Reaction of Hydrogen Atoms with Halogeno-Methanes

Part 1 *.--Carbon Tetrachloride

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Hydrogen atoms, generated in a Wood's tube, have been allowed to react with carbon tetrachloride vapour. The products of the reaction have been analyzed and found to be hydrogen chloride, chloroform, methylene dichloride and traces of methyl chloride. The effect of the relative concentrations of the reactants, of an inert gas and of added hydrogen chloride on the ratio of the principal products has been investigated. From these data it is possible to build up a complete picture of the reaction sequences. The initial step is chlorine abstraction by a hydrogen atom; the trichloromethyl radical so produced reacts with a further hydrogen atom to yield an excited chloroform molecule which either undergoes collisional deactivation or loses hydrogen chloride to yield dichlorocarbene.

Previous work from this laboratory has been devoted to a study of the abstraction of hydrogen atoms from substituted alkanes, and a fairly complete picture of this process has been developed. The present investigation is the second in a series in which the abstraction of halogen atoms from halogeno-alkanes will be investigated.¹

Chadwell and Titani reacted the methyl halides with hydrogen atoms produced in a discharge tube and identified the products of the reaction.² The reaction of hydrogen atoms with carbon tetrachloride was studied by Polanyi and co-workers,³ by Smyser and Smallwood,⁴ and by Vance and Baumann.⁵ The first authors used conditions such that hydrogen chloride was the only identified product, but Smyser and Smallwood reported obtaining an unidentified solid product as well. The most detailed study was that of Vance and Baumann who generated their hydrogen atoms in a Wood's tube and analyzed the hydrogen chloride produced. These authors report Arrhenius parameters for reaction (1),

$$CCl_4 + H \cdot \rightarrow CCl_3 \cdot + HCl. \tag{1}$$

Their results have little meaning since no attempt was made to investigate the mechanism of the reaction, and in some runs the amount of hydrogen chloride produced represented more than 100 % consumption of carbon tetrachloride according to eqn. (1).

It is clear from this previous work that no further progress can be made in the study of the reaction of hydrogen atoms with halogeno-alkanes until the mechanism of the reaction has been elucidated. It is the purpose of the present paper to describe the elucidation of the reaction of hydrogen atoms with carbon tetrachloride vapour at normal temperatures.

EXPERIMENTAL

The basic layout of the apparatus is shown in fig. 1. The main reaction vessel was 2 ft. \times 3 in. diam. and the inlet from the discharge tube ($\frac{7}{8}$ in. diam.) continued 6 in. down the

* This paper is also considered to be part 8 of a series entitled, Free Radical Substitution in Aliphatic Compounds.

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length of the reactor. The reaction vessel and discharge tube were acid-washed prior to assembly to poison the surfaces to hydrogen-atom recombination. Tubes subsequent to the reactor were not treated in order to assist in the recombination of any remaining hydrogen atoms. All the reported experiments were performed at room temperature. The carbon tetrachloride vapour was introduced by bubbling a stream of hydrogen through liquid carbon tetrachloride maintained at a known temperature. The carbon tetrachloride vapour was thus introduced into the hydrogen atom stream diluted by molecular hydrogen and, unlike the previous work, there was no local heating in the mixing zone. The concentration of carbon tetrachloride was calculated from the known vapour pressure at that temperature, assuming saturation. Flow rates of hydrogen, both through the discharge tube and through



FIG. 1.—Apparatus for studying hydrogen atom reactions.

the carbon tetrachloride trap, were measured using gas burettes. The flow in both streams was controlled by needle valves, and this in turn controlled the pressure in the apparatus which was measured by a vacustat connected to the apparatus just beyond the discharge tube (all runs were carried out at 0.23 mm). The products of a run were collected in the large traps at the end of the reactor, which contained powdered sodium hydroxide to remove the hydrogen chloride and which were surrounded with liquid nitrogen. At the end of a run the traps were isolated from the reactor and discharge tube, and a diffusion pump was

TABLE 1

expt. no.	in second- ary, mA	A×104	$B \times 10^4$	E C×10 ⁵	ICI adde H ₂	d CCl ₄	CHCl3	CH ₂ Cl ₂	CHCl ₃ CH ₂ Cl ₂	% reaction	no. of runs
1	300	5.2	2.5	3.3	—	32.7 ± 1.2	1.09	0.274 ± 0.014	3·99±0·19	4 ·19±0·16	5
2	300	5.2	2.5	1.3		17.1 ± 1.0	1.09	0.258 ± 0.014	4.26 ± 0.26	7.32 ± 0.32	6
3	105	5.2	2.5	3.3		62.5 ± 2.7	1.09	0.263 ± 0.014	4.15 ± 0.19	2.12 ± 0.09	5
4	320	5.2	2.5	3.3		23·96±0·70	1.09	0.249 ± 0.03	4.39 ± 0.44	5.30 ± 0.16	7
5*	200	5.2	2.5	3.3		39.00 ± 2.3	1.09	0.23 ± 0.02	4.75 ± 0.29	3.30 ± 0.14	5
6	310	5.2	2.5	3.3	5.80	23.45 ± 1.6	1.09	0.17 ± 0.014	6.42 ± 0.53	5.10 ± 0.15	5
7	300	5.2	2.5	3.3	10.1	$28 \cdot 1 \pm 1$	1.09	$0{\cdot}145\pm0{\cdot}01$	7.54 ± 0.32	$4\cdot22\pm0\cdot14$	6

A, flow rate of hydrogen through the discharge tube moles \min^{-1} ;

B, flow rate of hydrogen through the reactant bubbler moles \min^{-1} ;

C, flow rate of reactant moles \min^{-1} ;

* In this experiment the reactant was entrained in argon instead of hydrogen.

connected into the line so that a high vacuum was obtained. The products of the reaction were then transferred to a small trap from which samples could be taken for injection into the gas chromatography apparatus. The chromatography apparatus was a Griffin and George D6 instrument in which the detector is a gas-density balance. As the molecular weight of all the products was known, it was possible to calculate the relative concentration of each of the components directly from the peak areas on the chromatogram, and no calibration was necessary. The column was packed with 10 % silicone on Celite.

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DISCUSSION

The products of the reaction were hydrogen chloride, chloroform, methylene dichloride and traces of methyl chloride (methane if formed in trace amounts would not have been detected). Although the exact concentration of hydrogen atoms was not determined, the apparatus was very similar to that of previous workers, and from their data it may be assumed that the hydrogen from the discharge tube was about 20 % dissociated in the mixing zone. This represents approximately an eight-fold excess over the carbon tetrachloride in the mixing zone. The overall consumption of carbon tetrachloride never exceeded 8 %.

The first feature of the results is, therefore, the relatively large amount of methylene dichloride produced (approximately 25 % of the chloroform). If the methylene dichloride is formed as a result of attack by hydrogen atoms on chloroform produced in the reaction, this means that the rate of attack on chloroform must be much greater than that on carbon tetrachloride because of the relative concentrations. Apart from the improbability of this on the grounds of the relative bond strengths in chloroform and carbon tetrachloride, we have found that in separate experiments chloroform is *less* readily attacked by hydrogen atoms than carbon tetrachloride (see Part 2). It is clear, therefore, that the methylene dichloride must be formed by some other mechanism.

The second feature of the results is the constancy of the ratio of chloroform to methylene dichloride in the products. In expt. 1 and 2 the concentration of carbon tetrachloride was varied, and in expt. 3 and 4 the relative concentration of hydrogen atoms was varied by altering the current through the discharge tube. The extent of reaction varies from $2 \cdot 1$ % in expt. 3 to $7 \cdot 3$ % in expt. 2. In all four experiments the ratio of chloroform to methylene dichloride remained within experimental error the same. The simplest interpretation that can be put on these results is that chloroform and methylene dichloride are derived from a common intermediate, and the conversion of this intermediate into chloroform or methylene dichloride is independent of the concentration of hydrogen atoms or carbon tetrachloride.

The first step in the reaction sequence is undoubtedly the abstraction of a chlorine atom

$$CCl_4 + H \cdot \rightarrow CCl_3 \cdot + HCl. \tag{1}$$

Three reactions seem open to the CCl₃ radicals so generated.

$$CCl_{3} + H_2 \rightarrow CCl_3H + H$$
 (2)

$$CCl_3 + H \rightarrow CCl_3 H^*$$
 (3)

$$\operatorname{CCl}_{3} + \operatorname{CCl}_{3} \to \operatorname{C}_2 \operatorname{Cl}_6. \tag{4}$$

Reaction (2) is endothermic to approximately 14 kcal/mole, and therefore insignificant at the temperature studied. Goldfinger 6 found no activation energy for reaction (4) and reported a rate constant of $k_4 = 6.3 \times 10^8$ l. mole⁻¹ sec⁻¹. However, no hexachloroethane has been detected in any of the present experiments, so we conclude that reaction (3), which is exothermic to 90 kcal/mole, is the predominant reaction of the

* indicates vibrationally excited molecule,

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trichloromethyl radicals. We therefore consider possible reactions of the vibrationally excited chloroform molecules so produced.

$$\operatorname{CCl}_{3}\operatorname{H}^{*} \rightarrow \operatorname{CCl}_{3} + \operatorname{H}^{\bullet}$$
 (-3)

$$CCl_{3}H^{*} + M \rightarrow CCl_{3}H + M \tag{5}$$

$$CCl_{3}H^{*} \rightarrow CCl_{2}:+HCl$$
(6)

$$\operatorname{CCl}_{3}\operatorname{H}^{*} \to \operatorname{CCl}_{2}\operatorname{H}^{\bullet} + \operatorname{Cl}^{\bullet} \tag{7}$$

If reaction (-3) occurs, it generates the same starting species and cannot be detected. Evidence presented in part 3, from the reactions of hydrogen atoms with deuterochloroform shows that reactions similar to (-3) are unimportant. Reaction (5), the collisional deactivation of the excited chloroform molecules, may be expected to be rapid. In studies involving the reactions of hydrogen atoms with alkanes, collisional deactivation of vibrationally excited alkanes (formed by the combination of alkyl radicals and hydrogen atoms) under similar conditions was of the same order as the rate of unimolecular decomposition.^{7, 8} Neglecting reaction (-3), reactions (6) and (7) represent the two most probable modes of unimolecular decomposition of the excited chloroform molecules. The thermal decomposition of chloroform has been investigated by Semeluk and Bernstein 9 and by Shilov and Sabirova.¹⁰ The Russian workers, who made the more thorough investigation, provided good evidence that the reaction proceeds via dichlorocarbene giving a rate constant of $k_8 = 2.6 \times 10^{11} \exp -47,000/RT \sec^{-1}$ for this unimolecular reaction: $CCl_3H \rightarrow CCl_2$:+HCl. (8)

The vibrationally excited chloroform produced in reaction (3) has 90 kcal excess energy, so it is not possible to discriminate between reactions (6) and (7) without recourse to experimental data, although the Russian work discussed above and their data on the unimolecular decomposition of carbon tetrachloride and methyl chloride indicates that reaction (6) is the more probable.

Returning to the experimental data, we can now see that vibrationally excited chloroform molecules formed in reaction (3) are the common intermediates from which both chloroform and methylene dichloride are derived. The important feature in expt. 1-4 was that the ratio of chloroform to methylene dichloride in the products remained constant when the concentration of the reactants was varied. In expt. 5-7 the ratio of chloroform to methylene dichloride does vary. In expt. 5 the gas entraining the carbon tetrachloride into the reactor was argon in place of hydrogen. Effectively this represents keeping the concentration of all the species constant, except molecular hydrogen which was reduced by a factor of two. In this experiment the ratio of chloroform to methylene dichloride is slightly greater. effect might be due to argon being a more effective third body (reaction (5)), but the change in the chloroform/methylene dichloride ratio, although small, is larger than would be expected on this hypothesis. Probably, therefore, methylene dichloride is derived from the reaction of some reactive intermediate with molecular hydrogen. When the concentration of molecular hydrogen is reduced, then this reactive intermediate undergoes reaction with some other species to yield chloroform. Although both dichlorocarbene produced in reaction (6) and the dichloromethyl radical produced in reaction (7) could lead to methylene dichloride, only dichlorocarbene is consistent with the results of expt. 5.

If we now consider the possible reactions that dichlorocarbene may undergo;

$$\operatorname{CCl}_2: + \operatorname{H}_2 \to \operatorname{CCl}_2\operatorname{H}_2^* \tag{9}$$

$$CCl_2:+HCl \rightarrow CCl_3H^*$$
(10)

$$\operatorname{CCl}_2:+\operatorname{CCl}_4\to 2\operatorname{CCl}_3. \tag{11}$$

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reactions (9) and (10) are exothermic to approximately 65 and 45 kcal/mole respectively, while reaction (11) is probably slightly endothermic and is therefore unlikely to be important with reaction (9). The concentration of hydrogen chloride is normally much less than molecular hydrogen, so that the majority of any dichlorocarbene formed by reaction (6) may be expected to yield vibrationally excited methylene dichloride by reaction (9). The excess energy possessed by the excited methylene chloride is between 15 and 20 kcal less than that possessed by the excited chloroform produced in reaction (3), so it is reasonable to assume there will be less decomposition.

$$CCl_2H_2^* + M \rightarrow CCl_2H_2 + M \tag{12}$$

i.e., reaction (12) represents the principal fate of the excited methylene dichloride molecules. There are three modes of decomposition of excited methylene dichloride :

$$\operatorname{CCl}_2\operatorname{H}_2^* \to \operatorname{CCl}_2\operatorname{H}_{\bullet} + \operatorname{H}_{\bullet} \tag{13}$$

$$CCl_2H_2^* \to CClH_2 \bullet + Cl \bullet \tag{14}$$

$$CCl_2H_2^* \to CClH: + HCl \tag{15}$$

By analogy with the excited chloroform, we may expect reaction (15) to be the predominant. The very small amount of chlorocarbene so produced will then react with molecular hydrogen to yield methyl chloride, and further reaction becomes exceedingly unlikely. We thus have a complete reaction sequence.

Expt. 6 and 7, in which hydrogen chloride was added to the reactants, verify this sequence. If the methylene dichloride is derived from the reaction of dichlorocarbene with molecular hydrogen, we may expect the addition of hydrogen chloride to the reactants to increase the importance of reaction (10) at the expense of reaction (9) and so increase the chloroform/methylene dichloride ratio in the products. The addition of hydrogen chloride might introduce a number of additional complications as a result of reaction (16) (and (-16)):

$$\mathrm{HCl} + \mathrm{H} \cdot \to \mathrm{H}_2 + \mathrm{Cl} \cdot \tag{16}$$

However, taking Steiner and Rideal's data for these reactions,¹¹ and assuming that Vance and Baumann's figures for reaction (1) ⁵ are of the right order, we find that at room temperature reaction (1) is approximately 20 times faster than reaction (16), and as reaction (-16) is about the same rate as (16) at room temperature, the concentration of chlorine atoms is so small that it can be neglected. From the results of expt. 6 and 7, we see that the addition of hydrogen chloride causes a marked increase in the chloroform/methylene dichloride ratio as required by the proposed sequence.

We can now summarize the entire reaction sequence.



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When hydrogen chloride is added or the molecular hydrogen concentration is reduced, we have to include (10),

$$CCl_2:+HCl \rightarrow CCl_3H^{\dagger}$$
(10)

$$CCl_{3}H^{\dagger} + M \rightarrow CCl_{3}H + M \tag{17}$$

Precise derivation of rate expressions in a flow system is difficult. As a first step we treat reactions (3), (5) and (6) as two separate reactions (5') and (6'). In the same way, we treat reactions (9) and (12) and reactions (10) and (17) as single reactions (12') and (10'). These composite reactions are represented by the dotted lines in the reaction sequence.

If we consider a segment of the reaction vessel of length δl , then in this segment we have pseudo-steady state conditions,

$$(\partial [\mathrm{H}\cdot]/\partial t)_l = 0; \quad (\partial [\mathrm{CCl}_3\cdot]/\partial t)_l = 0; \quad (\partial [\mathrm{CCl}_2:]/\partial t)_l = 0$$

Since the concentrations of trichloromethyl radicals and dichlorocarbene are extremely small, we can consider them as being present in steady-state concentrations throughout the main part of the reactor : i.e.,

 $d[CCl_3 \cdot]/dt = 0; \quad d[CCl_2 :]/dt = 0.$

We now obtain a rate expression for the ratio of chloroform to methylene dichloride

$$d[CHCl_3]/d[CH_2Cl_2] = k_5'M/k_{6'} + (1 + k_5'M/k_{6'})(k_{10'}/k_{12'})([HCl]/[H_2]).$$

In expt. 1-5, the concentrations of hydrogen chloride is extrmely small, and so the integrated form of the rate expression reduces to

 $[CHCl_3]/[CH_2Cl_2] = k_5 M/k_{6'}$

i.e., the ratio of chloroform to methylene dichloride is independent of the relative concentrations of the reactants exactly as observed. In expt. 6 and 7 the concentration of hydrogen chloride was appreciable, and the concentrations of both hydrogen chloride and molecular hydrogen remain virtually constant throughout the reactor, so the integrated form of the rate expression becomes

$$[CHCl_3]/[CH_2Cl_2] = k_5' M/k_6' + (1 + k_5' M/k_6')(k_{10'}/k_{12'})([HCl]/[H_2]).$$

When the results of expt. 1, 6 and 7 are plotted in the form $[CHCl_3]/[CH_2Cl_2)$ against $[HCl]/[H_2]$, a straight line is obtained with an intercept of $k_5'M/k_6' = 4.30$ and a slope $(k_5'M/k_6')(k_{12'}/k_{12'}) = 33.5$, i.e., $k_{10'}/k_{12'} = 6.34$. The ratio $k_{10'}/k_{12'}$ is in accord with Semeluk and Bernstein's observations of rapid exchange between chloroform and hydrogen chloride ⁹ when these workers' results are re-interpreted according to the unimolecular decomposition mechanism (reaction (8)) of Shilov and Sabirova.¹⁰ These results as a whole provide a good confirmation of the reaction sequence proposed.

† indicates vibrationally excited molecule.

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