[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IMPERIAL COLLEGE, LONDON]

The Pyrolysis of 1,1,1-Trichloroethane[1]

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In the previous papers of this series[3] the mechanisms of the thermal decompositions of ethyl chloride,[3c] 1,1-[3c] and 1,2-dichloroethane,[3b] *t*-butyl chloride[3d] and 2-chloro-[3e] and 1,2-dichloropropane[3e] have been elucidated. It has been pointed out[3d] that saturated chlorinated hydrocarbons undergo thermal decomposition to the corresponding olefin or chloroölefin and hydrogen chloride by two easily distinguishable homogeneous mechanisms. The first of these, the radical chain mechanism, undoubtedly involves the participation of chlorine atoms in one of the two propagation steps of the reaction. The second, the unimolecular mechanism, is shown by those compounds which either are themselves, or decompose to give, inhibitors for the chain type decomposition. Clearly the definition of substances which are likely inhibitors is of fundamental importance and has, in fact, already been adequately discussed.[3d]

Although the molecular structure of a saturated chlorinated hydrocarbon may be such as to allow its decomposition by a chain mechanism, yet one is able to conceive the existence of a competition between the probable chain method of decomposition and a unimolecular mechanism,[4a] for there are no obvious restrictions on the latter[4b] arising from structural causes.[3e] 1,1,1-Trichloroethane, the pyrolysis of which would be expected[3d] to proceed by a chain mechanism, has now been shown to be a case in point.

Experimental

Materials.—Eastman Kodak Co. technical 1,1,1-trichloroethane[5] was washed with concentrated hydrochloric acid, water, 10% aqueous potassium carbonate solution, 10% aqueous sodium chloride and then dried over calcium chloride. It was fractionated through an 18″ column packed with Fenske rings and the main fraction, b. p. 73.9° (cor.) was fractionally crystallized three times, the lower freezing fractions being rejected on each occasion. The following constants were recorded and are compared with the mean of the best literature values (in parentheses): b. p. 73.9° cor. (74.0° cor.); from 74.1°[6]; 74.0°[7]; 73.9°[8]; 73.8-74.0°[9]; 73.86-73.94°[12a]; 73.8°.[12b] M. p. (sulfur dioxide vapor pressure thermometer), −32.0° (−32.8°); from: −32.7°[7]; −30.4°[8]; −33.0°[9]; −32.3°.[10] $d^{23}{}_4$ 1.3269 (1.3242); interpolated from $d^{20}{}_4$ 1.3492[8]; $d^{25}{}_{25}$ 1.31144.[11] $n^{23}\mathrm{D}$ 1.4360; compare $n^{20}\mathrm{D}$ 1.4379[7]; $n^{20}\mathrm{D}$ 1.4384[8]; $n^{21}\mathrm{D}$ 1.4377[12a]; $n^{20}\mathrm{D}$ 1.4384.[12c]

Apparatus.—The apparatus and general technique have already been described in detail by Barton and Howlett.[3b] In the work with 1,1,1-trichloroethane it was found necessary to evacuate the reactor using a 2-stage mercury vapor pump backed by the Hyvac oil-pump used previously. In this way the pressure in the reactor was reduced to about 10^{-3} mm. A uniform period of ten minutes of evacuation before each run was adopted. This change in technique was required because a relatively non-volatile inhibitor is produced during the 1,1,1-trichloroethane decomposition. If the reactor is not properly evacuated the succeeding run is slower than usual and the reproducibility of results becomes very unsatisfactory. In this respect 1,1,1-trichloroethane is in strong contrast with 1,2-dichloroethane.[3b]

Results

In general[3] when a saturated chlorinated hydrocarbon is pyrolyzed in a clean-walled reactor the rate of decomposition is fast and heterogeneous.[3d] As the walls of the reactor become covered with a carbonaceous film the heterogeneous mechanism is suppressed, the rates of decomposition fall, and eventually reproducible results are attained.[13] These effects were also noted with 1,1,1-trichloroethane and all the results recorded below refer to experiments made after this initial period of irreproducibility.

Stoichiometry.—Although the decomposition of 1,1,1-trichloroethane was not studied from the stoichiometric point of view in an earlier paper,[3a] it would be expected[3] that the first stage would be represented by (A) and the much slower, second stage by (B). Figure 1 where the line is drawn at the theoretical slope of 45°, shows that

$$CH_3CCl_3 \longrightarrow CH_2{=}CCl_2 + HCl \qquad (A)$$
$$CH_2{=}CCl_2 \longrightarrow CH{\equiv}CCl + HCl \qquad (B)$$

the increase in pressure during the pyrolysis is a direct measure of the hydrogen chloride produced. The data refer to various temperatures between 640 and 685°K. and to various initial pressures in the range 35 to 120 mm. The percentage decomposition, assuming stoichiometry represented by (A), varied from 50 to 70%. These results are in agreement with (A) but do not, of course, exclude

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(1) This paper is Part VI in our series on "The Kinetics of the Dehydrochlorination of Substituted Hydrocarbons."

(2) Harvard University, Visiting Lecturer, 1949-1950.

(3) (a) Barton, *J. Chem. Soc.*, 148 (1949); (b) Barton and Howlett, *ibid.*, 155 (1949); (c) *ibid.*, 165 (1949); (d) Barton and Onyon, *Trans. Faraday Soc.*, **45**, 725 (1949); (e) Barton and Head, *ibid.*, in press.

(4) (a) The question of heterogeneous decomposition, which experimentally may be a complicating factor, is excluded in the present discussion. (b) A hydrogen atom must, of course, be attached to the adjacent carbon atom in *all* cases, and the four centers involved in the reaction must be free to assume a planar conformation.[3e]

(5) We are much indebted to Dr. K. C. D. Hickman of Distillation Products, Inc., for a generous supply of this compound.

(6) "International Critical Tables," Vol. III, p. 216.

(7) Turkevich and Smyth, THIS JOURNAL, **62**, 2468 (1940).

(8) Henne and Hubbard, *ibid.*, **58**, 404 (1936).

(9) Rubin, Levedahl and Yost, *ibid.*, **66**, 279 (1944).

(10) Van der Vloed, *Bull. soc. chim. Belg.*, **48**, 229 (1939).

(11) Perkin, *J. Chem. Soc.*, **45**, 531 (1884).

(12) (a) Maryott, Hobbs and Gross, THIS JOURNAL, **63**, 659 (1941); (b) Kohlrausch and Köppl, *Monatsh.*, **65**, 198 (1935); (c) Wiswall and Smyth, *J. Chem. Phys.*, **9**, 357 (1941).

(13) It is desirable to emphasize at this point that the pyrolytic decompositions studied in Part I of this series,[3a] using clean-walled reactors and no inducing agent, were undoubtedly heterogeneous reactions. Thus the rates of decomposition were much faster than for the corresponding homogeneous reactions in packed reactors,[3b,3c] and the non-exponential terms and activation energies in the relevant rate equations were both much lower[3d] than for the corresponding homogeneous processes.[3b,3c]

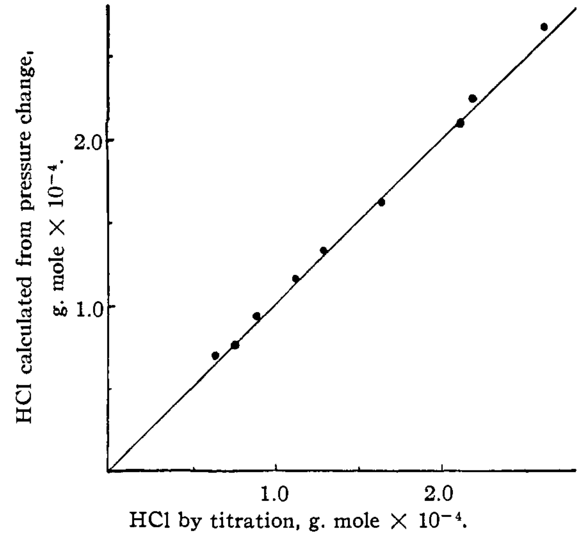

Fig. 1.

the participation of (B). However a separate experiment with vinylidene dichloride[14] ruled out this possibility: 61.7 mm. of vinylidene dichloride at 685°K. showed no pressure increase after fifteen minutes (> the half-life of 1,1,1-trichloroethane at this temperature).

A series of overnight (sixteen-hour) runs at various initial pressures in the range 30 to 90 mm., summarized in Fig. 2, showed that only at the lower temperatures was the final pressure that to be expected from the stoichiometry (A). The discrepancy at higher temperatures is presumably due to vinylidene dichloride decomposition as in (B).

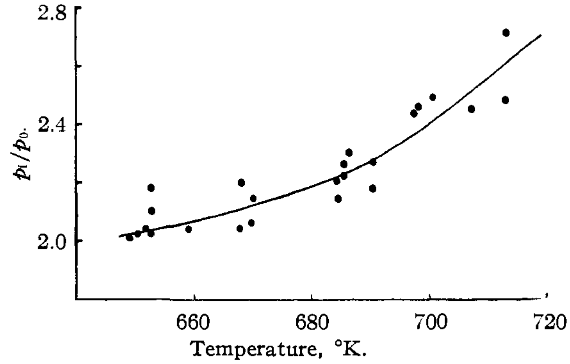

Fig. 2.—Plot of final (p_f) over initial (p_0) pressure against temperature.

Kinetics.—As usual[3] the course of the reaction was followed by the increase in pressure at constant volume. Two different Pyrex glass reactors were employed; one empty, the other packed with open glass tubing. The surface area:volume ratios were 2.72 and 9.98 cm.$^{-1}$, respectively. The over-all dimensions of the reactor were as described previously.[3b]

At 70–80 mm. initial pressure the over-all reaction followed first order kinetics only up to about 40% decomposition. Typical runs in the packed reactor are shown in Fig. 3. In all cases there were well-defined induction periods, which are also illustrated in Fig. 3.

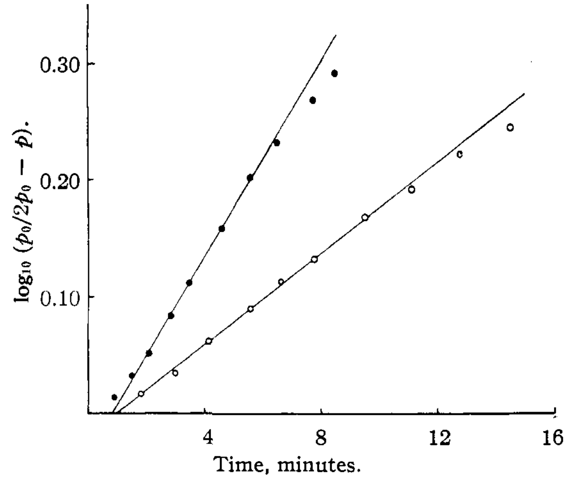

Fig. 3.—Plot of first order logarithmic function against time for the over-all reaction: —●— at 685.0°K.; —○— at 670.2°K.

In marked contrast to the decompositions studied previously in this series[3] the 1,1,1-trichloroethane pyrolysis showed a variation of first order velocity constant with initial pressure. This is illustrated in Fig. 4. Between 70 and 100 mm. initial pressures the velocity constants were nearly independent of initial pressure, but at lower pressures the variation was significant. *From now on, unless initial pressures are specifically mentioned, the data discussed are to be taken as referring to runs in the 70 to 80-mm. range.* A few runs were made in the empty reactor above 110 mm. initial pressure at 681.5°K. and are not shown in Fig. 4. They indicated (Table I) a slow increase in velocity constant with increase in initial pressure. The induction periods, which were less reproducible than the rate constants, were substantially independent of initial pressure (Fig. 4). If anything, there was a tendency for them to be longer at the lower pressures. The adherence to first order kinetics was better over the lower part of the initial pressure range. Thus at initial pressures over 100 mm. the obedience to first order kinetics

TABLE I

VARIATION OF VELOCITY CONSTANT WITH INITIAL PRESSURE

p_0, mm.	$k_0 \times 10^3$, sec.$^{-1}$
121.4	2.00
162.0	2.15
167.6	2.24
175.8	2.27

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[14] We are much indebted to Dr. H. M. Stanley of the Distillers' Co., Ltd., England, for a supply of monomeric vinylidene dichloride. This was stabilized by thymol, which was, of course, removed before making the experiments described in this paper.

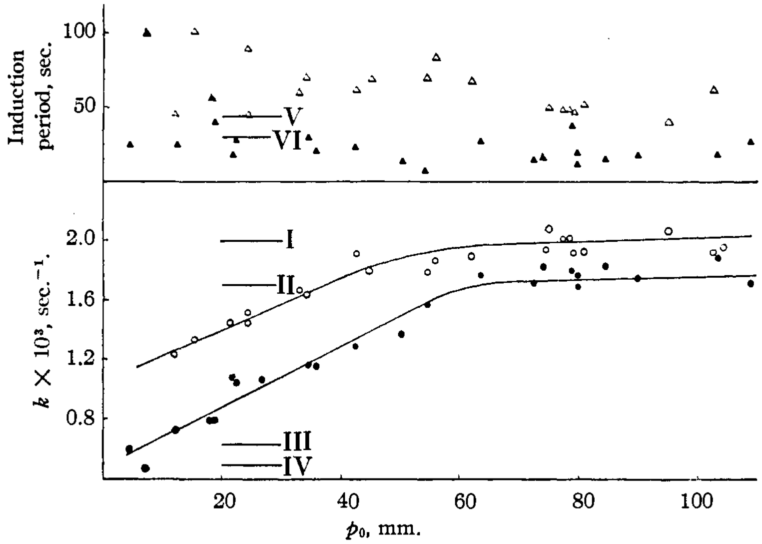

Fig. 4.—Variation of first order rate constant with initial pressure and (upper) corresponding variation of induction periods: —●— and ▲ for packed reactor at 684.0°K.; —○— and △ for empty reactor at 681.5°K. The short lines marked I (empty reactor) and II (packed reactor) represent k_0 calculated from the appropriate rate equation for the over-all reaction; those marked III (packed reactor) and IV (empty reactor) represent k_i calculated from the appropriate rate equation for the maximally inhibited reaction; those marked V (empty reactor) and VI (packed reactor) represent the induction periods of the over-all reaction calculated from the appropriate equation.

was only followed up to about 25% decomposition.

TABLE II

VARIATION OF VELOCITY CONSTANTS AND INDUCTION PERIODS WITH TEMPERATURE

Temp., °K.	No. of runs	Mean k_0, sec.$^{-1}$ × 10^3	% Mean error of mean k_0[a]	Mean I, sec.	% Mean error of mean I[a]
		Empty Reactor			
661.0	5	0.643	1.0	154	3.3
668.0	5	1.04	2.0	98	7.0
681.5	5	1.76	1.5	49	1.8
682.2[b]	4	1.84	1.4	48	4.9
682.0[b]	3	2.03	3.2	68	3.9
682.0[c]	2	2.17	..	..	..
696.0	4	4.25	1.9	22	12.1
696.5	2	4.41	..	19	..
		Packed Reactor			
635.7	2	0.122	..	321	..
650.0	4	.245	4.0	187	4.7
658.0	3	.407	3.4	111	6.8
670.0	5	.766	1.0	59	9.1
672.0	6	.96	2.1	62	7.2
675.0	3	1.03	4.1	53	..
681.0	6	1.48	2.3	39	3.5
688.5	5	2.23	1.5	26	14.6
698.5	9	3.85	1.5	13	8.1
707.0	3	5.24	4.9	12	..

[a] Calculated from the formula $100\sqrt{\Sigma(x-\bar{x})^2/n(n-1)}/\bar{x}$ where the symbols have the obvious significance. [b] Runs performed at the beginning of the series. [c] Runs performed at the end of the series.

With these features of the over-all reaction established the variation of velocity constant with temperature was studied. The results, together with the calculated error limits, are summarized in Table II and Fig. 5. The decomposition proceeded at a *faster* rate in the empty reactor than in the packed reactor (Table II and Fig. 5); the respective rate equations were

$$k_0 = 10^{13.34}e^{-50,000/RT} \text{ sec.}^{-1}$$

and

$$k_0 = 10^{13.21}e^{-50,000/RT} \text{ sec.}^{-1}$$

The latter equation only has been calculated by the least squares method giving the same statistical weight to *every* observation. Table II also summarizes the observed induction periods,[15] together with the corresponding error limits. The induction periods varied regularly with temperature and a plot of the $\log_{10}$ of the reciprocal of the mean induction period against the reciprocal of the absolute temperature gave a straight line (Fig. 6). The variation of the induction periods with temperature can, therefore, be summarized by the equations

$$\text{I (empty reactor)} = 10^{-14.4}e^{50,000/RT} \text{ sec.}$$

$$\text{I (packed reactor)} = 10^{-13.4}e^{46.500/RT} \text{ sec.}$$

The induction periods in the empty reactor were approximately 30% longer than in the packed reactor.

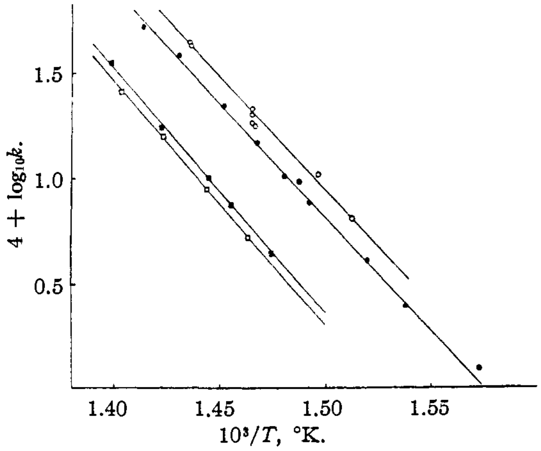

Fig. 5.—Variation of first order velocity constants with temperature: —●— for over-all rate in packed reactor; —○— for over-all rate in empty reactor; —◆— for maximally inhibited rate in packed reactor; —◇— for maximally inhibited rate in empty reactor.

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[15] The induction period (I) is defined (arbitrarily) as the intercept of the first order plot on the time axis. This definition also applies for 1,2-dichloroethane.[3b]

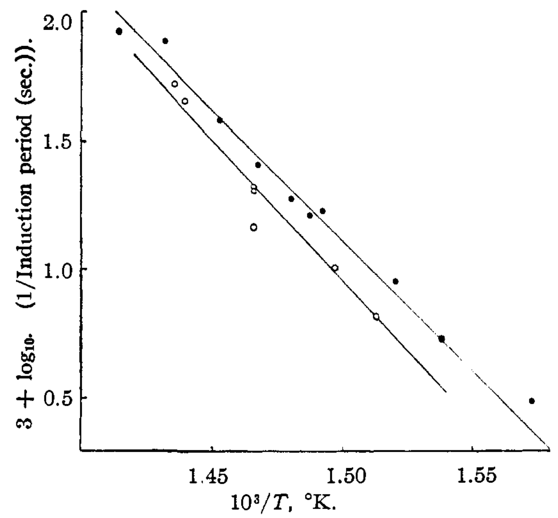

Fig. 6.—Variation of induction periods with temperature: —●— for packed reactor; —○— for empty reactor.

Effect of Vinylidene Dichloride.—The early deviation of the kinetics from first order suggested that the reaction products were exerting an inhibiting effect. It seemed unlikely that hydrogen chloride could be responsible and therefore attention was directed to the effects produced by added vinylidene dichloride. As the data in Table III indicate, the inhibition produced was approximately proportional to the amount of vinylidene dichloride added. As the amount of vinylidene dichloride added was increased the deviation from first order kinetics became more marked and with $p_0(CH_2{=}CCl_2)$ about 20 mm. the first order rate equation was only obeyed up to about 25% decomposition.

TABLE III[a]

VARIATION OF VELOCITY CONSTANT ON ADDITION OF VINYLIDENE DICHLORIDE

$p_0(CH_2{=}CCl_2)$, mm.	k_0'/k_0[b]	$(1 - k_0'/k_0)/p_0(CH_2{=}CCl_2)$, mm.$^{-1}$
12.0	0.86	0.012
13.6	.81	.014
14.0	.83	.012
14.2	.80	.014
20.5	.82	.009
21.5	.77	.011
21.5	.74	.012
21.8	.74	.012
23.0	.77	.010
28.0	.64	.013

[a] All experiments at 686.0°K. in the empty reactor. [b] k_0'/k_0 = first order velocity constant with added vinylidene dichloride over first order velocity constant calculated from appropriate rate equation.

In confirmation of the above experiments a number of runs were made in which a proportion of the reaction products from a previously completed run were left in the reactor. As Table IV indicates the extent of the inhibition produced by the reaction products, calculated on the basis of the vinylidene dichloride content, was of the same order as that observed with pure vinylidene dichloride (Table III). In these experiments deviations from first order kinetics were more pronounced than with the normal runs.

TABLE IV[a]

INHIBITING EFFECT OF REACTION PRODUCTS

Products left in from previous run, mm.	Calcd. $p_0(CH_2{=}CCl_2)$, mm.	k_0'/k_0	$(1 - k_0'/k_0)/p_0(CH_2{=}CCl_2)$, mm.$^{-1}$
25.0	11.5	0.83	0.015
25.7	11.7	.73	.023
27.8	12.8	.76	.019
32.7	14.3	.80	.014

[a] All experiments at 686.0°K. in the empty reactor.

Effect of Propylene.—Propylene is a powerful inhibitor[3b,3d] for those decompositions of saturated chlorinated hydrocarbons which proceed by a radical chain mechanism. The effect of propylene on the 1,1,1-trichloroethane pyrolysis was similar to its behavior with 1,2-dichloroethane, as illustrated in Fig. 7. The partially inhibited reactions followed first order kinetics to higher percentage decompositions than the uninhibited reaction. The maximally inhibited reactions followed first order kinetics up to at least 60% decompositions. The addition of propylene caused a progressive diminution (Fig. 8) in the length of the induction periods, until they disappeared altogether with the maximally inhibited reaction.

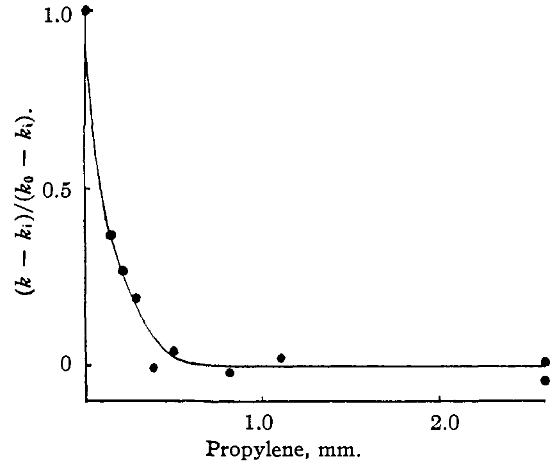

Fig. 7.—Effect of propylene on the 1,1,1-trichloroethane decomposition: k represents the observed first order rate constant, k_0 the rate constant for the over-all reaction (from the appropriate rate equation) and k_i the rate constant for the maximally inhibited reaction (also from the appropriate rate equation). All experiments in the packed reactor at 678.0°K. using initial pressures of 1,1,1-trichloroethane from 70 to 80 mm.

Unlike the over-all reaction, the maximally inhibited reaction showed no significant variation of first order velocity constant with initial pressure. This is illustrated by the data summarized

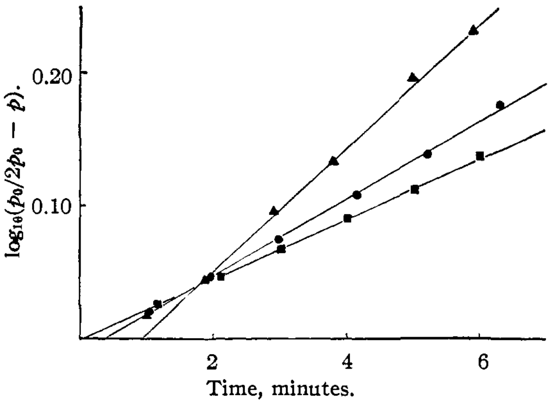

Fig. 8.—Plot of first order logarithmic function against time for partially inhibited decompositions: —▲— without propylene; —●— with 0.16 mm. propylene; —■— with 0.20 mm. propylene. All data for the packed reactor at 687.0°K. using an initial pressure of 1,1,1-trichloroethane of 70 to 80 mm.

in Fig. 9. A number of experiments at varying temperatures, which are summarized in Table V and in Fig. 5, enabled the rate equations again calculated, for the packed reactor, by the least squares method giving the same statistical weight to every run, to be obtained

$$k_i \text{ (empty reactor)} = 10^{14.07}e^{-54,200/RT} \text{ sec.}^{-1}$$
$$k_i \text{ (packed reactor)} = 10^{13.95}e^{-53,650/RT} \text{ sec.}^{-1}$$

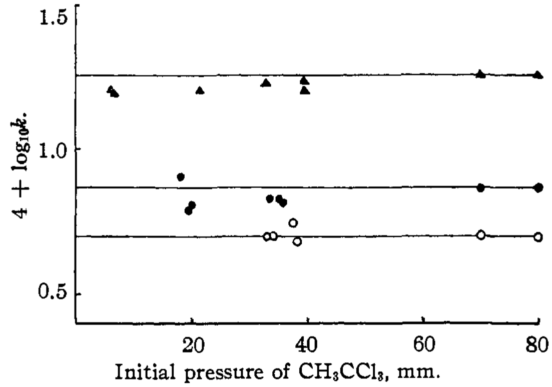

Fig. 9.—Plot of first order velocity constants for the maximally inhibited reaction against initial pressure of 1,1,1-trichloroethane.

Table V

Variation of Velocity Constants of Maximally Inhibited Reaction with Temperature

Temp., °K.	No. of runs	Mean k_i, sec.$^{-1}$ × 10^3	% Mean error of mean k_i
	Empty reactor		
683.3	4	0.523	2.1
692.5	3	0.892	...
702.5	4	1.58	2.2
712.5	3	2.52	...
	Packed reactor		
678.0	6	0.440	1.9
687.0	3	0.740	...
692.0	4	1.015	1.7
703.0	5	1.74	0.8
715.0	4	3.56	1.9

Thus at 695°K. the rate in the packed reactor was approximately 12.5% faster than in the empty reactor.

Since the over-all velocity constant varied rapidly with initial pressure below initial pressures of 70–80 mm., similar variation would be expected in the partially inhibited reactions. To some extent this is allowed for in the more complex function $(k - k_i)/(k_0 - k_i)$ used in Fig. 7 for expressing the results. Nevertheless this function also varied with the initial pressure of 1,1,1-trichloroethane as shown with the typical data summarized in Figs. 10 and 11.

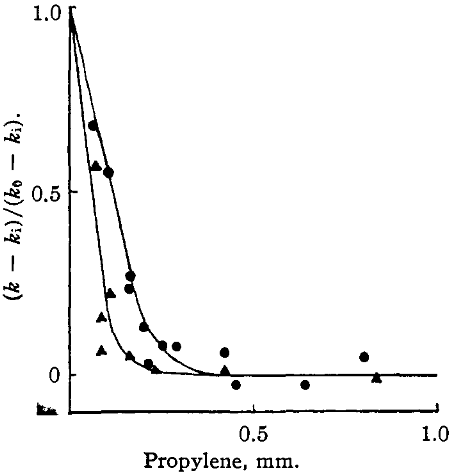

Fig. 10.—Effect of propylene on the 1,1,1-trichloroethane decomposition: —●— using 70–80 mm. initial pressures; —▲— using 35–40 mm. initial pressures. All experiments in the packed reactor at 687.0°K.

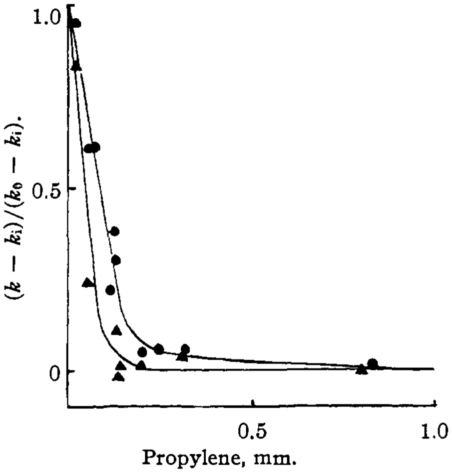

Fig. 11.—Effect of propylene on the 1,1,1-trichloroethane decomposition: —●— using 70–80 mm. initial pressures; —▲— using 35–40 mm. initial pressures. All experiments in the empty reactor at 682.0°K.

Discussion

As will be clear from the results detailed above the thermal decomposition of 1,1,1-trichloroethane is, from the mechanistic point of view, a reaction of considerable complexity. Over the temperature range studied the reaction proceeds by two simultaneously operating mechanisms, one of which is suppressible by the addition of propylene, the other not. It is convenient to consider the latter first.

The maximally inhibited reaction shows good obedience to first order kinetics. There is no variation of the velocity constant with initial pressure and there is no indication of any induction periods even at the lowest temperature studied. The maximally inhibited reaction is substantially homogeneous. The non-exponential term of the relevant rate equation is within a power of ten of 10^{13}, the value usually accepted as normal for unimolecular reactions.[3e] All these experimental features are identical with those established previously for ethyl chloride,[3c] 1,1-dichloroethane,[3c] *t*-butyl chloride,[3d] 2-chloropropane[3e] and 1,2-dichloropropane,[3e] and we regard them as proving that the maximally inhibited reaction is unimolecular in mechanism.

The rate equation for the mechanism of decomposition which is suppressible by propylene can be calculated by subtracting the rate constant for the maximally inhibited reaction from that for the over-all reaction.[16,17] The data thus obtained are summarized in Fig. 12. The relevant rate equations, calculated by the least squares method, are

$$(k_0 - k_i) = k_c = 10^{12.53}e^{-47,900/RT} \text{ sec.}^{-1}$$

in the empty reactor and

$$(k_0 - k_i) = k_c = 10^{12.51}e^{-48,400/RT} \text{ sec.}^{-1}$$

in the packed reactor, where k_0 is the velocity constant of the over-all reaction, k_i that of the maximally inhibited reaction and k_c that of the suppressible (radical chain) mechanism of decomposition.

The ease with which less than 1 mm. of propylene completely inhibits the decomposition of very much larger amounts of 1,1,1-trichloroethane, the fact that the reaction is *slower* in the packed than in the empty reactor, and the characteristic temperature dependent induction periods are a proof[3b,3d] that the suppressible non-unimolecular part of the decomposition must have a radical chain mechanism.

In discussing the more detailed mechanism of the 1,1,1-trichloroethane decomposition, it is convenient to treat the chain part of the reaction under these headings: (I) initiation, (II) propagation and (III) termination.

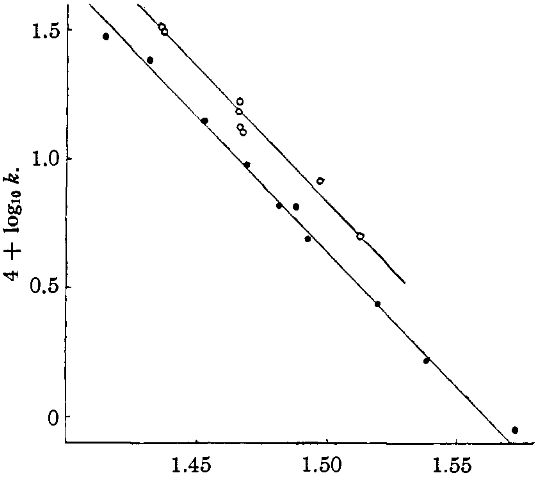

Fig. 12.—Variation of the rate constant of the chain type decomposition with temperature: —●— in packed reactor; —O— in empty reactor. All data for initial pressures of 1,1,1-trichloroethane from 70 to 80 mm.

(I). The Initiation Process.—There are only three obvious ways in which a chain reaction could be initiated in 1,1,1-trichloroethane.

$$CH_3CCl_3 \xrightarrow{k_1} CH_3CCl_2 + Cl \qquad (a)$$

$$CH_3CCl_3 \xrightarrow{k_1} CH_3 + CCl_3 \qquad (b)$$

$$CH_3CCl_3 \xrightarrow{k_1} CH_2CCl_3 + H \qquad (c)$$

Of these (c) can be excluded on energetic grounds.[18] If the succeeding reactions of the methyl and trichloromethyl radicals produced in (b) are as indicated below.

$$CH_3 + CH_3CCl_3 \longrightarrow CH_4 + CH_2CCl_3$$

and

$$CCl_3 + CH_3CCl_3 \longrightarrow CHCl_3 + CH_2CCl_3$$

followed by $CH_2CCl_3 \rightarrow CH_2{=}CCl_2 + Cl$, then it is not possible, without further evidence, to distinguish between (a) and (b).[19]

II. The Propagation Process.—The stoichiometry of the reaction makes it certain that the chain propagation steps must be represented by

$$Cl + CH_3CCl_3 \xrightarrow{k_2} HCl + CH_2CCl_3 \qquad (a)$$

and

$$CH_2CCl_3 \xrightarrow{k_3} CH_2{=}CCl_2 + Cl \qquad (b)$$

III. The Termination Process.—In general[3d] the termination process in the chain decomposi-

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(16) In theory a composite reaction involving two or more reactions of different activation energy should not give a straight line Arrhenius plot. It happens, however, in this case, that (Fig. 5) the sum of the velocity constants for the maximally inhibited reaction and for the competitive chain reaction give a plot of such slight curvature that there would be no possibility of detecting it experimentally.

(17) The treatment of the experimental data is justified only if both the maximally inhibited reaction and the competitive chain reaction are of the first order.

(18) Thus the calculated activation energies for the three processes, assuming zero activation energy for the reverse reaction and with no allowance for substitution as compared with ethane and ethyl chloride, are (a) 80 kcal. (b) 85 kcal. and (c) 97 kcal. (Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., 1946, p. 73 ff.).

(19) In so far as the fate of the CH_3CCl_2 radical is not adequately explained otherwise, the initiation process (b) seems preferable.

tions of saturated chlorinated hydrocarbons comprises interaction between a chlorine atom and the "large" chlorine containing radical. In the case of 1,1,1-trichloroethane this would imply

$$CH_2CCl_3 + Cl \longrightarrow \text{products}$$

Now the 1,1,1-trichloroethane decomposition is peculiar in two respects. Firstly, the radical mechanism rate is about 55% faster in the *empty* than in the packed reactor and, secondly, the rate constant varies with initial pressure, especially below 70 mm. Both these facts are best explained if the termination process occurs partly homogeneously and partly heterogeneously. Lowering the initial pressure would favor the latter and thus decrease the rate constant, but above a certain pressure most of the chains would end in the gas phase and thus the rate constant would tend to remain pressure invariant. This theory can be placed on a quantitative basis. Let the two competing termination processes be

$$CH_2CCl_3 + Cl\ (\text{wall}) \xrightarrow{k_4} \text{products} \qquad (a)$$

and

$$CH_2CCl_3 + Cl\ (\text{homogeneously}) \xrightarrow{k_4''} \text{products} \quad (b)$$

Then application of the stationary state method using equations I(a), (II)(a), II(b), (III)(a) and III(b) leads to the expression

$$\frac{-\mathrm{d}\ [CH_3CCl_3]}{\mathrm{d}t} = [CH_3CCl_3] \left(\frac{k_1k_2k_3}{2(k_4 + k_4'')}\right)^{1/2}$$

If I(b) were taken as the initiating step then the factor 2 in the denominator of the above equation would be deleted. The general treatment[20] of chain reactions, where the termination process involves combination of radicals on the walls, assumes that the Einstein–Smoluchowski relationship (or its equivalent) is applicable and that the rate of the total reaction varies as the product of the squares of the reactor diameter and reactant pressure. In the particular case of 1,1,1-trichloroethane it is a reasonable assumption that k_4 varies *inversely* as this product. As far as initial pressures (p_0) are concerned this can be expressed by writing $k_4 = k_4'/p_0^2$, where k_4' is a constant independent of p_0.[21]

Taking the first order velocity constant of the over-all reaction as representing the initial stages of decomposition, where vinylidene dichloride inhibition is not serious, we have

$$k_0 = k_i + k_c = k_i + \left(\frac{k_1k_2k_3}{2k_4'}\right)^{1/2} \Big/ \left(\frac{1}{p_0^2} + \frac{k_4''}{k_4'}\right)^{1/2} = k_i + C_1 \Big/ \left(\frac{1}{p_0^2} + C_2\right)^{1/2}$$

If suitable values of C_1 and C_2 (Table VI) are taken, then a very close fit to the experimental data of Fig. 5, for both packed and empty reactors, is obtained. This is shown by comparison of calculated and observed k_0 values (Table VI), the data for k_i being taken from the relevant rate equations.

TABLE VI

Empty reactor, T = 681.5°K. C_1 = 5.0 × 10^{-5}, sec.$^{-1}$: C_2 = 9.0 × 10^{-4}				Packed reactor, T = 684.0°K. C_1 = 1.87 × 10^{-5} sec.$^{-1}$: C_2 = 1.4 × 10^{-4}			
p_0, mm.	k_c, sec.$^{-1}$ × 10^3 calcd.	$k_0 = k_i + k_c$, sec.$^{-1}$ × 10^3 Calcd.	Obsd.	p_0, mm.	k_c, sec.$^{-1}$ × 10^3 calcd.	$k_0 = k_i + k_c$, sec.$^{-1}$ × 10^3 Calcd.	Obsd.
10	0.48	0.95	1.22	10	0.19	0.82	0.68
20	0.86	1.33	1.40	20	.36	0.99	0.88
30	1.11	1.58	1.57	30	.54	1.17	1.08
50	1.37	1.84	1.88	50	.81	1.44	1.49
70	1.51	1.98	1.98	70	1.02	1.65	1.72
80	1.53	2.00	1.99	80	1.09	1.72	1.74
90	1.56	2.03	2.01	90	1.16	1.79	1.75
110	1.57	2.04	2.05	110	1.21	1.84	1.77
200	1.63	2.10	2.30[a]	200	1.42	2.05	2.10[a]

[a] Extrapolated.

That our interpretation of the experimental results is substantially correct can be checked in the following way. Since

$$C_1^2/C_2 = k_1k_2k_3/2k_4''$$

an expression involving the velocity constants of homogeneous reactions only, it should be the same for both empty and packed reactors. The values of C_1^2/C_2 are 2.78 × 10^{-6} and 2.50 × 10^{-6} sec.$^{-2}$, respectively, in agreement with theory. The values of C_1 and C_2 provide two independent methods of calculating k_4' (packed reactor)/k_4' (empty reactor). The values obtained, 6.4 and 7.2, are in good agreement. According to the argument given above k_4' is inversely proportional to the square of the reactor diameter. The mean ratio of d(empty reactor):d(packed reactor) calculated in this way is 2.6. This is in agreement with the surface area:volume ratios in the two reactors, which are 9.98 cm.$^{-1}$ and 2.72 cm.$^{-1}$, a ratio of 3.7. The method of packing adopted (see Results section) is such that 3.7 is an upper limit to the ratio of the two effective diameters.

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Summary

1,1,1-Trichloroethane decomposes in the temperature range 635.7 to 707.0°K. to give vinylidene dichloride and hydrogen chloride. The decomposition proceeds by a unimolecular and by a radical chain mechanism, both of which occur simultaneously. The chain process involves 2,2,2-trichloroethyl radicals and chlorine atoms, and, in the empty reactor, represents in the initial stages of decomposition about 75% of the total rate.

The homogeneous unimolecular mechanism obeys first order kinetics and the rate constant, which is independent of initial pressure, can be represented by $10^{14}e^{-54,000/RT}$ sec.$^{-1}$.

The radical chain mechanism follows first order

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[20] Semenoff, "Chemical Kinetics and Chain Reactions," Oxford University Press, 1935, p. 23 ff.

[21] Since only the initial stages of decomposition are involved, it is convenient to take p_0 instead of the total pressure.

kinetics only over the initial stages of the decomposition. This is because the vinylidene dichloride produced partially inhibits the reaction. The velocity constant falls off at initial pressures below 70 mm., but increases only slowly at initial pressures above this. In the 70 to 80 mm. range it can be represented by $10^{12.53}\, e^{-47,900/RT}$ sec.$^{-1}$ in the empty reactor. The radical chain mode of decomposition is completely suppressed by small additions of propylene and is decreased by packing.

All the facts with regard to the radical chain mechanism can be explained quantitatively in terms of a chain termination process involving CH_2CCl_3 and Cl, which occurs either in the gas phase or on the walls of the reactor.

The radical chain mechanism exhibits well defined induction periods which, in the empty reactor, can be represented by the equation $I = 10^{-14.4} e^{50,000/RT}$ sec. These are independent of initial pressure and only slightly dependent on packing. The unimolecular mechanism does not show induction periods.

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Meta Rearrangement in the Reaction of Triphenyl-(*p*-bromophenyl)-silane with Lithium Dimethylamide

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In earlier communications it has been reported that *o*- and *p*-haloanisoles and related types undergo rearrangement reactions with metal amides in liquid ammonia and with lithium dialkylamides in ether to yield *m*-amino- and *m*-dialkylaminoanisoles, respectively.[1] It has also been observed that α-halonaphthalenes form β-dialkylaminonaphthalenes in their reaction with lithium dialkylamides in ether,[2] and β-aminonaphthalene is obtained when these halogen compounds are treated with metal amides in liquid ammonia.[3] When sulfur-containing compounds were investigated, *o*-halophenyl methyl sulfides and *o*-bromophenyl methyl sulfone were found to react with metal amides in liquid ammonia to yield *m*-amino derivatives.[4]

$$p\text{-}BrC_6H_4OCH_3 + LiN(C_2H_5)_2 \longrightarrow m\text{-}(C_2H_5)_2NC_6H_4OCH_3 + LiBr$$

During the course of our investigations of organosilicon compounds, triphenyl-(*p*-bromophenyl)-silane was treated with lithium dimethylamide in ether, and in a benzene–ether mixture. The compound obtained was triphenyl-(*m*-dimethylaminophenyl)-silane.

$$(C_6H_5)_3SiC_6H_4Br\text{-}p + LiN(CH_3)_2 \longrightarrow (C_6H_5)_3SiC_6H_4N(CH_3)_2\text{-}m + LiBr$$

The product of this rearrangement reaction was identified through its synthesis in accordance with the scheme

$$(C_6H_5)_3SiCl + m\text{-}(CH_3)_2NC_6H_4Li \longrightarrow (C_6H_5)_3SiC_6H_4N(CH_3)_2\text{-}m + LiCl$$

Experimental

Triphenyl-(*p*-bromophenyl)-silane.—*p*-Bromophenyllithium[5] was prepared in ether by treating 13 g. (0.055 mole) of 1,4-dibromobenzene with 0.05 mole of *n*-butyllithium.[6] Color Test II-A[7] was negative immediately upon the conclusion of the addition of *n*-butyllithium. Then, 13.3 g. (0.045 mole) of triphenylchlorosilane dissolved in ether was added at such a rate as to maintain a gentle reflux, and a precipitate was promptly formed. After refluxing the mixture for one hour, it was hydrolyzed with 1:3 hydrochloric acid and most of the solid product settled at the ether-water interface. This material was collected on a filter. After the ether layer was separated and dried, the solvent was removed by distillation and a small quantity of solid remained. The total product was dissolved in the minimum volume of hot benzene and 95% ethanol was added until the hot solution began to assume a cloudy appearance. After cooling the solution, the solid that precipitated was collected on a filter and dried in a vacuum desiccator over sulfuric acid. The yield of triphenyl-(*p*-bromophenyl)-silane, melting at 167–168°, was 14.5 g. (78%, based on the quantity of triphenylchlorosilane used).

Anal. Calcd. for $C_{24}H_{19}BrSi$: Br, 19.3; Si, 6.7. Found: Br, 19.2; Si, 6.7.

In two other preparations, the yields were 73 and 77%, respectively.

Triphenyl-(*p*-bromophenyl)-silane and Lithium Dimethylamide.—Lithium dimethylamide was prepared by passing dimethylamine through an ether solution containing 0.03 mole of *n*-butyllithium against a pressure of 2–3 cm. of mercury.[2] Color Test II-A[7] was negative at the end of the reaction and Color Test IV[8] was positive.

To the suspension of lithium dimethylamide was added 10 g. (0.024 mole) of solid triphenyl-(*p*-bromophenyl)-silane and the mixture was refluxed for thirty-six hours. The usual procedure was followed in working up the reaction, and a viscous oil which could not be resolved by crystallization was obtained. This material was then suspended in ether, in which some of the product was sol-

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[1] Gilman and Kyle, THIS JOURNAL, **70**, 3945 (1948). Earlier references may be traced from this citation.

[2] Gilman, Crounse, Massie, Benkeser and Spatz, *ibid.*, **67**, 2106 (1945).

[3] Urner and Bergstrom, *ibid.*, **67**, 2108 (1945).

[4] Martin, Doctoral Dissertation, Iowa State College, 1945.

[5] Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).

[6] *n*-Butyllithium was prepared in accordance with the recent directions of Gilman, Beel, Brannen, Bullock, Dunn and Miller, *ibid.*, **71**, 1499 (1949). The titer was determined by the double-titration method of Gilman and Haubein, *ibid.*, **66**, 1515 (1944).

[7] Gilman and Swiss, *ibid.*, **62**, 1847 (1940).

[8] Gilman and Woods, *ibid.*, **65**, 33 (1943).