6 mm.) and melting at 0–1° was taken.[6]

Anal. Calcd. for $C_6H_5CHBr_2$: side chain bromine, 63.95. Found: Br, 63.00.

Benzodichlorobromide.[5]—For 3 hours, a mixture of 266 g. (1.4 moles) of benzotrichloride, 20 g. (0.056 mole) of mercuric bromide, and 490 g. (4.9 moles) of sodium bromide was stirred at 150–160°. Filtration and fractional distillation yielded 25 g. of benzodichlorobromide, boiling at 98° (4.2 mm.) and m.p. 4–7°.

Anal. Calcd. for $C_6H_5CCl_2Br$: equivalent wt. (as an acid, after hydrolysis), 60.00. Found: equiv. wt., 60.87.

Benzochlorodibromide.—Benzal chloride was brominated at 140° in the presence of light.[5] Material boiling at 110–111° (4.5 mm.) and melting at 27–30° was used.

Anal. Calcd. for $C_6H_5CClBr_2$: equiv. wt., 71.10. Found: equiv. wt., 71.01.

Benzotribromide.—Benzyl bromide was brominated in the presence of light.[5] The material boiling at 123° at 4.5 mm. was recrystallized from hexane yielding white crystals, m.p. 56–57°.

Anal. Calcd. for $C_6H_5CBr_3$: equiv. wt., 82.21. Found: equiv. wt., 81.55.

Molecular Refractivity.—It was thought desirable to further characterize the lesser known compounds by their molecular refractivities. The observed values were in all cases somewhat higher than the calculated. However, this was also found to be the case when the densities and indices of refraction (either ours or the best values from the literature) were used in determining the molecular refractivity of the well known halides. The data obtained are shown in Table II.

Determination of Rate Constants.—The following is an example of the method used. A mixture of 20 ml. of acetone and 25 ml. of water in a 100-ml. volumetric flask was allowed to reach thermal equilibrium in a well-stirred water-bath at 30 ± 0.02°. To this, 5 ml. of a solution of 0.04872 g. of benzotrichloride in acetone was added, and the flask shaken.

TABLE II

MOLECULAR REFRACTIVITIES OF α-HALOTOLUENES

Compound	Temp., °C.	n^t_D	$d^t_{4°}$	M_k Found	Calcd.
$C_6H_5CH_2Cl$	17.4	1.5391	1.1015	36.00	35.79
$C_6H_5CH_2Br$	22	1.5742	1.4380	39.26	38.69
$C_6H_5CHCl_2$	19.4	1.5515	1.2502	41.13	40.66
$C_6H_5CHClBr$	25	1.5808	1.5478	44.23	43.56
$C_6H_5CHBr_2$	28	1.6106	1.8365	47.22	46.46
$C_6H_5CCl_3$	19.2	1.5584	1.3733	45.92	45.53
$C_6H_5CCl_2Br$	28	1.5846	1.6379	49.07	48.42
$C_6H_5CClBr_2$	32	1.6089	1.9017	51.77	51.31

After 30 minutes, the flask was removed from the constant temperature bath and vigorously swirled in a Dry Ice-acetone-bath. (Trial experiments showed that this brought the temperature below 0° in less than 15 seconds.) Two drops of phenolphthalein indicator was added, and the cold solution titrated with 0.0502 N NaOH. Other points were taken similarly at different intervals of time. The rate constant for each point was calculated from the first order rate equation

$$k = \frac{2.303}{t} \log \frac{\text{ml.}_\infty}{\text{ml.}_\infty - \text{ml.}_t}$$

and the values obtained are shown in Table III.

TABLE III

Time, min.	$k \times 10^4$
15	111.9
30	110.0
60	111.5
105.25	109.4
130	109.8
Av.	110.5 ± 0.9

Summary

The rates of hydrolysis in 50% aqueous acetone have been determined for all of the side-chain chloro and bromo derivatives of toluene. From the data, it appears that as α-substituents both halogens cause increased S_N1 reactivity (as compared to hydrogen). It is thought that this is largely due to resonance stabilization of the carbonium ions. This occurs to a greater extent with chlorine, due to the greater ease of double bond formation.

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(5) L. S. Heble, D. R. Nadkarni and T. S. Wheeler, *J. Chem. Soc.*, 1322 (1938).

(6) The only values of the density and index of refraction of benzal bromide were recorded by T. Curtius and E. Quedenfeldt, *J. prakt. Chem.*, [2] **58**, 389 (1898). It is obvious that these workers must have had some other compound (see also D. Vorländer, *Ann.*, **341**, 22 (1905).)