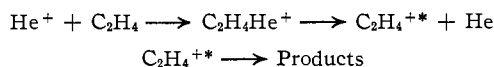


known to be below the ionization potential of Ne, and indeed it is not far different from that of  $\text{CH}_2^+$ . Also  $\text{C}_2\text{H}^+$  is present in the primary spectrum in greater abundance than  $\text{CH}_2^+$ . We cannot explain its absence.

It is interesting that, with both neon and helium, the ratio of  $\text{CH}_2^+$  to  $\text{CH}_3^+$  is the same as it is in the primary mass spectrum of ethylene. Indeed, the proportions of  $\text{C}^+$ ,  $\text{CH}^+$ ,  $\text{CH}_2^+$  and  $\text{CH}_3^+$  produced by charge exchange with neon are rather similar to those in the primary spectrum of ethylene. This may, of course, be merely a coincidence, since similar relations to the primary spectrum are not observed with the other rare gases. However, it suggests the possibility that a different mechanism is involved, *i.e.*, that the reaction may be



Under these circumstances one would expect the products to occur in the same proportion as in the

primary spectrum for similar amounts of excitation.

No clear relation between  $\Delta E$  and relative abundance is observable. It does appear that charge exchange reactions can occur only if they are exothermic (or at least not endothermic). Also, we do not note any reactions in Table II where  $-\Delta E$  is as great as five volts. We do not know, however, whether reactions having this much excess energy are not favored or whether, with so much excess energy, other preferred modes of reactions are induced. It does appear that considerations other than energy are of importance. Thus, the formation of  $\text{C}_2\text{H}_2^+$ , which occurs *via* a four-center reaction, is less favored than either  $\text{C}_2\text{H}_3^+$  or  $\text{C}_2\text{H}_4^+$ . Further, where enough energy is available it appears that the formation of  $\text{C}_2\text{H}_3^+$  is favored above that of  $\text{C}_2\text{H}_4^+$ . Although one cannot be certain, these results may be attributed to differences in entropy in the activated complex.

**Acknowledgments.**—We wish to acknowledge the assistance of Mr. W. C. Gieger who made all of the measurements upon which this study is based.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION OF THE HUMBLE OIL AND REFINING COMPANY, BAYTOWN, TEXAS, AND THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

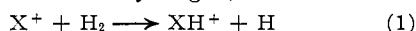
## Hydrogen Inhibition of the Rare Gas Sensitized Radiolysis of Cyclopropane

BY C. F. SMITH, B. G. CORMAN AND F. W. LAMPE<sup>1</sup>

RECEIVED MARCH 1, 1961

Argon, krypton and xenon sensitize the gas-phase radiolysis of cyclopropane. Hydrogen also acts as a sensitizer but in moderate quantities inhibits the rare gas sensitization; in larger quantities, it inhibits its own sensitization. A sensitization and inhibition mechanism is proposed from which specific reaction rates for the radiolysis sensitization by argon and hydrogen are derived.

The fact that the rare gases will sensitize the gas-phase radiolysis of various compounds such as acetylene,<sup>2</sup> butadiene,<sup>2b</sup> ethylene<sup>3</sup> and several inorganic gases,<sup>2b</sup> by some energy transfer process or processes, is well known in radiation chemistry. In addition, it has been shown recently that irradiated rare gases will sensitize the formation of hydrogen atoms and consequently the hydrogenation of ethylene.<sup>4</sup> Moreover, it was strongly suggested that this hydrogen atom sensitization occurred by means of the known reaction of the rare gas ions with molecular hydrogen,<sup>5</sup> *viz.*

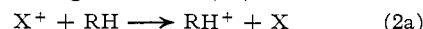


If we consider for simplicity that the rare gas sensitized radiolysis of some hydrocarbon, RH, also occurs *via* reaction with  $\text{X}^+$ , *viz.*

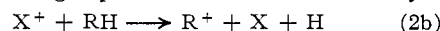


then addition of hydrogen to a constant composition radiolysis mixture of X and RH would result in a competition for  $\text{X}^+$  between  $\text{H}_2$  and RH and would

retard the rate of reaction of RH, provided that the hydrogen atoms produced in (1) do not react appreciably with it. Reaction 2 might be thought of as a simple charge transfer, (2a)



or as a dissociative charge transfer reaction,<sup>6</sup> (2b); (2b) can be considered as being related to the hydride transfer processes recently shown to be important in gas-phase radiation chemistry.<sup>7-9</sup>



For the purpose of this paper it is sufficient to know only that RH is consumed in (2). Since (1) and (2) are in direct competition (as long as H-atoms do not react with RH) a study of the retardation effect of hydrogen on the rare gas sensitized radiolysis of RH should yield the ratio of rate constants  $k_1/k_2$ . As  $k_1$  is known from mass spectrometric measurements,<sup>5</sup> such studies should in principle permit calculation of  $k_2$ , the over-all specific reaction rate for the sensitized radiolysis.

Cyclopropane seemed a good choice for RH as its inertness to hydrogen atom attack at room temperature has been demonstrated.<sup>10</sup>

(1) Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania.

(2) (a) S. C. Lind and D. C. Bardwell, *J. Am. Chem. Soc.*, **48**, 1575 (1926); (b) R. C. Palmer and D. C. Bardwell, Paper presented at 134th National Meeting of the American Chemical Society, Chicago, Illinois, September 7-12, 1958.

(3) F. W. Lampe, *Radiation Research*, **10**, 691 (1959).

(4) F. W. Lampe, *J. Am. Chem. Soc.*, **82**, 1551 (1960).

(5) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

(6) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *J. Chem. Phys.*, **25**, 790 (1956).

(7) F. H. Field and F. W. Lampe, *J. Am. Chem. Soc.*, **80**, 5587 (1958).

(8) J. H. Futrell, *ibid.*, **81**, 5921 (1959).

(9) J. H. Futrell, *J. Phys. Chem.*, **64**, 1634 (1960).

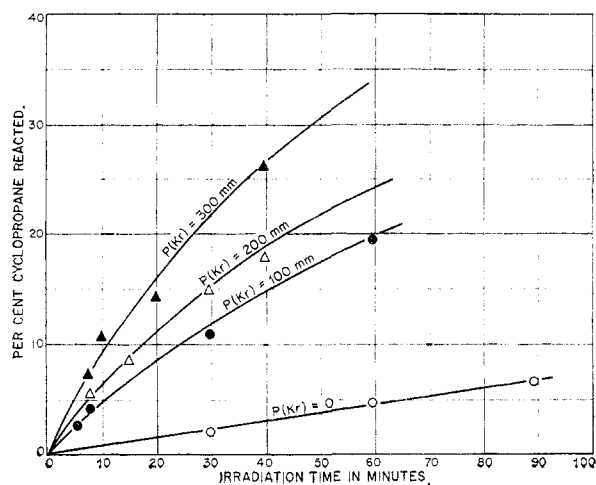


Fig. 1.—Effect of krypton on radiolysis of cyclopropane.

### Experimental

**Radiation Source.**—The source of high-energy electron radiation was a 2-million volt Van de Graaff electrostatic accelerator, Type AK, Model S, manufactured by High Voltage Engineering Co. In all experiments the accelerating voltage was maintained at 2.0 million volts and the electron beam current at approximately  $10 \mu\text{a}$ .

**Radiation Vessels.**—The vessel in which the irradiations were carried out consisted of a heavy walled stainless steel cylinder, of 10 cm. internal diameter and 30 cm. length. The flange closing the end of the reactor had three independent holes for an aluminum foil window, an inlet tube and a small diameter sampling line to the gas sample bombs. The aluminum foil window was 5 mils thick and 1 inch in diameter. The inlet tube was fitted with a stainless steel valve and a machined brass 14-35  $\frac{1}{8}$  joint and was used for loading and unloading the reactor. The five gas sample bombs, each with a capacity of 45 ml., were attached to the sampling line by a low volume manifold. The entire sample system, exclusive of the stainless steel bombs, had a capacity of less than 5 ml. Provision was made for evacuation of the line after each sample was taken to ensure that the next sample would be representative of the gaseous mixture in the reactor at that time.

**Materials.**—Matheson cyclopropane, stated to have a purity of 99.5%, was frozen out in liquid nitrogen in such a way that more cyclopropane than was required to fill the storage bulb was contained in the trap. The gas was then expanded with the collection of a middle fraction in a bulb previously evacuated to  $10^{-6}$  mm. Air Reduction Company Research grade argon (stated purity 99.9 mole %), krypton (99.5%) and xenon (99.5%) were used without further purification, as was Matheson research grade hydrogen (99.9%).

**Procedure.**—In carrying out an irradiation, the reaction vessel was first evacuated to  $10^{-6}$  mm. and this pressure maintained by pumping for approximately 8 hr. It was filled to the desired partial pressures always with a positive pressure differential to minimize back diffusion of components already present. The reactor then was placed in position on an electrically insulated support and the irradiation begun. The current collected from the reactor body was used to monitor the incident beam intensity. At predetermined intervals the irradiation was stopped and a sample withdrawn into a sample bomb. At the conclusion of the irradiation, the sample bombs were attached to a gas handling system, their pressures measured and the samples transferred to evacuated Pyrex sample bulbs by means of a Toepler pump. Quantitative analysis of the reaction products was accomplished by gas-liquid partition chromatography. Two columns, hexadecane and benzyl Cello-solve substrates on 40- to 60-mesh crushed firebrick support, permitted complete separation and determination of all components boiling below hexane. Energy absorption

(10) (a) H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **17**, 351 (1949). (b) J. K. Lee, B. Musgrave and F. S. Rowland, *Can. J. Chem.*, **38**, 1756 (1960).

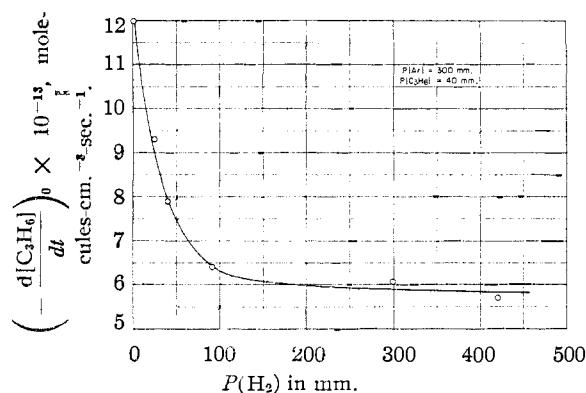


Fig. 2.—Inhibition of argon-sensitized radiolysis of hydrogen.

rates were calculated by means of methane dosimetry ( $G_{\text{C}_2\text{H}_6} = 2.1$ )<sup>11</sup> and the standard corrections for stopping power.

### Results

That rare gases will sensitize the radiolysis of cyclopropane can be seen in Fig. 1 in which the percentage of cyclopropane reacting is plotted as a function of irradiation time for several partial pressures of krypton and fixed partial pressures of 20 mm. of cyclopropane and about 85 mm. of hydrogen; also shown is similar data for irradiation of pure cyclopropane. Argon exhibits similar behavior and a few experiments with xenon served to indicate that the degree of rare gas sensitization is in the order expected from their energy absorption characteristics, namely,  $\text{Xe} > \text{Kr} > \text{A}$ . The products of the radiolysis are identical with the radiation damage products observed in studies of the reactions of recoil tritium with cyclopropane,<sup>12</sup> while the relative amounts of the various products vary with cyclopropane conversion as expected from considerations of the olefinic scavenging effect at all but extremely low concentrations.<sup>13</sup> Since, however, cyclopropane reacts negligibly slowly with H-atoms at this temperature,<sup>10</sup> olefinic scavenging should have no effect on consideration of the rate of cyclopropane disappearance.

When hydrogen is added to a constant composition radiolysis system of rare gas and cyclopropane, the rate of disappearance of cyclopropane is retarded. This can be seen in Fig. 2 in which is plotted the initial rate of consumption of cyclopropane as a function of the partial pressure of hydrogen. The observed products are qualitatively independent of hydrogen pressure (that is, no new products appear with hydrogen), although for a given conversion of cyclopropane the relative amounts of saturated to unsaturated products would be expected to increase with increasing hydrogen pressure. Typical product distributions for various times of irradiation of a system of 400 mm. of argon, 30 mm. of cyclopropane and 40 mm. of hydrogen are shown in Table I. Other products noted but not analyzed quantitatively included methane, acetylene, allene, methylacetylene and *n*-hexane. A material balance showed that a large amount of polymerization to higher molecular weight products must have occurred.

(11) F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 1055 (1957).

(12) J. K. Lee, B. Musgrave and F. S. Rowland, *ibid.*, **81**, 3803 (1959).

(13) R. A. Back, *J. Phys. Chem.*, **64**, 124 (1960).

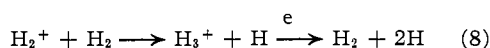
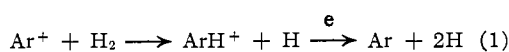
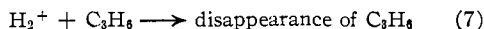
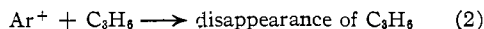
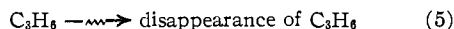
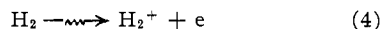
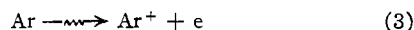
TABLE I  
PRODUCTS OF THE RADIOLYSIS OF CYCLOPROPANE, HYDROGEN AND ARGON

Component	Irradiation time			
	30 min.	60 min.	90 min.	120 min.
Ethylene	Trace	0.15	0.28	0.34
Ethane	0.15	.31	.49	.61
Propylene	.18	.23	.25	.25
Propane	.41	.94	1.15	1.27
Isobutane	.18	.30	0.42	0.44
n-Butane	.37	.79	.96	1.03
Methylcyclopropane	Trace	.11	.24	0.29
2-Methylpentane	Trace	.12	.21	.24
n-Pentane	Trace	.09	.15	.15

In Fig. 3, the initial rates of disappearance of cyclopropane are plotted as a function of  $[H_2]^{-1}$ , the dotted portion indicating that the rate must asymptotically approach the intercept of Fig. 2 as  $1/[H_2]$  tends toward infinity. Such a plot enables us to obtain the completely inhibited rate of the sensitized radiolysis.

### Discussion

As shown in Fig. 2 the addition of hydrogen to irradiated mixtures of argon and cyclopropane retards the rate of reaction of cyclopropane to a limiting value. To attempt a kinetic description of the hydrogen retardation effect let us consider for simplicity only ionization processes stemming from the primary act. Excitation processes are not ruled out but in their totality would probably be kinetically equivalent. The probable reactions are



A kinetic analysis of the above reactions yields an expression for the initial rate of disappearance of cyclopropane

$$\left(-\frac{d[\text{C}_3\text{H}_6]}{dt}\right)_{t=0} = \alpha + \frac{\beta}{1 + \gamma_1[\text{H}_2]} + \frac{\xi[\text{H}_2]}{1 + \gamma_2[\text{H}_2]} \quad (\text{E1})$$

where by definition

$$\alpha = \frac{Q_{\text{C}_3\text{H}_6}[\text{C}_3\text{H}_6]G_{-\text{C}_3\text{H}_6}}{100}, \quad \beta = \frac{Q_{\text{Ar}}[\text{Ar}]}{W_{\text{Ar}}}, \quad \gamma_1 = \frac{k_1}{k_2[\text{C}_3\text{H}_6]},$$

$$\gamma_2 = \frac{k_8}{k_7[\text{C}_3\text{H}_6]}, \quad \xi = \frac{Q_{\text{H}_2}}{W_{\text{H}_2}}$$

and

$Q_i$  = rate of absorption of energy by the  $i$ th component at unit concn.  
 $G_{-\text{C}_3\text{H}_6}$  = the 100 e.v. yield for the disappearance of cyclopropane in the radiolysis of pure cyclopropane  
 $W_i$  = av. energy expended in forming an ion-pair in component  $i$

Since, in the hydrogen inhibition experiments under discussion,  $[\text{C}_3\text{H}_6]$ ,  $[\text{Ar}]$  and the radiation intensity are held constant, the only variable in (E1) is  $[\text{H}_2]$ . Moreover,  $\beta$ ,  $\xi$  and  $Q_{\text{C}_3\text{H}_6}$  are deter-

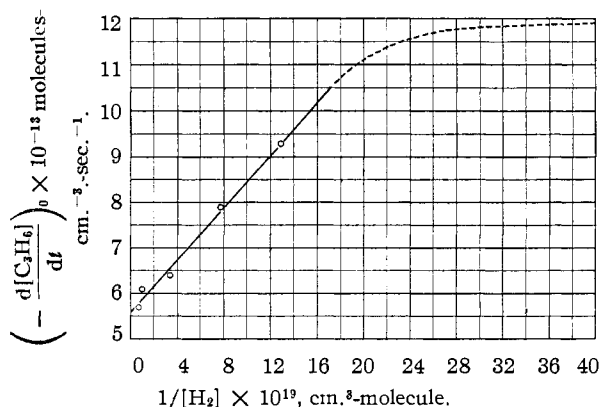


Fig. 3.—Limiting inhibition by hydrogen.

mined independently from the methane dosimetry irradiations as described briefly in the Experimental section.

The linearity of the plot in Fig. 3 is in agreement with the above inhibition mechanism (E1) for the case when  $\gamma_1[\text{H}_2] \gg 1$ . Within our experimental precision this appears to be true for all hydrogen concentrations studied. To obtain values for  $\alpha$ ,  $\gamma_1$  and  $\gamma_2$  we have simply to consider these three limits of (E1)

$$\lim_{[\text{H}_2] \rightarrow 0} \left(-\frac{d[\text{C}_3\text{H}_6]}{dt}\right)_{t=0} = \alpha + \beta \quad (\text{E2})$$

$$\lim_{[\text{H}_2] \rightarrow \infty} \left(-\frac{d[\text{C}_3\text{H}_6]}{dt}\right)_{t=0} = \alpha + \frac{\xi}{\gamma_2} \quad (\text{E3})$$

$$\lim_{[\text{H}_2] \rightarrow \infty} \frac{d}{d\left(\frac{1}{[\text{H}_2]}\right)} \left(-\frac{d[\text{C}_3\text{H}_6]}{dt}\right)_{t=0} = \frac{\beta}{\gamma_1} - \frac{\xi}{\gamma_2} \quad (\text{E4})$$

As  $\beta$  and  $\xi$  are known,  $\alpha$  is determined from (E2) utilizing the intercept of Fig. 2, following which  $\gamma_1$  and  $\gamma_2$  are obtained from the slope and intercept, respectively, of Fig. 3 in accordance with E3 and E4.

The values of  $\beta$  and  $\xi$  from the dosimetry irradiations are  $9.3 \times 10^{12}$  ions-cm.<sup>-3</sup>-sec.<sup>-1</sup> and  $3.3 \times 10^{-4}$  ions-molecule<sup>-1</sup>-sec.<sup>-1</sup>, respectively. When these values and the cyclopropane concentration ( $1.30 \times 10^{18}$  molecules-cm.<sup>-3</sup>) are combined with the appropriate limits, as described above, we obtain values for the rate constant ratios

$$\frac{k_1}{k_2} = 4.2$$

$$\frac{k_8}{k_7} = 0.15$$

Taking reported values for  $k_1^{15}$  and  $k_8^{14}$  we obtain finally the specific reaction rates of the sensitization by argon and hydrogen of cyclopropane radiolysis, namely

$$k_2 = 2.7 \times 10^{11} \text{ l.-mole}^{-1} \text{ sec.}^{-1}$$

$$k_7 = 8.4 \times 10^{12} \text{ l.-mole}^{-1} \text{ sec.}^{-1}$$

Molecular hydrogen thus appears to be a much more efficient radio-sensitizer for cyclopropane than is argon. Simple ion-molecule reaction rate theory<sup>14</sup> which predicts that

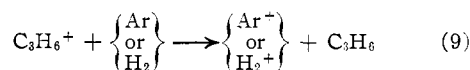
$$\frac{k_2}{k_7} = \sqrt{\frac{\mu_{\text{H}_2-\text{C}_3\text{H}_6}}{\mu_{\text{Ar}-\text{C}_3\text{H}_6}}} = 0.31$$

where  $\mu$  is the reduced mass, is clearly not able to explain the much greater effectiveness of  $\text{H}_2$  as a sensitizer.

(14) H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

When the value of  $\alpha$ , obtained as described above ( $2.7 \times 10^{13}$  molecules-cm.<sup>-2</sup>-sec.<sup>-1</sup>), 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  $\alpha$  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.

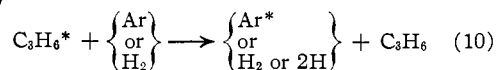
In the inhibition mechanism, and hence in the derivation of (E1), we have implicitly assumed that  $G(-C_3H_6)$  (defined as the number of molecules of cyclopropane consumed per 100 electron-volts absorbed by cyclopropane) is independent of hydrogen and argon pressure. To be valid this requires that 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.*



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



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  $\gamma_1$  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  $\gamma_2$  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,  $\xi$  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.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS, CALIFORNIA]

## 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

RECEIVED FEBRUARY 9, 1961

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,<sup>1</sup> 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<sup>1</sup> 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.

$$R = -d[Br_2]/dt = k_0[ArH][Br_2] \quad (1)$$

This decrease has been attributed to inhibition of the reaction by a substance, probably  $HZnCl_2Br$ , formed by coordination 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.<sup>1,2</sup>

(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<sup>1</sup> 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  $H_2ZnCl_3Br(OAc)$  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).