Acetyl Hyprobromite as an Intermediate in the Mercuric Acetate Induced Bromination of Alkylbenzenes

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In acetic acid solutions of mercuric acetate and bromine an equilibrium is established with respect to the formation of acetyl hypobromite and acetoxymercuric bromide [$Hg(OCOCH_3)Br$]. The equilibrium constant for this reaction has been evaluated by spectrophotometric methods. A kinetic study of the halogenation of benzene and some of the methylbenzenes in such solutions has been conducted. Evidence has been obtained that the reactions are polar rather than radical in character and that acetyl hypobromite is the brominating agent.

Mixtures of bromine and silver acetate are known to be effective as aromatic brominating agents and as reagents for the conversion of olefins to bromoacetates[1] [$>C(OCOCH_3)C(Br)<$]. Presumably acetyl hypobromite functions as an intermediate in these reactions. The zinc chloride catalyzed bromination of alkylbenzenes in acetic acid is subject to inhibition by hydrogen bromide, a fact which has tentatively been explained on the assumption that acetyl hypobromite, formed as shown in eq. 1, is an effective brominating agent[2]—and much more so than bromine itself. It has previously been established that acetyl hypochlorite is more reactive than chlorine as an electrophile in aromatic substitution processes.[3]

$$CH_3COOH + Br_2 + ZnCl_2 \rightleftarrows CH_3COOBr + ZnCl_2 \cdot HBr \quad (1)$$
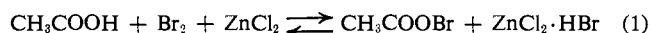
A detailed study of the function of acetyl hypobromite as a brominating agent for alkylbenzenes in acetic acid has now been conducted. Both the reaction products and reaction kinetics have been investigated. So far a pure sample of acetyl hypobromite has not been prepared. A satisfactory procedure for generation of the hypobromite in equilibrium with free bromine in acetic acid solutions of mercuric acetate has been employed in connection with this investigation.

Experimental Section

Materials. Allied Chemical Co. reagent grade acetic acid was further purified by the method of Orton and Bradfield.[4] Reagent grade bromine (J. T. Baker Chemical Co.) was used without additional treatment. The benzene used in kinetic experiments was Fisher Scientific Co. spectroanalyzed material. Samples of toluene, *m*- and *p*-xylene, the isomeric bromotoluenes, and 2-bromo-*p*-xylene and bromobenzene were of the best grade obtainable either from

Eastman Organic Chemicals or Matheson Coleman and Bell. Silver acetate (Mallinckrodt Chemical Co.) was dried in a vacuum oven at 60° for 24 hr. before use. Mercuric acetate (J. T. Baker Chemical Co. reagent grade) was used after drying under vacuum at 50° for 4 to 5 hr. That the dried salt was of analytical grade was established by titration of weighed samples in acetic acid solution with standard potassium thiocyanate solution.

In connection with gas chromatographic analyses of the products of competitive brominations of methylbenzene mixtures, a sample of bromo-*m*-xylene was prepared under conditions similar to those employed in the kinetic studies later described. To a solution of 60 g. (0.19 mole) of mercuric acetate and 20 ml. (0.16 mole) of *m*-xylene in 1000 ml. of acetic acid a solution of 8 ml. (0.15 mole) of bromine in 100 ml. of acetic acid was added dropwise over a 3-hr. period. The product mixture was washed with 1 l. of water. The aqueous extract was washed with two 100-ml. portions of petroleum ether. The combined organic phases of these several extractions were washed with water, dried over sodium sulfate, and freed of petroleum ether by distillation at atmospheric pressure. The residue was distilled at 55–56° (5 mm.). An initial fraction of 5-ml. volume was discarded. Gas chromatographic analysis (under conditions later described) of a sample of the second (7 ml.) fraction showed only one major peak for the product of monobromination of *m*-xylene.

Determination of Equilibrium Constants for Formation of Acetyl Hypobromite in Acetic Acid. Solutions of bromine in acetic acid were prepared at 25.0° and standardized by iodometric methods. Stock solutions of mercuric acetate in acetic acid, prepared at 25.0°, were analyzed for mercuric ion content by titration with potassium thiocyanate in the presence of ferric ion. Aliquots of the bromine and mercuric acetate solutions were mixed, and samples of the mixtures were transferred to silica absorption cells of known path length (0.1–2.0 cm.). The cells were stored in a temperature-controlled (25.0°) housing of a Beckman DU spectrophotometer. After temperature equilibration of the cells and housing, the content of free bromine in the reaction mixtures was established through optical density measurements at 400 mμ using pure acetic acid as a blank. It was assumed in making this calculation that of all the reactants and products, free bromine was the only one which absorbed at this wave length. It was established by separate measurement that at 400 mμ $\epsilon_{Br_2} = 185$ in acetic acid. The data thus obtained and interpreted were used to evaluate equilibrium constants for acetyl hypobromite formation on the assumption that in acetic acid an equilibrium is established as indicated

(1) (a) L. Birckenbach and J. Goubeau, *Ber.*, **66B**, 1280 (1933); (b) W. G. Dauben and H. J. Tilles, *J. Am. Chem. Soc.*, **72**, 3185 (1950); (c) D. C. Abbott and C. L. Arcus, *J. Chem. Soc.*, 1515 (1952).
(2) R. Josephson, R. M. Keefer, and L. J. Andrews, *J. Am. Chem. Soc.*, **83**, 3562 (1961).
(3) P. B. D. de la Mare, I. C. Hilton, and S. Varma, *J. Chem. Soc.*, 4044 (1960).
(4) K. J. P. Orton and A. E. Bradfield, *ibid.*, 983 (1927).

by eq. 2 (see Results section). Inclusion in the reaction mixtures of minor amounts of water (0.3 *M*) or acetic anhydride (1 vol. %) had no significant effect on the equilibrium position.

Preparation of t-Butyl Hypobromite Solutions. The procedure followed was similar to that employed by Walling and Padwa.[5] To a stirred mixture of 200 ml. of water and 32 g. (0.20 mole) of bromine was added 77 g. (0.245 mole) of silver sulfate. Stirring was continued for 2 hr. To ensure completion of the reaction an additional 2.5 g. of silver sulfate was added, and stirring was resumed for 0.5 hr. Precipitated silver bromide and unreacted silver sulfate were removed by centrifugation. To the resultant solution 10 ml. (0.105 mole) of *t*-butyl alcohol was added. The mixture was then extracted with 150 ml. of carbon tetrachloride. The organic phase was washed with 100 ml. of water, dried over sodium sulfate, and concentrated under vacuum. No significant separation of *t*-butyl hypobromite and carbon tetrachloride was accomplished because of the close similarity in their boiling points. A fraction of b.p. 28–32° (28–30 mm.) which was collected for infrared spectrum measurement was found by iodometric analysis to contain 7.8% *t*-butyl hypobromite by weight.

Infrared Spectra of Acetyl Hypobromite and t-Butyl Hypobromite Solutions. The infrared spectrum of the carbon tetrachloride solution of *t*-butyl hypobromite was determined using a sodium chloride cell. Measurements on solutions of *t*-butyl hypobromite in carbon tetrachloride–acetic acid mixtures and of acetyl hypobromite solutions in acetic acid were conducted using Throwaway IR Liquid Cells obtained from Limit Research Corp., Darien, Conn.

Rate Studies of Benzene Bromination in Acetic Acid Solutions of Mercuric Acetate and Bromine. Stock solutions of benzene and mercuric acetate were prepared by dilution of weighed samples of the reactants to known volumes with acetic acid at 25°. Solutions of bromine in acetic acid, temperature controlled to 25°, were standardized by iodometric methods.

Rate runs were started by mixing known volumes of the solutions of the three reactants in 10-ml. volumetric flasks. The bromine solutions were added last and zero times were noted at the time of half-addition of the halogen. Samples of these solutions were transferred to 1-cm. glass-stoppered silica absorption cells. The cells were stored in the temperature-controlled Beckman spectrophotometer housing, and the optical densities of the cell contents at 400 mμ were determined at appropriate intervals using pure acetic acid in the blank cells. The bromine concentrations of the reaction mixtures at various times were calculated from the measured optical densities and the 400-mμ value for bromine in acetic acid. The acetyl hypobromite concentrations of the rate samples were calculated at various reaction times using the appropriate free bromine concentrations and the equilibrium constant *K* (Results section, eq. 3) for reaction of bromine and mercuric acetate.

Relative Bromination Rates of Benzene and Methylbenzenes in Solutions of Mercuric Acetate and Bromine in Acetic Acid. To 100 ml. of a stock solution of

(5) C. Walling and A. Padwa, *J. Org. Chem.*, 27, 2976 (1962).

bromine in acetic acid was added 100 ml. of a solution of 5.0 g. (0.016 mole) of mercuric acetate in acetic acid. To the resultant solution was added 25 ml. of a two-component mixture of aromatic hydrocarbons of known composition by weight. The mixture was shaken and stored in the dark at 25° for at least 5 hr. It was then extracted with 600 ml. of water. The aqueous phase was extracted several times with a total of 200 ml. of petroleum ether. The organic phase and petroleum ether extracts were washed several times with small amounts of water and dilute sodium bicarbonate and dried over sodium sulfate. The petroleum ether was removed by slow distillation using a Vigreux column. The temperature of the condensing vapor was kept below 60° throughout the distillation. In runs in which benzene and toluene mixtures were used the distillate generally contained a small amount of benzene. In such runs the distillate was redistilled, and the pot residues from the first and second distillations were combined for analysis of the bromoaromatic products through vapor phase chromatography.

To check the accuracy of the analytical procedure, known mixtures of the two aromatic compounds and their monobromination products in acetic acid, which were similar in composition to the product mixtures in the competition experiments, were prepared. These were extracted and the extracts concentrated and analyzed for their bromoaromatic content as described above. Generally the recovery of the bromo compounds, as based on analysis of the concentrated petroleum ether extracts, was of the order of 80–90% (somewhat better than in the actual competition experiments, in which usually from 75–80% of the initial bromine could be accounted for by chromatography of the concentrate of the products and unreacted aromatics). In experiments in which only one aromatic hydrocarbon was used (benzene or toluene) the recovery of product (bromobenzene or bromotoluene) rose as high as 95%. Generally, however, in the control experiments the mole ratios of the bromoaromatic components, as determined by chromatography of the concentrate, was in excellent agreement with the ratio of these materials in the original mixture irrespective of the per cent recovery. In a typical control experiment in which the initial acetic acid solution contained bromotoluene and bromobenzene in the mole ratio 1.39, a figure of 1.37 was obtained by application of the analytical procedure.

Chromatographic Analyses. The vapor phase chromatographic separations of the mixtures of unreacted aromatic hydrocarbons and bromination products were accomplished using a 10-ft. column packed with Chromosorb W (60–80 mesh) impregnated with SE-30 silicone gum rubber. The column temperature was in the range of 120–190° and the carrier gas (helium) flow rate was fixed at 110 ml./min. Under these conditions the unreacted hydrocarbons and bromo compounds were readily separated. Bromobenzene, bromotoluene, and bromoxylene also gave well-resolved peaks. The emergence times of bromobenzene and bromotoluene, for example, differed by about 1 min. The isomeric bromotoluenes and also the isomeric bromoxylenes were not separated under the operating conditions which were used. Rather the isomeric mixtures were characterized by single peaks in the
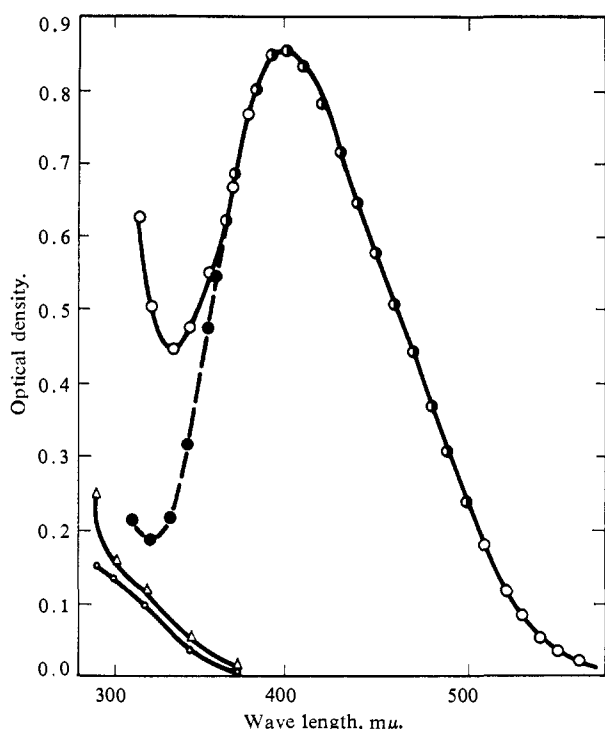
Figure 1. The spectra of solutions of bromine and mercuric acetate in acetic acid solutions (1-cm. cells, acetic acid blanks): O, 0.01 M bromine and 0.05 M mercuric acetate; $\triangle$, the preceding solution after the addition of m-xylene (0.5 M) to the mixture; ●, 0.0046 M Br$_2$; O, 0.05 M mercuric acetate.

chromatograms. Experiments with synthetic mixtures of o- and p-bromotoluene and benzyl bromide indicated that the side-chain halogenated toluene derivative emerged from the chromatograph column (as a separate peak) after the ring brominated toluenes. No benzyl bromide peak was detected in any of the chromatograms of the products of reaction of toluene with bromine and mercuric acetate in acetic acid.

Results

Acetyl Hypobromite. The ultraviolet spectrum of acetyl hypobromite in carbon tetrachloride has been described previously,[6] although the details of preparation of the organic hypohalite have not been reported. In the course of the present investigation an unsuccessful attempt has been made to isolate the compound in pure form through the addition of solid silver acetate to a solution of bromine in carbon tetrachloride followed by distillation of the greenish yellow liquid phase of the resultant mixture under reduced pressure. No fractions which could be characterized as acetyl hypobromite were obtained. The greenish yellow solutions resulting from the reaction of the halogen in carbon tetrachloride with the silver salt were found to display absorption maxima in the same region (320 mμ) as that reported for the hypobromite. That the compound is relatively unstable in carbon tetrachloride is suggested by the fact that the oxidizing power, as determined iodometrically, and the ultraviolet absorption intensity of these solutions were found to diminish relatively rapidly, though somewhat erratically, with time at room temperature.

(6) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).

It has been found that the brown-red color of an acetic acid solution of bromine decreases in intensity when mercuric acetate is added, but the color does not disappear completely nor is there a change in oxidizing power. No further alteration in color or oxidizing power occurs as the resultant solution stands at room temperature. A typical spectrum of an acetic acid solution containing bromine and mercuric acetate at concentrations of 0.01 and 0.05 M, respectively (before reaction), is compared in Figure 1 with the spectrum of a dilute solution (0.0046 M) of bromine in acetic acid. At wave lengths above 380 mμ the spectra are identical, but the mercuric acetate solution contains a substance, presumably acetyl hypobromite, which absorbs much more strongly than bromine below 320 mμ. Mercuric acetate itself absorbs feebly in the 300–400-mμ region.

The spectral changes accompanying the addition of mercuric acetate in varying quantity to a series of solutions of bromine in acetic acid have been explained on the assumption that under such conditions the equilibrium

$$Hg(OCOCH_3)_2 + Br_2 \rightleftharpoons Hg(OCOCH_3)Br + CH_3COOBr \quad (2)$$
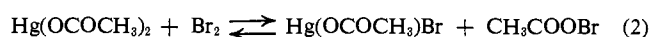
is established. The optical densities of the equilibrium mixtures at 400 mμ have been used to calculate free bromine concentrations, on the assumption that the free halogen is the only substance in the solutions which absorbs at this wave length. The concentrations of the other components have been calculated from the initial reactant and free bromine concentrations, and the resultant values have been applied in the calculation of equilibrium constants, K.

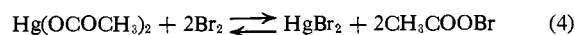$$K = [Hg(OCOCH_3)Br][CH_3COOBr]/[Hg(OCOCH_3)_2][Br_2] \quad (3)$$

Typical K values are listed in Table I (fourth column from the left) along with values of K' which are calculated on the assumption, obviously erroneous,

Table I. The Equilibrium Constant for Acetyl Hypobromite Formation in Acetic Acid at 25°[a]

| [Hg(OCO-CH$_3$)$_2$]$_i$, mole/l.	[Br$_2$]$_i$, mole/l.	[Br$_2$], mole/l.	K	K'
0.159	0.050	0.0250	0.187	0.085
0.159	0.0050	0.00065	0.188	0.672
0.146	0.0917	0.0562	0.204	0.055
0.146	0.00917	0.00188	0.203	0.386
0.0729	0.00903	0.00286	0.200	0.206
0.0795	0.00493	0.00099	0.207	0.401
0.0438	0.00925	0.00384	0.198	0.131
0.0292	0.00903	0.00443	0.194	0.092
0.0146	0.00925	0.00567	0.205	0.056
			Av.[b] = 0.198 ± 0.006	

[a] The subscripts on the columns labeled [Hg(OCOCH$_3$)$_2$]$_i$ and [Br$_2$]$_i$ refer to concentrations of materials prior to the establishment of equilibrium. The term [Br$_2$] refers to the equilibrium concentration of the free halogen. [b] The average of sixteen determinations including those in the table was 0.197 ± 0.010.

that the reaction of bromine and mercuric acetate proceeds according to eq. 4. Other evidence, qualitative in nature, has been obtained which indicates that

$$Hg(OCOCH_3)_2 + 2Br_2 \rightleftharpoons HgBr_2 + 2CH_3COOBr \quad (4)$$

$$K' = [HgBr_2][CH_3COOBr]^2/[Hg(OCOCH_3)_2][Br_2]^2 \quad (5)$$

acetoxymercuric bromide rather than mercuric bromide should be the major mercury-containing product of the reactions summarized in Table I. Mercuric bromide, which is only sparingly soluble in pure acetic acid, is appreciably soluble in acetic acid solutions of mercuric acetate. This is ascribed to the formation (eq. 6) of a significantly soluble product (acetoxy-

$$Hg(OCOCH_3)_2 + HgBr_2 \rightleftharpoons 2Hg(OCOCH_3)Br \qquad (6)$$
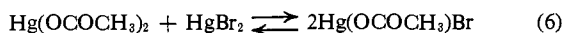
mercuric bromide). It appears that reaction 6 provides for quantitative conversion of mercuric bromide to acetoxymercuric bromide only when the mercuric acetate is in substantial excess of the bromide. A number of measurements to determine K, similar to those summarized in Table I, have been conducted with mercuric bromide as an additional component of the reaction mixtures. As the initial concentration ratios of mercuric acetate to mercuric bromide are reduced to relatively low values (below 4), apparent K values (eq. 3), calculated on the assumption that reaction 6 is complete, are observed to increase. The K value increases slightly with temperature (from about 0.20 at 25° to 0.21 at 45°). The enthalpy of the reaction to form acetyl hypobromite is, therefore, of the order of +1 kcal.

Further evidence that solutions of mercuric acetate and bromine in acetic acid contain a hypobromite exists in the fact (see Figure 2) that such mixtures show an infrared peak at 15.0 μ which is not found in the spectra of the separate components. A peak at this wave length has been reported previously[5] in the spectrum of a solution of t-butyl hypobromite in carbon tetrachloride and has been ascribed to the O–Br bond. The presence of this band in the spectrum of t-butyl hypobromite in carbon tetrachloride, as well as in solutions obtained by dilution of carbon tetrachloride solutions of the alkyl hypobromite with acetic acid, has been confirmed in the present investigation. In this connection it should be noted that it has been established by iodometric methods that the dilution with acetic acid does not affect the over-all oxidizing power of solutions of t-butyl hypobromite in carbon tetrachloride.

Kinetics of Halogenation of Alkylbenzenes by Acetyl Hypobromite. As indicated in the Experimental section it has been found that in acetic acid solutions of mercuric acetate and bromine, toluene reacts at room temperature to give high yields of ring, as contrasted to side chain, bromination product. It is assumed, therefore, that the reaction is polar rather than radical in character. Toluene itself is sufficiently reactive so that direct studies of the kinetics of its halogenation under these conditions cannot be conducted by ordinary methods.[7] The corresponding reaction of benzene has, however, proved to be slow enough for direct rate study.

Generally the initial reaction mixtures in the benzene bromination rate study contained the aromatic hydrocarbon in at least tenfold excess of bromine, and the mercuric acetate was also in substantial excess of the halogen. In analyzing the results of a series of runs in which the changes in the free bromine concentrations of

(7) In the absence of mercuric acetate toluene is brominated at a very slow rate in acetic acid at room temperature. Even mesitylene is not highly reactive under these conditions; *cf.* R. M. Keefer, L. J. Andrews, and A. Ottenberg, *J. Am. Chem. Soc.*, **78**, 255 (1956).
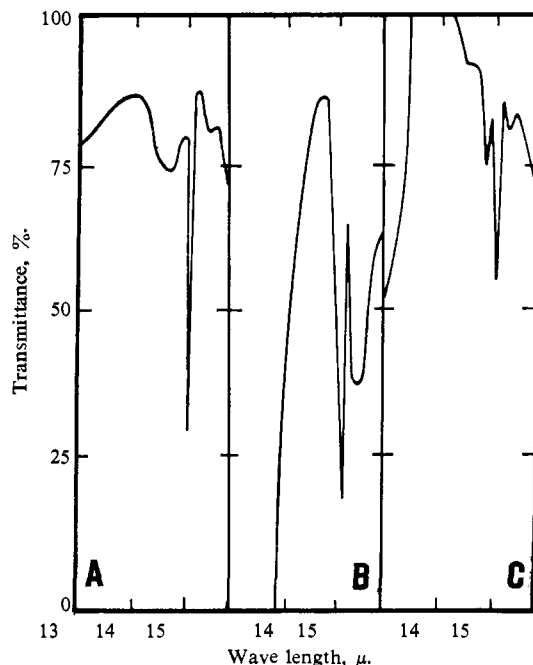

Figure 2. Infrared spectra of acetyl hypobromite and t-butyl hypobromite: A, 0.048 M CH₃COOBr in acetic acid (a solution of 0.160 M mercuric acetate and 0.150 M bromine in acetic acid); B, 0.08 M t-butyl hypobromite in carbon tetrachloride; C, 0.016 M t-butyl hypobromide in a 4:1 volume mixture of acetic acid and carbon tetrachloride. Cells with silver chloride windows (1.0 mm.) were used with double beam operation and acetic acid in the blanks.

the reaction mixtures, [Br₂], were determined spectrophotometrically, it has been assumed that bromobenzene is formed according to the rate law

$$d[ArBr]/dt = -d[Br_2]_T/dt = k[ArH][CH_3COOBr] \qquad (7)$$

The term [Br₂]$_T$, the total concentration of brominating agents at any time, is defined by eq. 8.

$$[Br_2]_T = [Br_2] + [CH_3COOBr] \qquad (8)$$

The initial concentrations of free bromine ([Br₂] at time = zero) in the reaction mixtures have been determined by extrapolation of plots of log [Br₂] *vs.* time to zero time. Equation 9 has been used in calculating [CH₃COOBr] from the corresponding values of [Br₂] and the initial concentrations of mercuric acetate and bromine as based on the amount of salt and halogen added to the reaction mixture ([Hg(OCOCH₃)₂]ᵢ and [Br₂]ᵢ).

$$[CH_3COOBr] = \frac{K[Br_2]([Hg(OCOCH_3)_2]_i - [Br_2]_i + [Br_2])}{[Br_2]_i - [Br_2]} \qquad (9)$$

$$[Br_2]_i - [Br_2] = [Hg(OCOCH_3)Br] \qquad (10)$$

$$[Hg(OCOCH_3)_2] = [Hg(OCOCH_3)_2]_i - [Hg(OCOCH_3)Br] \qquad (11)$$

$$[ArH] = [ArH]_i - [Br_2]_i + [Br_2]_T \qquad (12)$$

Because of the complexity of the integrated rate law based on eq. 7 which relates rate constants to experimental values of [Br₂], K, [Hg(OCOCH₃)₂]ᵢ, [Br₂]ᵢ, and [ArH], a graphical procedure has been employed in the interpretation of the runs. Values of $-d[Br_2]_T/dt$ at various times during the course of the runs have been determined from the slopes of plots of [Br₂]$_T$ *vs.* time. The rate constants k have been calculated by dividing these slopes by the corresponding values of [ArH]·[CH₃COOBr].

The results of a series of runs in which [Hg-(OCOCH₃)₂]ᵢ and [Br₂]ᵢ were held constant but benzene concentration was varied by a factor of 8 are summarized in Table II. As is required if eq. 7 is the

Table II. Rate Constants (Eq. 7) for Bromination of Benzene at 25.0° with Runs at Varying Benzene Concentration[a]

[C₆H₆], mole/l.	Extent of reaction, %	$-10^6 d$-[Br₂]$_T$/dt, mole/l. sec.	10^3[AcOBr], mole/l.	$10^3 k$, l./mole sec.
0.5520	0	10.0	6.28	2.9
	30	6.7	4.31	2.8
	60	3.7	2.40	2.8
0.2760	0	5.0	6.28	2.9
	30	3.5	4.31	3.0
	60	1.4	2.40	3.0
0.1380	0	3.00	6.28	3.5
	30	2.00	4.31	3.4
	60	1.12	2.40	3.5
0.0690	0	1.50	6.28	3.5
	30	1.00	4.31	3.5
	60	0.53	2.40	3.5
			Av.	3.2 ± 0.3

[a] In all runs [Hg(OCOCH₃)₂]ᵢ = 0.1060 M and [Br₂]ᵢ = 0.00828 M.

correct rate law, the experimental values of k remain relatively constant during the course of individual runs. The values of k, as reported in this table, appear to increase slightly with decreases in [C₆H₆]. Although no further supporting evidence has been obtained, it is possible that this drift in rate constants may be the result of feeble complexing of acetyl hypobromite by benzene.

A summary of the results of a series of runs at constant benzene but varying initial concentrations of mercuric acetate and bromine is given in Table III.

Table III. Rate Constants for Bromination of Benzene at 25.0° with Runs at Varying Initial Concentrations of Bromine and Mercuric Acetate[a]

[Hg(OCO-CH₃)₂]ᵢ, mole/l.	10^3[Br₂]ᵢ, mole/l.	Extent of reaction, %	$-10^6 d$-[Br₂]$_T$/dt, mole/l. sec.	10^3[AcOBr], mole/l.	$10^3 k$, l./mole sec.
0.1630	10.50	0	6.2	9.03	2.5
		30	4.5	5.70	2.9
		60	2.35	3.18	2.7
0.1060	8.28	0	5.0	6.28	2.9
		30	3.5	4.31	3.0
		60	1.40	2.40	3.0
0.0530	8.05	0	4.0	5.20	2.8
		30	2.7	3.46	2.9
		60	1.40	1.86	2.8
0.0265	8.05	0	3.0	4.15	2.6
		30	1.80	2.59	2.5
		60	0.95	1.28	2.7
0.0265	4.14	0	2.00	2.66	2.7
		30	1.20	1.76	2.5
		60	0.70	0.95	2.7
0.0133	4.14	0	1.50	2.12	2.6
		30	0.85	1.31	2.4
		60	0.45	0.64	2.5

[a] In all runs [C₆H₆]ᵢ = 0.276 M.

It can be seen by reference to the values of d[Br₂]$_T$/dt for the second, third, and fourth runs in this listing

that there is no simple dependence of initial rate on mercuric acetate concentration; that is, at 0% reaction $-$d[Br₂]$_T$/dt varies by less than a factor of two as [Hg(OCOCH₃)₂]ᵢ varies by a factor of over four. Neither is there any simple relationship between initial rate and the free bromine concentration ([Br₂]). The initial rates of the fourth and fifth runs of Table III are not radically different, but the initial free bromine concentrations are 0.0391 and 0.0015 M, respectively. The only satisfactory explanation of these observations is based on the assumption that acetyl hypobromite (or possibly its conjugate acid) attacks benzene in the slow step of the bromination reaction. Rate constants k (eq. 7) reported in Table III, and calculated in the manner described above, are gratifyingly invariant during the course of individual runs, and the average value of k for the several runs is in good agreement with that listed in Table II.

The relative reactivities of benzene, toluene, and m- and p-xylene have been established by means of experiments in which mixtures of two of the aromatic hydrocarbons have competed for limited amounts of acetyl hypobromite in acetic acid. Ratios of the rate constants for the hydrocarbons have been calculated using eq. 13. The product concentration ratios, [BrAr₁]/

$$[ArH_2]_{av} [BrAr_1]/[ArH_1]_{av}[BrAr_2] = k_{ArH_1}/k_{ArH_2} \qquad (13)$$

[BrAr₂], have been determined by vapor phase chromatography. This equation is strictly applicable only in situations in which the hydrocarbon concentrations do not change appreciably during the competition reactions. In those cases in which significant changes occurred, the average of the initial and final hydrocarbon concentrations have been used in calculating the rate constant ratios. These ratios are summarized in Table IV. These rate ratios are independent of the ratio of initial concentrations of the competing hydrocarbons and of the initial concentration of bromine. However, it should be noted for the m-xylene–toluene competition experiments that the reaction time is very fast and that a good portion of the reaction takes place during the mixing process. For this reason the m-xylene–toluene ratio must be regarded as tentative at this time.

Table IV. Competition Experiments to Determine Relative Reactivities of Aromatic Hydrocarbons and Acetyl Hypobromite (Acetic Acid, 25°)

Initial concn., mole/l.		Product concn., mole/l.		
[ArH₁]	10^3[ArH₂]	10^4[ArBr₁]	10^4[ArBr₂]	k_{ArH_2}/k_{ArH_1}
ArH₁ = Benzene		ArH₂ = Toluene		
0.278	1.35	1.36	2.80	4.7 × 10²
0.278	2.15	1.75	5.6	4.8 × 10²
0.273	4.47	1.93	13.0	4.8 × 10²
ArH₁ = Toluene		ArH₂ = p-Xylene		
0.214	17.7	18.1	6.8	4.6
0.201	28.6	17.0	10.4	4.2
0.205	32.2	12.7	9.2	4.5
ArH₁ = Toluene		ArH₂ = m-Xylene		
0.230	1.52	0.70	1.83	4.2 × 10²
0.230	2.33	0.82	3.24	4.2 × 10²
0.229	4.17	0.98	7.2	4.4 × 10²

The relative reactivities of the hydrocarbons with respect to attack by acetyl hypobromite in acetic acid

at 25° fall in the order benzene (1), toluene (4.8 × 10^2), p-xylene (2.1 × 10^3), m-xylene (2.0 × 10^5). The observation that the reaction rate is highly sensitive to changes in the number of ring methyl substituents adds support to the conclusion that acetyl hypobromite is a polar rather than a radical brominating agent in acetic acid. Variations in hydrocarbon reactivity very similar to those encountered in the present study have been observed with certain polar halogenating agents other than acetyl hypobromite. The reactivity ratios benzene (1), toluene (6.1 × 10^2), p-xylene (2.2 × 10^3), m-xylene (2.1 × 10^5)—and benzene (1), toluene (3.4 × 10^2), p-xylene (2.1 × 10^3), m-xylene (1.9 × 10^5)—have been reported, respectively, for reaction with bromine in 85% acetic acid and with chlorine in pure acetic acid.[8] That is, the electrophilicities of acetyl hypobromite and chlorine in acetic acid (and also of bromine in 85% acetic acid) are about the same.

Chlorination Studies of Unsaturated Materials in Nonpolar Media. IV. The Ionic Pathway for Alkylated Ethylenes. Products and Relative Reactivities[1]

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The rapid chlorination of neat alkylethylenes at ambient temperatures in the presence of oxygen as a radical inhibitor is considered. 1-Substituted or 1,2-disubstituted olefins (no branching at the double bond) (allyl chloride, 1-butene, cis- and trans-2-butene, and cyclohexene) had been found previously to give predominantly addition products, stereospecifically trans for the 1,2-cases, accompanied by very minor amounts of allylic substitution products. t-Butylethylene gave largely the unrearranged dichloride II, but 10% of 4-chloro-2,3-dimethyl-1-butene (I), a result of methyl migration, was detected. In contrast, it had been found previously that isobutylene gave predominantly the substitution product, 3-chloro-2-methyl-1-propene, with a shifted double bond. This apparently general tendency for branched olefins to react by substitution rather than addition has now been demonstrated for 2-methyl-1-butene, trimethylethylene, and tetramethylethylene. The respective products are: 2-(chloromethyl)-1-butene (III), 1-chloro-2-methyl-cis-2-butene (IV), 1-chloro-2-methyl-trans-2-butene (V), and 1,2-dichloro-2-methylbutane (VI) (58:29:8:5); 3-chloro-2-methyl-1-butene (VII) and 2,3-dichloro-2-methylbutane (IX) (85.5:1.45); and 3-chloro-2,3-dimethyl-1-butene (X) and 2,3-dichloro-2,3-dimethylbutane (XI) (99.7:0.3). Relative reactivities of the olefins toward chlorine were determined by competitive experiments and found to correlate with the sum of Taft's σ* constants for the alkyl substituents regardless of their orientation on the double bond. For both the linear cis-2-butene and the branched trimethylethylene, the addition process is favored by the energy of activation; hence the predominant substitution observed in the latter case is the result of an over-compensating entropy effect. The results are discussed in terms of electrophilic attack by chlorine, and possible transition states and intermediates are considered.

Introduction

Chlorination of simple olefins in nonpolar media can follow either a free-radical or ionic pathway dependent on the structure and concentration of the olefin.[1,2] One can isolate the ionic pathway by use of radical inhibitors such as oxygen. This paper deals with products and relative reactivities of ionic chlorination of a series of ethylenes substituted with successively larger numbers of alkyl groups. Each of these substrates has been chlorinated previously[3-8]; however, because of ambiguities owing to mixed reaction pathways, secondary reactions, and lack of sensitive analytical tools, a systematic reinvestigation was undertaken.

Results

Product Compositions. Product distributions from chlorination of ten representative olefins are given in Table I. Each reaction was carried out by passing a limited amount of chlorine (ca. 1%) in an oxygen gas stream into neat olefin at −9 or 25° in the dark; reaction mixtures were analyzed directly by use of a g.l.p.c. instrument equipped with a flame ionization detector; g.l.p.c. areas were converted to molar quantities by means of calibration factors determined from synthetic mixtures of authentic compounds except

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