When the value of α, obtained as described above $(2.7 \times 10^{13}$ molecules-cm.$^{-3}$-sec.$^{-1})$, is combined with $Q_{C_3H_6}$ determined from dosimetry, we get for a pure cyclopropane radiolysis $G(-C_3H_6)$ = 6.6. Although this is a very reasonable value for a saturated hydrocarbon, it is quite uncertain since the error arising in α is determined as a relatively small difference between two much larger numbers. By comparison $G(-C_3H_6)$ obtained from the radiolysis of pure cyclopropane (Fig. 1) is 4.0.
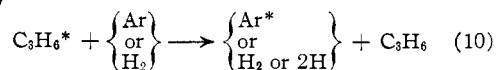
In the inhibition mechanism, and hence in the derivation of (E1), we have implicitly assumed that $G(-C_3H_6)$ (defined as the number of molecules of cyclopropane consumed per 100 electron-volts absorbed by cyclopropane) is independent of hydrogen and argon pressure. To be valid this requires that there be no reaction of $C_3H_6^+$ with argon or hydrogen that regenerates C_3H_6. That is, this assumption requires that there be no simple charge exchange reaction, viz.

$$C_3H_6^+ + \begin{Bmatrix} Ar \\ or \\ H_2 \end{Bmatrix} \longrightarrow \begin{Bmatrix} Ar^+ \\ or \\ H_2^+ \end{Bmatrix} + C_3H_6 \qquad (9)$$
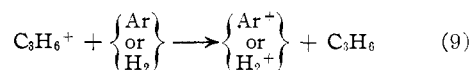
As these reactions are highly endothermic and, therefore, very improbable our assumption appears to be valid.

As mentioned before this mechanism does not preclude the participation by excited species. In fact, as written the scheme would be kinetically equivalent if $*$ were substituted for $+$. However, in this case our implicit assumption discussed above would most likely break down because of the intrinsic plausibility of the analog of (9), namely

$$C_3H_6^* + \begin{Bmatrix} Ar \\ or \\ H_2 \end{Bmatrix} \longrightarrow \begin{Bmatrix} Ar^* \\ or \\ H_2 \text{ or } 2H \end{Bmatrix} + C_3H_6 \qquad (10)$$

In fact, the plausibility of (10) suggests that excited species could not produce the entire phenomena observed, because as $[H_2] \rightarrow \infty$ one would not expect the completely hydrogen-inhibited rate to be 46% of the uninhibited rate. Rather one might think it considerably closer to zero.

One further word about the linearity of Fig. 3 over the experimental range of hydrogen pressure: within our experimental error the value of γ_1 is such that the approximation of neglecting unity with respect to $\gamma_1[H_2]$ is valid over the whole range of $[H_2]$. On the other hand the value of γ_2 is such that this is not true even at the highest $[H_2]$, so that unity in the third term on the right of (E1) cannot be neglected. However, hydrogen absorbs energy so slowly, that is, ξ is so small, that at the lower hydrogen pressures employed, the third term in (E1) is negligible. At the higher pressures, the rate is still insensitive enough to the third term that, within our experimental error, the third term behaves essentially as a constant even though unity cannot be neglected with respect to $\gamma_2[H_2]$. For these reasons then (E1) accounts for the linear plot of the data in Fig. 3.

Acknowledgments.—We wish to thank Messrs. T. P. Gorman and C. W. Bell for their very valuable assistance with the experimental work.

Hydrogen Bromide Inhibition in the Zinc Chloride Catalyzed Bromination of Polyalkylbenzenes in Acetic Acid. The Effect of Ring Deuteration on Reactivity

BY ROY JOSEPHSON, R. M. KEEFER AND L. J. ANDREWS

The effect of hydrogen bromide, over a wide concentration range, on the rate of the zinc chloride catalyzed bromination of o-xylene in acetic acid has been investigated. The second-order rate constants $(R = k_0[ArH][Br_2])$ show linear dependence on the reciprocal of the hydrogen halide concentration, and they approach a minimum (non-zero) value as the inhibitor content of the medium becomes appreciable. Apparently reaction occurs by two different processes, only one of which is subject to influence by hydrogen bromide. A similar, though less complete, series of observations has been made concerning the reactivity of toluene and pentamethylbenzene. The reactivities of $C_6D_5CH_3$ and of $C_6D(CH_3)_5$ are approximately the same as those of their unlabeled analogs over a wide range of hydrogen bromide concentrations. The suggestion, made earlier,[1] that the reaction product is formed directly through decomposition of an intermediate $(ArHBr^+OAc^-)$ in a slow step, is subject to reconsideration. Two alternate reaction schemes are suggested, both of which are in accord with the present results. Brief consideration is also given to the nature of the halogen free product obtained when hexamethylbenzene reacts with bromine in acetic acid solutions of zinc chloride.

It has been reported[1] previously that the apparent rate constants for the zinc chloride catalyzed bromination of an alkylbenzene in acetic acid, as defined in eq. 1, decrease as reaction proceeds.
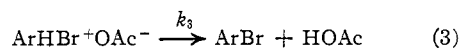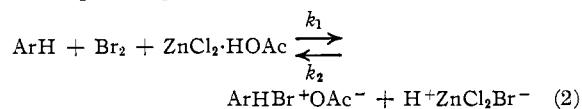
$$R = -d[Br_2]/dt = k_0[ArH][Br_2] \qquad (1)$$

This decrease has been attributed to inhibition of the reaction by a substance, probably $HZnCl_2Br$, formed by coördination of zinc chloride with the hydrogen bromide generated as a reaction product. It has been shown that in the presence of excess

zinc chloride, the conversion of the hydrogen halide to the complex, is essentially quantitative.[1,2]

(2) D. Bethell, V. Gold and D. P. N. Satchell. *J. Chem. Soc.*, 1918 (1958), have presented evidence that two complexes, probably H_2ZnCl_4 and $H_2ZnCl_3(OAc)$, are produced from hydrogen chloride and zinc chloride in acetic acid. The former is replaced by the latter as the zinc chloride concentration of the medium is increased. It has been assumed in the earlier[1] as well as in the present investigation that in acetic acid solutions in which zinc chloride is in substantial excess of hydrogen bromide, the mole ratio of the components in the complex which is formed is 1:1. It should be noted that the formulas H_2ZnCl_3-$Br(OAc)$ and $H_2ZnCl_2(OAc)_2$ rather than $HZnCl_2Br$, may be correct for the complex and for solvated zinc chloride. The arguments which are presented concerning the reaction mechanism are not materially influenced by the choice of formulas.

(1) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **78**, 4549 (1956).

The hydrogen bromide effect on the rate constant has been explained on the assumption that a steady state is established with respect to the concentration of $ArHBr^+OAc^-$, which is presumed to be a reaction intermediate. In accord with the suggested reaction mechanism (equations 2 and 3) is the fact that the reciprocals of experimental values of the rate constants k_0 for a particular run (or for a series of runs at fixed zinc chloride concentration) increase in linear fashion with the corresponding $[HZnCl_2Br]$ values.

$$ArH + Br_2 + ZnCl_2 \cdot HOAc \underset{k_2}{\overset{k_1}{\rightleftarrows}}$$
$$ArHBr^+OAc^- + H^+ZnCl_2Br^- \quad (2)$$

$$ArHBr^+OAc^- \overset{k_3}{\longrightarrow} ArBr + HOAc \quad (3)$$

If the proposed mechanism is entirely adequate, the observed rate constant k_0 for the zinc chloride catalyzed reaction should decrease continuously as the hydrogen bromide content of the medium is increased to high levels. Also it may be expected that the substitution of deuterium for hydrogen on the aromatic nucleus should result in a reduction of the polymethylbenzene bromination rate. That is, the rate constant k_0 should vary (eq. 4) with changes in the rate constant k_3 (eq. 3); and since proton removal occurs in the breakdown of $ArHBr^+OAc^-$ to product, k_3 should be subject to an isotope effect.

$$k_0 = k_1k_3[ZnCl_2 \cdot HOAc]/(k_3 + k_2[HZnCl_2Br]) \quad (4)$$

With these points in mind an investigation has now been conducted of the effects of hydrogen bromide, over a wide range of initial concentrations, on the rate of the zinc chloride catalyzed bromination of o-xylene in acetic acid. Also the relative reactivities of toluene-2,3,4,5,6-d_5 and toluene and of pentamethylbenzene-1-d_1 and of pentamethylbenzene with respect to zinc chloride catalyzed bromination in acetic acid have been determined. In addition, the nature of the product formed when hexamethylbenzene and bromine react in acetic acid in the presence of the metal halide catalyst has been investigated.

Experimental

Materials.—The aromatic hydrocarbons of normal isotopic composition and the acetic acid were purified before use as described earlier.[1] Reagent grade (Mallinckrodt Chemical Works) zinc chloride was dried for 8 hr. at 160°. Reagent grade bromine (J. T. Baker Chemical Co.) was used without further purification. The authors are indebted to Professor F. R. Jensen of the University of California, Berkeley, for providing a sample of gallium bromide which had been purified by sublimation.

As starting material for the preparation of ring deuterated pentamethylbenzene, 1-bromo-2,3,4,5,6-pentamethylbenzene was prepared by the iodine bromide catalyzed bromination of pentamethylbenzene in chloroform.[3] The Grignard reagent was prepared under dry nitrogen from 25.0 g. (0.110 mole) of the bromo compound and 3.3 g. (0.126 g. atom) of magnesium in 200 ml. of tetrahydrofuran. The solvent previously had been exposed to metallic sodium and finally was dried with lithium aluminum hydride and distilled before use. The Grignard reagent was treated dropwise over a several minute period with 7.5 ml. (0.43 mole) of deuterium oxide (Stuart Oxygen Co. material of greater than 99.5% purity). The mixture then was re-

fluxed for 0.5 hr., cooled and treated with 200 ml. of 10% aqueous ammonium chloride. The organic matter was removed from the mixture by repeated extraction with petroleum ether. The combined extracts were evaporated to dryness, and the residue was crystallized from ethanol. A total of 14.0 g. (85% yield) of material which varied in melting point from 49.0–53.0° was obtained through repeated concentration of the mother liquors. A sample of m.p. 52.0–53.0° for use in rate work was obtained through recrystallization.

A rough estimate of the isotopic purity of this sample of pentamethylbenzene-1-d_1 was obtained through comparison (against a solvent blank) of its infrared spectrum in a 10% solution in carbon disulfide with that of a similar solution of the unlabeled hydrocarbon. The unlabeled material has a strong band at 11.6 μ which is greatly diminished in the deuterated material. On the assumption that the weak band in the latter sample results from contamination with the protonated material, it was calculated using the absorption intensities of the two samples at 11.6 μ that the pentamethyl-deuteriobenzene was 94 atom % with respect to deuterium on the open position on the ring. Another sample of this material, which was analyzed by mass spectrometry through the courtesy of Mr. Seymour Meyerson of the Standard Oil Co. of Indiana, was found to be 93.6 atom % labeled at the unsubstituted ring position.

A sample of 6-methylbenzene-1,2,3,4,5-d_5 (pentadeuterio-toluene) was prepared by a procedure devised by Professor Jensen.[4] The method involved the slow gassing of a sample of toluene with a large excess of deuterium chloride at 0° in the presence of gallium bromide as a catalyst. The deuterium chloride was generated from benzoyl chloride and deuterium oxide. After the product was washed free of inorganic matter, it was subjected to high precision fractionation. Material of b.p. 110.2–110.6° was obtained which, according to the mass spectrometric analysis of Mr. Seymour Meyerson, was composed of 97.4 mole % d_5 and 2.6 mole % d_4 labeled toluene.

The Kinetics of the Bromination Reactions.—A spectrophotometric procedure similar to that employed in the earlier investigation[1] of zinc chloride catalyzed aromatic bromination in acetic acid was used. The changes in bromine concentration during the course of reaction were determined by noting changes in the optical density of the reaction mixtures at 440 mμ. The extinction coefficient of the halogen in acetic acid at this wave length is 135. In all runs the aromatic hydrocarbon was in large excess of the bromine. To provide for a large initial concentration of hydrogen bromide in the reaction mixture, it proved convenient to generate it by adding the appropriate excess of bromine to the reaction mixture. Spectrophotometer readings then were begun when the hydrogen bromide content of the mixture had reached the desired level. In most instances the reactions were carried to completion using 10 cm. absorption cells as reaction vessels, although the cell size was varied to provide initial optical density readings ranging between 0.4–1.0. Usually the reactions were started by mixing samples of stock solutions of the reactants directly in the absorption cells. The stock zinc chloride solutions were standardized by the Volhard method for chloride ion. The stock bromine solutions were standardized spectrophotometrically. The concentrations of other stock solutions were established by the appropriate dilution of weighed samples.

The Product of Bromination of Pentamethylbenzene.—As has been demonstrated previously, very little side chain substitution occurs when mesitylene is subjected to zinc chloride catalyzed bromination.[1] Because hexamethylbenzene is reactive with respect to bromine in zinc chloride (see below), it seemed worthwhile to check the identity of the product of bromination of pentamethylbenzene (as it is formed under conditions similar to those of the rate runs). Accordingly a solution of 0.50 g. (0.00338 mole) of pentamethylbenzene in 50 ml. of 0.6 M zinc chloride in acetic acid was treated with 200 λ (0.0039 mole) of bromine. Five minutes later the mixture was poured into dilute aqueous sodium bisulfite solution. The white solid which separated was recrystallized from ethanol. The 6-bromo-1,2,3,4,5-pentamethylbenzene thus obtained weighed 0.59 g. (76% yield), m.p. 160–161.5° (lit.[5] m.p. 160°).

(3) R. Josephson, R. M. Keefer and L. J. Andrews, J. Am. Chem. Soc., **83**, 2128 (1961).

(4) F. R. Jensen, private communication. The details of the method have not yet been published.

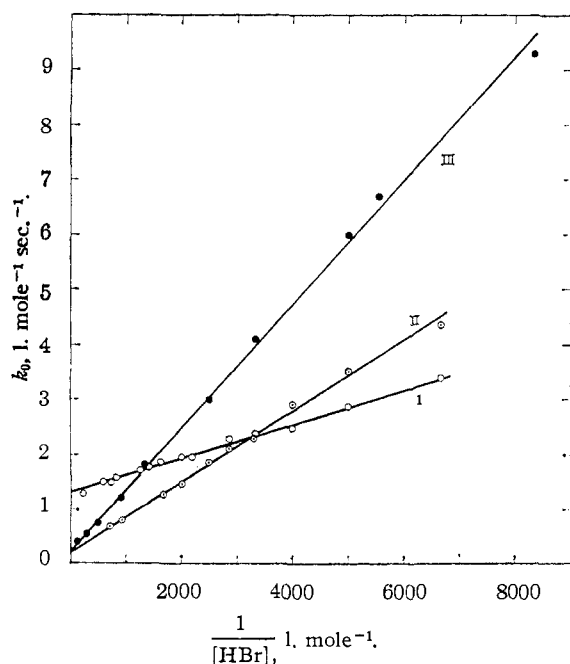(5) E. H. Huntress and S. P. Mulliken, "Identification of Pure

Fig. 1.—The effect of [HBr] on k_0 at 25.0°: Lines I, II and III apply, respectively, to the reactions of penta-methylbenzene, toluene and o-xylene. Line I is based on four runs at $[ZnCl_2] = 0.0197\ M$ in which [Br$_2$] varied from 1.23×10^{-4} to $7.0 \times 10^{-4}\ M$ and [ArH] from 8.1×10^{-4} to $20 \times 10^{-4}\ M$. Line II is based on four runs at $[ZnCl_2] = 0.375\ M$ in which [Br$_2$] varied from 1.26×10^{-8} to $6.0 \times 10^{-8}\ M$ and [ArH] from 79.1×10^{-8} to $93.6 \times 10^{-8}\ M$. Line III is based on eighteen runs at $[ZnCl_2] = 0.494\ M$ in which [Br$_2$] varied from 0.20×10^{-8} to $6.0 \times 10^{-8}\ M$ and [ArH] from 3.3×10^{-8} to $250 \times 10^{-8}\ M$. On line II the ordinates are 1,000 times and the abscissas are 10 times their actual values. On line III the ordinates are 100 times and the abscissas are 10 times their actual values.

The Stability of Pentadeuteriotoluene in Solutions of Zinc Chloride in Acetic Acid.—This experiment was performed to demonstrate that the ring deuterium atoms of 6-methylbenzene-1,2,3,4,5-d_5 are not exchanged for protium under the conditions of the rate runs. To 500 ml. of a solution of 0.36 M zinc chloride in acetic acid were added 150 λ (0.0030 mole) of bromine and 5.0 ml. (0.052 mole) of penta-deuteriotoluene. The mixture was allowed to stand for 100 minutes, by which time the bromine color had disappeared. Then it was treated with 1 l. of water, and the resultant mixture was extracted several times with a total of 300 ml. of carbon disulfide. The combined carbon disulfide extracts were washed with aqueous sodium hydroxide solution and dried over calcium chloride. The solution was concentrated to about 50 ml. by a distillation process in which a two and one-half foot Vigreux column was used. The infrared spectrum of the pot residue was identical (insofar as the location and relative heights of the absorption peaks is concerned) with that of the starting pentadeuteriotoluene in carbon disulfide.

Results

The Hydrogen Bromide Effect on Reaction Rate.—It has been found that the linear relationship, eq. 4, which was earlier reported to exist between $1/k_0$ and the concentration of HZnCl$_2$Br (as measured by the amount of hydrogen bromide in the reaction mixture), is apparent rather than real. This equation relating the rate constant

Organic Compounds, Order I," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 502.

k_0 to hydrogen halide concentration was incorrectly thought to apply because an insufficiently wide variation in inhibitor concentration was made in the rate runs which were conducted in the previous investigation. In no case did the hydrogen bromide concentration in these runs exceed $3.9 \times 10^{-3}\ M$. In the present work the maximum variation of the hydrogen bromide concentration, during the period of measurement, within individual rate runs was in some cases as much as 0.2×10^{-3} to $43 \times 10^{-3}\ M$. For such runs the lines obtained by plotting $1/k_0$ vs. the hydrogen bromide concentration bend markedly as the inhibitor content of the medium becomes appreciable.

Actually there is a linear dependence of the rate constants for aromatic bromination, at a given zinc chloride concentration, on the reciprocal of the hydrogen bromide concentration of the medium. This fact is illustrated in Fig. 1. The experimental rate constants on which these plots are based were calculated from R values as defined in eq. 1. These rates were obtained by measuring the slopes of plots of [Br$_2$] values, recorded during the course of the runs, versus time. It has been demonstrated specifically in the case of o-xylene that the new found linear relationship (Fig. 1) applies over wide ranges of hydrogen bromide concentration.

Alternately it can be shown that contrary to what is expected if the reaction proceeds according to equation 2 and 3, experimental k_0 values do not diminish continuously with increasing hydrogen bromide content of the medium. Rather they approach asymptotically a minimum value which is appreciable in magnitude. That is, the reactions of the hydrocarbons occur by two different processes, only one of which is subject to inhibition by HZnCl$_2$Br.

Typical rate constants calculated, as described above, from data taken during runs with o-xylene are given in Table I. The value of k_0 at a fixed

TABLE I

THE EFFECT OF HYDROGEN BROMIDE ON THE RATE OF THE ZnCl$_2$ CATALYZED REACTION OF BROMINE AND o-XYLENE AT 25.0°; $[ZnCl_2] = 0.494\ M$

$10^3[ArH]$,[a] mole/l.	$10^3[Br_2]$,[a] mole/l.	$10^3[HBr]$,[a] mole/l.	$\dfrac{10^3 R}{[ArH][Br_2]}$, l. mole^{-1} sec.$^{-1}$
13.05	0.236	0.20	48
3.12	0.236	0.20	38
40	4.1	43	5.6
123	4.1	43	5.1
205	4.1	43	5.1
78.9	1.40	4.0	29
95.4	0.36	4.0	31

[a] Values at the time at which R was measured.

catalyst concentration is independent of changes in the concentrations of the two reactants as long as the hydrogen bromide content of the medium remains fixed. That is, the reaction of o-xylene is first order in hydrocarbon and in halogen both when the hydrogen bromide concentration is small and also when the inhibitor is in large excess of the bromine. It follows, therefore, that the reaction which is insensitive to HZnCl$_2$Br, as well as that which is subject to inhibition, is first order with respect to each reactant. It should be noted

that plots of log $[Br_2]_T$ *versus* time for runs in which the hydrogen bromide concentration remained constant during the reaction were linear to high percentages of completion, in contrast to those for runs in which the inhibitor content increased appreciably with time.

The Reactions of Deuterated Hydrocarbons.—A series of rate runs on pentamethyldeuteriobenzene and on pentadeuteriotoluene (6-methylbenzene-1,2,3,4,5-d_5) were conducted, and each run was duplicated with the corresponding unlabeled hydrocarbon. Typical k_0 values determined at various stages of these runs are listed in Table II.

TABLE II

COMPARATIVE RATES OF REACTION OF PENTAMETHYLBENZENE AND OF TOLUENE AND THEIR DEUTERIUM ANALOGS (25.0°)

10^4[ArH], mole/l.	10^4[Br₂], mole/l.	10^4[HBr], mole/l.	$\dfrac{R}{[ArH][Br_2]}$, 1. mole⁻¹ sec.⁻¹ for C₆H(CH₃)₅	for C₆D(CH₃)₅
		[ZnCl₂] = 0.0197 M		
10.6	2.73	2.0	2.89	3.73
9.6	1.73	3.0	2.38	2.66
19.2	3.46	6.0	1.87	1.90
17.2	1.46	8.0	1.72	1.70
12.1	5.9	13.0	1.48	1.53
9.1	2.9	16.0	1.53	1.48
5.83	4.3	43.0	1.26	1.28

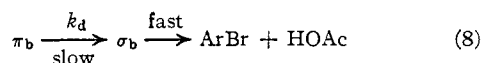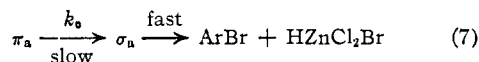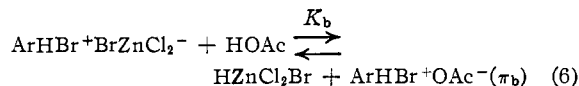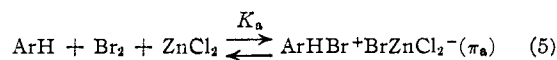|			$\dfrac{10^2 R}{[ArH][Br_2]}$ for C₆H₅CH₃	for C₆D₅CH₃
		[ZnCl₂] = 0.375 M		
93.1	3.78	1.0	5.4	5.9
92.6	3.28	1.5	4.3	4.4
92.1	2.78	2.0	3.5	3.5
91.1	1.78	3.0	2.2	2.5

Actually the differences in the rate constants, at the same hydrogen bromide concentrations, for the protium and deuterium analogs are small enough to be ascribed to experimental errors. In the case of the pentamethylbenzenes the reactivities of the two analogs have been found to be closely comparable over a wide range of hydrogen bromide concentrations. Apparently neither the HZnCl₂Br inhibited reaction nor the uninhibited process is subject to a deuterium isotope effect.

Certainly an extensive modification in the mechanism proposed previously (equations 2 and 3) for zinc chloride catalyzed aromatic bromination should be made even if only that phase of the reaction which is subject to inhibition by hydrogen bromide is to be considered. As noted in the Introduction, if a reaction such as that described by eq. 3, in which a proton is lost from the aromatic nucleus in a slow step, contributed significantly to the over-all bromination rate, the deuterated hydrocarbons would be less reactive than their unlabeled analogs.[6] Actually were there no contri-

bution from a reaction which was insensitive to hydrogen bromide and if equations 2 and 3 uniquely accounted for the bromination process, experimental k_0 values would be subject to an isotope effect, the intensity of which would increase with the hydrogen bromide content of the medium. This effect would be expected to reach a maximum value,[7] no larger than $k_H/k_D = 7$ at 25°. A mechanism similar to that of equations 2 and 3 has been proposed as one of two likely possibilities in accounting for the deuterium isotope effect observed for the iodination of 2,4,6-trideuterioanisole by iodine monochloride in aqueous solution.[8] It should be noted that the rates of certain iodination reactions of deuterium substituted phenols and amines also have been reported to be significantly less than those of their unlabeled analogs.[9,10] Apparently the presence of substituents such as –NH₂ or –OH (–OCH₃) on the aromatic nucleus provides for considerable stabilization of the reactive intermediate.[8,9]

The Mechanism of the Bromination Reaction.— Two reaction schemes can be suggested which in reality are very similar and both of which are in accord with the experimental observations concerning the effects of hydrogen bromide and of deuteration of the aromatic nucleus on the zinc chloride catalyzed bromination rate of methylbenzenes in acetic acid. In the first of these (equations 5–8) the slow steps are those in which two π complexes are converted to σ-complexes.[11]

$$ArH + Br_2 + ZnCl_2 \underset{}{\overset{K_a}{\rightleftharpoons}} ArHBr^+BrZnCl_2^-(\pi_a) \quad (5)$$

$$ArHBr^+BrZnCl_2^- + HOAc \underset{}{\overset{K_b}{\rightleftharpoons}}$$
$$HZnCl_2Br + ArHBr^+OAc^-(\pi_b) \quad (6)$$

$$\pi_a \xrightarrow[\text{slow}]{k_0} \sigma_a \xrightarrow{\text{fast}} ArBr + HZnCl_2Br \quad (7)$$

$$\pi_b \xrightarrow[\text{slow}]{k_d} \sigma_b \xrightarrow{\text{fast}} ArBr + HOAc \quad (8)$$

The corresponding π- and σ-complexes can be considered to differ in structure mainly in the degree to which the π-electron cloud of the aromatic nucleus has been penetrated. Presumably little progress toward cleavage of the C–H bond which is broken is made during these rate-determining steps (see ref. 6 for qualifying remarks). The reactions preceding the slow steps (equations 5 and 6) are considered to be at equilibrium at all times. Because of an adverse effect on the position of equilibrium 6, the relative importance of equation 8 as a rate-determining process should diminish with increasing hydrogen bromide concentration of the reaction mixtures.

If reaction proceeds by the second scheme (equations 9–11), the over-all rate should be unfavorably

(6) In discussing the significance of the observation that there is no deuterium isotope effect, it has been assumed that substantial weakening of the C–H bond should occur in the activation stage of a one-step process like that described by equation 3. The possibility that this bond would not be appreciably stretched in the transition state cannot, however, be entirely discounted [see G. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955)]. There is, nonetheless, considerable evidence that in certain closely related types of aromatic halogenation reactions, the C–H cleavage process is subject to a pronounced isotope effect.[7–9]

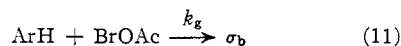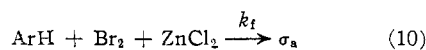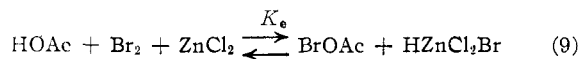(7) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(8) E. Berliner, *J. Am. Chem. Soc.*, **82**, 5435 (1960).

(9) E. Grovenstein, Jr., and D. C. Kilby, *ibid.*, **79**, 2972 (1957).

(10) E. Shilov and F. Weinstein, *Nature*, **182**, 1300 (1958).

(11) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

influenced by hydrogen bromide because of its effect on the equilibrium between bromine and acetyl hypobromite. Again it is presumed that

$$HOAc + Br_2 + ZnCl_2 \underset{}{\overset{K_e}{\rightleftarrows}} BrOAc + HZnCl_2Br \quad (9)$$

$$ArH + Br_2 + ZnCl_2 \xrightarrow{k_f} \sigma_a \quad (10)$$

$$ArH + BrOAc \xrightarrow{k_g} \sigma_b \quad (11)$$

little stretching of the C–H bond occurs in the slow steps (equations 10 and 11) of the reaction.

It is interesting that it recently[12] has been established that ClOAc is appreciably more reactive than chlorine as an electrophilic reagent in aromatic substitution processes. It can be concluded from the results of the present investigation that if the above mechanism (equations 9–11) applies, BrOAc is more electrophilic than bromine (over the range of zinc chloride concentrations which have been investigated).

The first scheme (equation 5–8) requires that the observed rate constant vary with hydrogen bromide produced as predicted by eq. 12. This variation should follow eq. 13 if the reactions take place by the second scheme (eq. 9–11). In either case

$$k_0 = k_c K_a[ZnCl_2] + k_d K_a K_b[ZnCl_2]/[HBr] \quad (12)$$

$$k_0 = k_f[ZnCl_2] + k_g K_e[ZnCl_2]/[HBr] \quad (13)$$

the predicted effect of the production of hydrogen bromide on the rate is in agreement with the experimental findings (Fig. 1).

Some of the experimental data from the previous investigation[1] of the kinetics of the zinc chloride catalyzed bromination of the polymethylbenzenes in acetic acid have been reinterpreted to conform to the findings of the present investigation. That is, plots of experimental k_0 values versus the corresponding reciprocals of the hydrogen bromide concentrations have been prepared. Inasmuch as the earlier experiments were concerned with reaction mixtures in which relatively small changes in hydrogen bromide concentrations took place, the fitting of straight lines to the plotted data cannot be carried out with high precision. Further information concerning reaction rates of the various alkylbenzenes at relatively high hydrogen bromide concentrations is required before the changes in reactivity with changes in the nature and position of ring substituents can be discussed extensively. It seems pertinent to attempt to decide which of the two mechanisms, eq. 5–8 or 9–11, correctly applies to these reactions before giving detailed consideration to the relative reactivities of the various hydrocarbons. With that point in mind an investigation of bromine acetate as an aromatic brominating agent is now underway.

A few representative values of the intercepts (I) and slopes (S) of plots of k_0 versus $1/[HBr]$, which are based on the data recorded previously,[1] are listed in Table III. These values, which are only of semi-quantitative significance, reflect the usual variations in susceptibility to electrophilic substitution which are generally observed for a series of polymethylbenzenes. They also illustrate

(12) P. B. D. de la Mare, I. C. Hilton and S. Varma, J. Chem. Soc., 4044 (1960).

TABLE III

THE INTERCEPTS AND SLOPES OF PLOTS[a] OF k_0 AT 25° versus $1/[HBr]$

Hydrocarbon	[HBr] range[b] × 10¹, mole/l.	[ZnCl₂], mole/l.	10³I, l. mole⁻¹ sec.⁻¹	10⁶S, l. mole⁻¹ sec.⁻¹
Benzene	0.35–1.05	0.500	0.037	0.037
Toluene	1.0–15.0	.375	.2[c]	6.36[c]
	0.13–3.0	.250	.2	1.7
	.5–1.5	.125	.05	0.31
o-Xylene	.1–7.5	.494	2.0[c]	6.36[c]
	.8–3.3	.250	0.4	15
p-Xylene	.4–3.0	.250	1.5	8.8
	.5–2.8	.125	0.25	1.7
m-Xylene	1.0–3.3	.250	20	256
	0.4–3.0	.0625	4.0	11.5
	0.4–3.4	.0313	1.75	2.5
Pseudocumene	1.2–3.3	.125	35	96
	0.6–3.3	.0625	16	18
Pentamethyl-benzene	0.4–4.5	.0197	1300[c]	312[c]

[a] Based on experiment data from the research described in ref. 1. [b] Range of concentrations over which the reaction was followed. [c] This research.

that the apparent orders of the reactions with respect to the catalyst are, contrary to what has been assumed for the sake of simplicity in the preceding discussion, higher than first. According to eq. 12 and 13 the slopes which are tabulated represent $k_d K_a K_b[ZnCl_2]$ or $k_g K_e[ZnCl_2]$. These slopes vary with the second power (or greater) of the zinc chloride concentration. The intercepts, which are presumed to represent $k_c k_a[ZnCl_2]$ or $k_f[ZnCl_2]$, show a similar dependence on zinc chloride when its concentration is relatively high, although at low catalyst concentrations (<0.030 M) the apparent order in zinc chloride for the reaction of mesitylene[1] and bromine is approximately one.

Actually these apparent orders probably are a composite of true reaction orders (which are for the moment unknown) and of salt effects on the magnitudes of the rate and equilibrium constants on which k_0 depends. It is, of course, also possible that at the higher concentrations the zinc chloride forms polymolecular aggregates which have catalytic activity.

The Hexamethylbenzene Reaction.—It has been found that in the presence of zinc chloride, hexamethylbenzene reacts rapidly with bromine in acetic acid. Originally a detailed study of the kinetics of this reaction was planned. However, because of uncertainties concerning the stoichiometry, only the most qualitative kind of information so far has been obtained. It seems worthwhile, nonetheless, to make a few general comments concerning the nature of this interesting reaction. In its initial phases the disappearance of halogen takes place by a process which is first order with respect to each of the two reactants and the catalyst and which is subject to hydrogen bromide inhibition. Considerably more than one mole of bromine is consumed per mole of hydrocarbon, and a mixture of organic products which are halogen-free is obtained. Attempts to isolate a single pure substance from the mixture by chromatography have so far been unsuccessful. Various fractions

have been obtained which show well defined carbonyl bands (5.7 μ). It seems most likely that these are acetoxy derivatives of hexamethylbenzene.

The Role of Non-bonded Repulsions in Secondary Isotope Effects. I. Alpha and Beta Substitution Effects.[1]

BY L. S. BARTELL

Beta deuterium isotope effects in reactions involving carbonium ions have been attributed almost universally to hyperconjugative weakening of C–H or C–D bonds. In view of recent calculations which indicate that structural and thermochemical effects in ground states of molecules previously ascribed to hyperconjugation can be correlated semiquantitatively in terms of non-bonded interactions, the non-bonded model is now extended to the treatment of isotope effects. Its basis is that repulsions involving deuterium atoms, when averaged over stretching and bending vibrations, are smaller than those for hydrogen which has a characteristically greater amplitude of vibration. Results are found to be sensitive to assumptions made about molecular structures. Nevertheless, results for several typical reactions strongly indicate that the isotopic differences in relief of non-bonded repulsions experienced by molecules going from crowded tetrahedral configurations to trigonal transition states or products, are quite comparable to the observed isotopic free energy differences. The alpha deuterium isotope effect, previously regarded as unrelated to the beta effect, is found to be accounted for semiquantitatively by the same model.

Several years ago Lewis and Boozer,[2] and Shiner[3] found that rates of solvolyses may be retarded appreciably if hydrogen atoms are replaced by deuterium atoms on carbon atoms β to the site of the leaving group. This secondary isotope effect has been attributed almost universally to the hyperconjugation presumably encountered in the carbonium ion transition state.[4] The associated withdrawal of electrons from C–H bonds has been considered to weaken the bonds and, accordingly, to lower zero point vibrational energies. Since the lowering would be less for the heavier deuteriums than for the hydrogens, the activation energy would be greater for the deuterated molecules. The effect has been studied extensively since its discovery with a view to elucidating the role of hyperconjugation in trigonal molecules and complexes. Analogous secondary isotope effects have been studied in rates of free radical reactions,[5] and even in the equilibrium constants of reactions involving transformations from tetrahedral to trigonal configurations.[6]

Whereas hyperconjugation currently is acknowledged to be important in transition states of molecules, its significance in ground states has been questioned seriously in the last two years, especially by Dewar. Dewar and Schmeising[7] showed that if the difference in bond energy between trigonal and tetrahedral σ bonds is taken into account, it is

no longer necessary to invoke hyperconjugation to account for heats of hydrogenation and bond lengths. Dewar ascribed the distinction between bonds in trigonal and tetrahedral molecules to differences in hybridization, which is plausible but not, at present, susceptible of a definitive formulation of meaning. Very recently it has been pointed out that non-bonded repulsions provide an alternative scheme for correlating effects customarily attributed to hybridization and hyperconjugation.[8] The number of non-bonded repulsions varies in the molecules concerned, decreasing in just those cases where bond lengths are observed to become shorter and bond energies increase. Furthermore, the magnitudes of non-bonded repulsions, as inferred from vibrational spectra, seem to be quite sufficient to account for the magnitudes of the observed effects in *ground states* of molecules. It is appropriate to inquire, then, whether considerations of non-bonded repulsions can offer an alternative explanation to hyperconjugation in secondary isotope effects involving *transition states* of molecules.

Model

The principle of the proposed argument is that the amplitudes of vibration of hydrogen atoms are larger than the amplitudes of the heavier deuterium atoms by a readily predictable amount. Non-bonded repulsions, averaged over the atomic vibrations, are greater for hydrogen atoms than for deuterium atoms since, in the range of interest, the second derivative of the non-bonded potential function is positive. Moreover, there are more and stronger non-bonded repulsions in a tetrahedral reactant than in a trigonal product or carbonium ion transition state. Accordingly, the relief of non-bonded repulsions associated with the transformation from a tetrahedral to a trigonal form is greater in molecules containing hydrogen than it is in those containing deuterium.

(1) (a) Research supported by the National Science Foundation; (b) presented at the 138th Meeting of the American Chemical Society, New York, N. Y., September 12, 1960.

(2) E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **74**, 6306 (1952); **76**, 794 (1954); **76**, 795 (1954).

(3) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); **76**, 1603 (1954).

(4) See, for example, E. S. Lewis, *Tetrahedron*, **5**, 143 (1959); V. J. Shiner, *ibid.*, **5**, 243 (1959).

(5) G. S. Hammond (private communication). In free radical reactions, however, the present "steric" arguments must be considered with greater reservation. In α substitution effects, at least, unshared electrons are sometimes considered to behave as if they are "bulkier" than adjacent bonded groups.

(6) P. Love, R. W. Taft, Jr., and T. Wartik, *Tetrahedron*, **5**, 116 (1959).

(7) M. J. S. Dewar and H. N. Schmeising, *ibid.*, **5**, 166 (1959).

(8) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).