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Mass Spectrometric Studies of Low Pressure Pyrolysis Reactions of Chlorinated and Fluorinated C₁ and C₂ Compounds on Graphite¹

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The pyrolysis behavior of chlorinated derivatives of methane, ethane and ethylene has been investigated in graphite ovens at pressures between 10⁻² and one mm. of Hg in the temperature range 450–1300°K. Several C₂ compounds studied transfer chlorine atoms from adjacent carbon atoms to the graphite surface. The pressure dependence of the yield of dechlorinated products indicated a first-order relationship between product and reactant. This is interpreted as evidence for the existence of an equilibrium reaction with graphite. Heats of reaction for the removal of two chlorine atoms from adjacent carbon atoms are found to vary between +12 and +25 kcal. The compound *sym*-tetrachloroethane pyrolyses to both *sym*-dichloroethylene and trichloroethylene, the latter by the elimination of HCl(g). The HCl elimination reactions are found to follow a more complex pressure dependence than those observed for dechlorination. Several fluoro-chloro C₁ and C₂ compounds also have been dehalogenated over graphite.

Introduction

A number of investigations of the pyrolysis of chlorine derivatives of methane and ethane have been quoted by Huntress.³ In general these studies have been concerned with the identification of new compounds as they exist in the condensed product resulting from the pyrolysis. The details of the pyrolysis occurring in the reaction chamber may not always be well defined since the products themselves may undergo further reaction on cooling.

A useful analytic technique is the direct mass spectrometric identification of the pyrolysis products as they are found in the reaction. The general limitation, however, is that gases cannot be injected at high pressures into the vacuum region of the mass spectrometer source. An advantage, on the other hand, of low pressure studies is that they offer a more thorough examination of the catalytic behavior of the reaction vessel. In this paper we will deal only with low pressure reactions in graphite ovens.

Experimental

Descriptions of the mass spectrometer and high temperature assembly for vaporization studies have been given

(1) Work supported by the Air Force Office of Scientific Research and the Advanced Research Projects Agency.

(2) (a) Air Research and Development Command, Research Associate, 1960–1961; (b) Alfred P. Sloan Fellow.

(3) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

earlier.⁴ The apparatus has been modified by enclosing the effusion cell in a chamber which permits differential pumping between the high temperature assembly and the ion source of the mass spectrometer. This arrangement is demonstrated in Fig. 1. A 3-mm. orifice in the top of the isolating chamber permits a beam of gas to flow directly from the reaction cell to the ion source at pressures of 10⁻⁶ mm. or lower. The graphite reaction vessel is connected by means of a stainless steel tube to the external gas handling system. A cross section of the graphite oven is reproduced in Fig. 2. The upper section is heated directly by radiation and electron bombardment from a helical tungsten filament. The long narrow neck on the cell serves to minimize heat transfer to the lower section. Several pieces of graphite were included in the upper chamber to provide a large surface area for reaction and to ensure that the gases attained the temperature of the cell. The temperature of the upper chamber was measured with a Pt–Pt,Rh thermocouple which was fastened to the side of the reaction cell. The area of the cell orifice (1 mm.²) is less than one thousandth that of the apparent internal area of the upper cell chamber. Under these conditions effusion by Knudsen flow is realized. Electrolytic-type graphite was used throughout.

Leak rates were controlled to maintain the cell pressures between 10⁻² and one mm. The cell pressure was estimated by calibrating with CCl₄ vapor in equilibrium with solid CCl₄ maintained at the Dry Ice–acetone temperature and observing the intensity of the CCl₄⁺ ion beam as a function of ionizing electron energy. As the temperature of the cell was raised the gas pressure dropped below its initial inlet value. This probably results from increased impedance due to thermal expansion of the furnace assembly.

Each new graphite oven installed in the mass spectrometer was cleaned by heating to 700–800° for about 2 hr. with subsequent heating to between 1000 and 1200° for 1 hr.

(4) R. F. Porter and R. C. Schoonmaker, *J. Phys. Chem.*, **62**, 234 (1958).

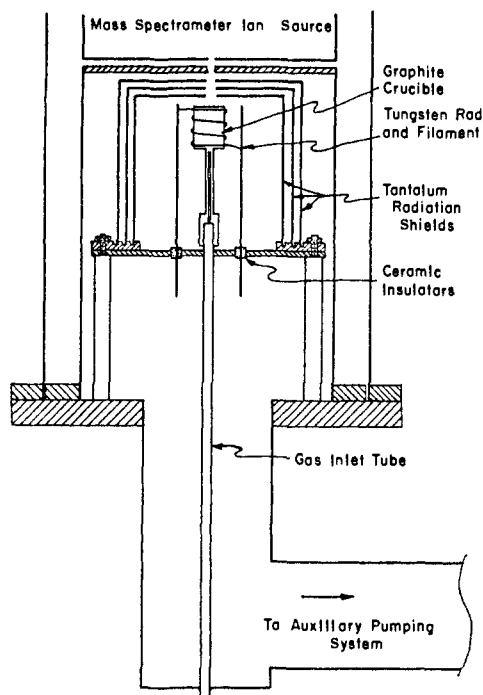


Fig. 1.—Pyrolysis assembly.

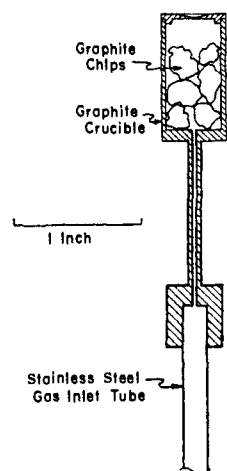
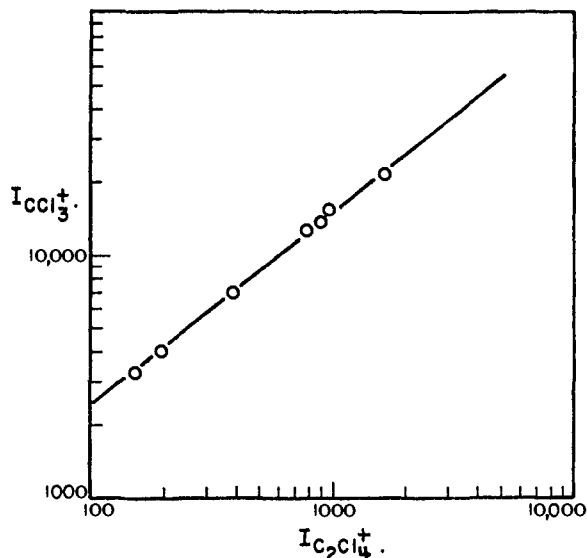
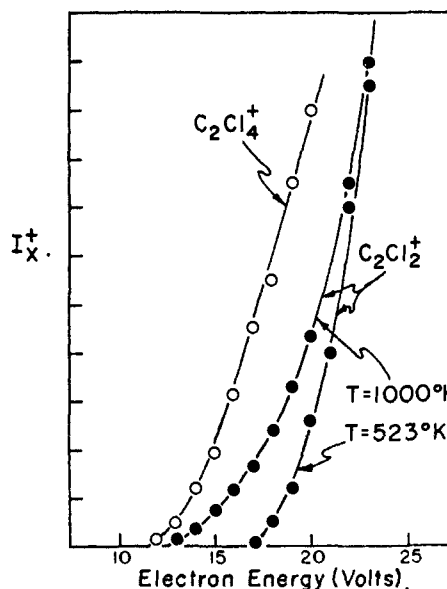


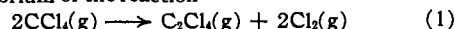
Fig. 2.—Graphite cell for pyrolysis reactions.

The purity of the materials employed was determined by running their mass spectra with the reaction chamber cold. The CCl_4 and C_2Cl_4 were Mallinckrodt Reagent Grade Chemicals. The C_2Cl_4 was redistilled. The $\text{CH}_3\text{-CCl}_3$ was Fisher Reagent Grade Material. The C_2HCl_3 , $\text{CHCl}_2\text{-CHCl}_2$, $\text{CF}_3\text{-CCl}_3$, CFCl_2 , $\text{CFCl}_2\text{-CFCl}_2$, $\text{CF}_2\text{=CCl}_2$ and CFCl=CFCl were kindly provided by Dr. W. T. Miller and Dr. A. C. Currie of the Chemistry Department of Cornell University. The $\text{CF}_2\text{Cl-CF}_2\text{Cl}$ was purchased from the Matheson Company and was purified by successive distillations from one cold trap to another in a vacuum system.

CCl_4 and C_2Cl_4 .—The pyrolysis of carbon tetrachloride at pressures higher than those attainable in an effusion cell has been studied by several investigators.⁵⁻⁷ The major products are known to be tetrachloroethylene, hexachloroethane and, to a lesser extent, hexachlorobenzene. In the present work, at temperatures above 500° , the major ionic species found by mass analysis were C_2Cl_4^+ , Cl_2^+ (from Cl_2) and CCl_2^+ which is the major ion fragment from CCl_4 . At temperatures around 600° C_2Cl_3^+ also began to appear

(5) C. G. Fink and C. F. Bonilla, *J. Phys. Chem.*, **37**, 1141 (1933).(6) H. B. Weiser and G. E. Wightman, *ibid.*, **23**, 415 (1919).(7) W. Lüb, *Z. Elektrochem.*, **7**, 903 (1901).Fig. 3.—Pressure dependence of $\text{C}_2\text{Cl}_4(\text{C}_2\text{Cl}_4^+)$ on $\text{CCl}_4(\text{CCl}_4^+)$; electron energy = 20 volts; $T = 800^\circ\text{K}$; pressure range 0.1 to 1 mm.Fig. 4.—Appearance potential curves for C_2Cl_3^+ and C_2Cl_4^+ showing second threshold for C_2Cl_3^+ at high cell temperatures.

in the mass spectra. The pressure dependence of $\text{C}_2\text{Cl}_4(\text{g})$ on CCl_4 is shown in Fig. 3 where the intensities of CCl_4^+ and C_2Cl_4^+ are taken as proportional to the pressures of CCl_4 and C_2Cl_4 , respectively. This line has a slope of 0.8 which is interpreted to indicate a first-order pressure relationship. The pressure of Cl_2 as indicated by the Cl_2^+ current was directly proportional to the C_2Cl_4^+ current from C_2Cl_4 . At 750° the $\text{Cl}_2^+/\text{C}_2\text{Cl}_4^+$ ratio varied between about 0.81 and 0.74 for an ionizing electron energy of 20 volts while the absolute intensities of Cl_2^+ and C_2Cl_4^+ changed by a factor over ten. On the basis of the preceding observations it is not possible to interpret the data in terms of the gas phase equilibrium of the reaction



The pressure dependence curve for this equilibrium has a theoretical slope of 1.5 which is well outside of the limits of reproducibility.

Consideration of a plausible mechanism for the pyrolysis of CCl_4 will be given in the discussion on the basis of subsequent observations with chlorinated ethanes.

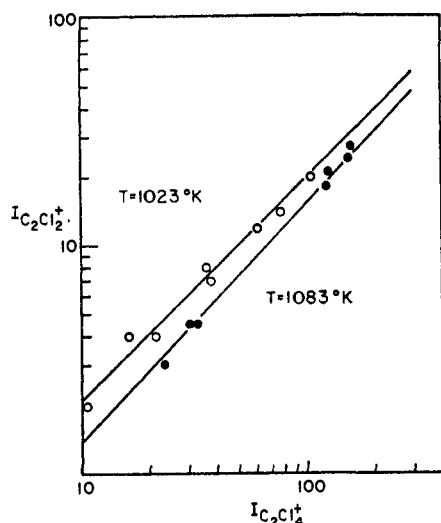
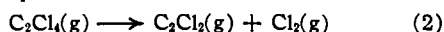


Fig. 5.—Pressure dependence of $C_2Cl_2(C_2Cl_2^+)$ on $C_2Cl_4(C_2Cl_4^+)$; upper curve obtained with CCl_4 as flow gas; lower curve obtained with C_2Cl_4 as flow gas. Ionizing electron energy = 15 volts; pressure range 0.025 to 0.25 mm.

At temperatures above 600° the $C_2Cl_2/C_2Cl_4^+$ ratio was found to increase with temperature. The same effect was observed when C_2Cl_4 was introduced through the leak. Appearance potential measurements for $C_2Cl_2^+$ in Fig. 4 show that $C_2Cl_2^+$ is formed by two processes. At high temperatures, $C_2Cl_2^+$ has an ionization threshold about 5 volts below that observed when the C_2Cl_4 sample was below 600° . This indicates that ion fragmentation of $C_2Cl_4(g)$ to form $C_2Cl_2^+$ is negligible at electron energies below 15 volts. The high temperature threshold for $C_2Cl_2^+$ is interpreted to indicate that a molecular species $C_2Cl_2(g)$ having a low appearance potential is produced by a high temperature reaction. It was thus imperative to compare $C_2Cl_2^+$ and $C_2Cl_4^+$ currents at electron energies of 15 volts or lower to eliminate ion fragmentation as a source of $C_2Cl_2^+$. The observed pressure dependence of C_2Cl_2 on C_2Cl_4 is shown in Fig. 5. Pressure data were obtained with CCl_4 and C_2Cl_4 as the flow gases. A simple first-order pressure dependence was observed in both cases (Fig. 5). Thus, chlorine gas, a by-product from the CCl_4 pyrolysis, had no discernible effect on the pressure dependence. This indicates that the pyrolysis of C_2Cl_4 in a graphite oven does not follow the simple gas phase reaction



This is also supported by the striking fact that Cl_2 was *not* observed as a product in the direct pyrolysis of C_2Cl_4 . A feasible interpretation of these results is that $C_2Cl_2(g)$ is generated by a surface reaction.

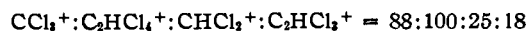


The only observable product beside C_2Cl_2 with C_2Cl_4 as the inlet gas was $HCl(g)$. It thus appears that surface chlorine was removed by a reaction involving hydrogen present in the graphite.

A plot of $\log(I_{C_2Cl_2^+}/I_{C_2Cl_4^+})$ which is proportional to $\log K_{eq}$ for reaction 3 is shown in Fig. 6. The slope of the curve can be seen to flatten off at highest temperatures. This effect is not clearly understood, although it may be due to the competing reaction of graphite that removes chlorine atoms from C_2Cl_2 .

The slope of the curve in the lower temperature range was reproducible and gave a heat of reaction of $+16.0 \pm 3.0$ kcal. This implies that the transfer of two chlorine atoms from C_2Cl_4 to the carbon surface is endothermic.

$CHCl_2-CCl_2$.—Mass spectra with $CHCl_2-CCl_2$ as reactant were obtained as a function of leak rate and cell temperature. The ion fragments from cold $CHCl_2-CCl_2$ were



for an ionizing electron energy of 20 volts. At high temperatures $C_2HCl_3^+$ became the ion of highest intensity.

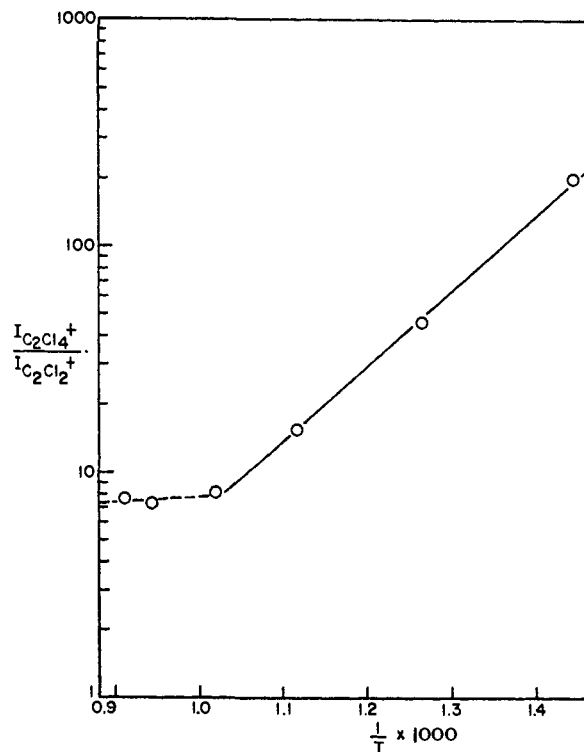
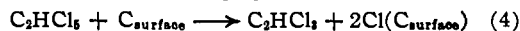


Fig. 6.—Temperature dependence of $C_2Cl_2(C_2Cl_2^+)$ on $C_2Cl_4(C_2Cl_4^+)$; electron energy = 15 volts; pressure range 0.3 to 0.8 mm.

This is interpreted as the ionization of $CHCl=CCl_2$ which is formed by the transfer of chlorine atoms from adjacent carbon atoms of the reactant to the hot graphite surface. The yield of C_2HCl_3 increased with temperature as indicated in Fig. 7 where $C_2HCl_4^+$ is used as a measure of the C_2HCl_3 pressure. In addition to $C_2HCl_3^+$ an ion current of $C_2Cl_4^+$ due to C_2Cl_4 was observed. The intensity of this $C_2Cl_4^+$ current, however, was insensitive to large variations in temperature, and it was therefore concluded that its presence is probably due to an impurity. Some elimination of HCl to give C_2Cl_2 cannot, however, be excluded. As in the case of the C_2Cl_4 reaction, no evidence for the formation of $Cl_2(g)$ was found. This suggests that the removal of chlorine atoms was occurring by a surface reaction similar to that for C_2Cl_4



The temperature dependence of this reaction (Fig. 7) gives $\Delta H = 21.0 \pm 3.0$ kcal.

$CHCl_2-CHCl_2$.—The mass spectrum of cold $CHCl_2-CHCl_2$ gave ion currents of $C_2H_2Cl_3^+ : CHCl_2^+ : C_2H_2Cl_2^+ : C_2HCl_3^+ = 9:100:7:3$ for 20 volt electrons. At high temperatures ion currents of $C_2H_2Cl_2^+$ and $C_2HCl_3^+$ became intense relative to $CHCl_2^+$ which was used as a measure of the $CHCl_2-CHCl_2$ pressure. The species $C_2H_2Cl_2^+$ and $C_2HCl_3^+$ are due to ionization of $CHCl=CHCl$ and $CHCl=CCl_2$, respectively. Under conditions where the pyrolysis is essentially complete, *i.e.*, above 1000° , the mass spectrum observed for $CHCl=CHCl$ agrees well with the reported spectrum for dichloroethylene.⁸ The temperature dependence of this system is shown in Fig. 8. As illustrated, the yield of $CHCl=CCl_2$ is more temperature dependent than that of $CHCl=CHCl$. The heat of reaction for the production of $CHCl=CHCl$ is $\Delta H = 14.2 \pm 3.0$ kcal. We do not attach quantitative significance to the temperature dependence of the $CHCl=CCl_2$ generation shown in Fig. 8. We comment later that the HCl elimination in $CH_2=CCl_2$ is too complex to be accounted for by a simple reaction eliminating HCl by surface adsorption.

$CH_2=CCl_2$.—Investigation of $CH_2=CCl_2$ appeared useful since one would assume that chlorine atoms would not be

(8) "Mass Spectral Data," American Petroleum Institute Research Project 44, National Bureau of Standards, Washington, D. C.

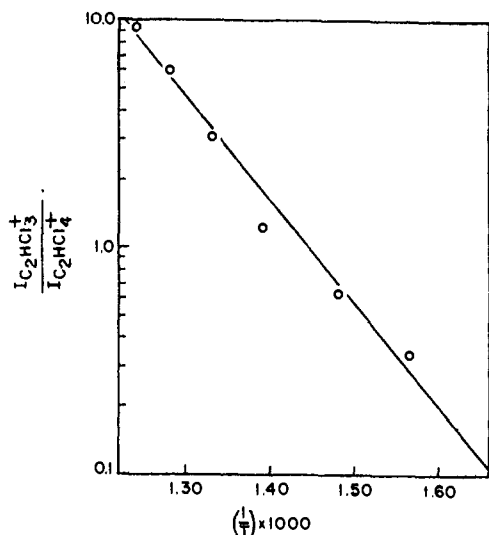


Fig. 7.—Temperature dependence of $C_2HCl_3(C_2HCl_3^+)$ on $C_2HCl_4(C_2HCl_4^+)$; electron energy = 20 volts; pressure range 0.07 to 1.0 mm.

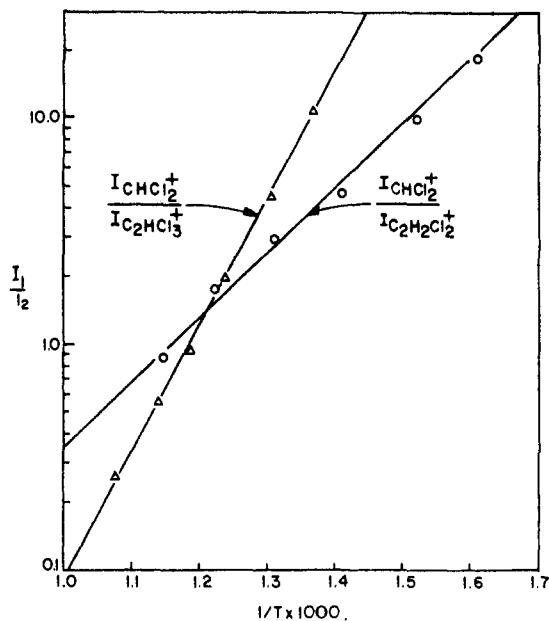


Fig. 8.—Temperature dependence of $C_2HCl_3(C_2HCl_3^+)$ on $CHCl_2-CHCl_2(CHCl_2^+)$ and $CHCl=CHCl(C_2H_2Cl_2^+)$ on $CHCl_2-CHCl_2(CHCl_2^+)$; electron energy = 20 volts; pressure range 0.09 to 1.2 mm.

removed by the surface reaction. The mass spectrum of cold CH_2-CCl_3 gave major ion currents in the ratio $C_2H_3-Cl_2^+ : CCl_3^+ : C_2H_2Cl_2^+ = 100:21:0$ at 20 electron volts. At high temperatures the current of $C_2H_2Cl_2^+$ increased relative to $C_2H_3Cl_2^+$ as indicated in Fig. 9. The appearance of $C_2H_2Cl_2^+$ is due to ionization of $CH_2=CCl_2$ which is produced in the oven at high temperatures. The pressure dependence of $C_2H_2Cl_2$ on $C_2H_3Cl_3$ is illustrated in Fig. 10, where the observed currents $C_2H_2Cl_2^+$ and $C_2H_3Cl_3^+$ are considered to be proportional to pressures of their respective gases. The experimental data give a slope of approximately 1.8 which implies a second-order pressure relationship of the reactant to the product. This is understandable if we assume that the $HCl(g)$ as split from the reactant molecule is not strongly chemically absorbed on the surface and may effect reversal of the reaction. This is also consistent with the observation of a high $HCl(g)$ concentration as indicated by an intense HCl^+ current.

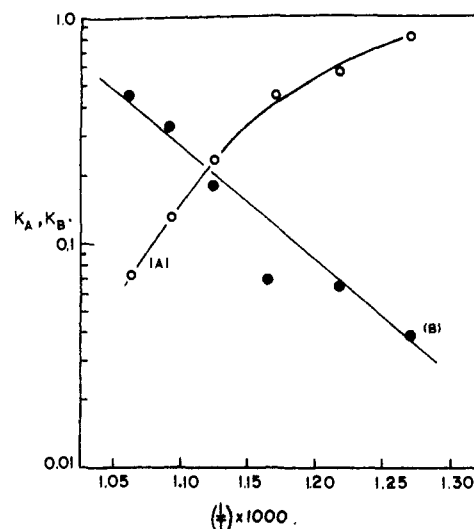


Fig. 9.—(A) Temperature dependence of $CH_2=CCl_2(C_2H_2Cl_2^+)$ on $CH_3-CCl_3(C_2H_3Cl_3^+)$; electron energy = 20 volts; pressure range 0.12 to 0.25 mm. (B) Temperature dependence of relative K_{eq} for $C_2H_3Cl_3(g) \rightleftharpoons C_2H_2Cl_2(g) + HCl(g)$. $K_A = I_{C_2H_3Cl_3^+}/I_{C_2H_2Cl_2^+}$; $K_B = (\text{constant}) T (I_{C_2H_2Cl_2^+})^2/I_{C_2H_3Cl_3^+}$.

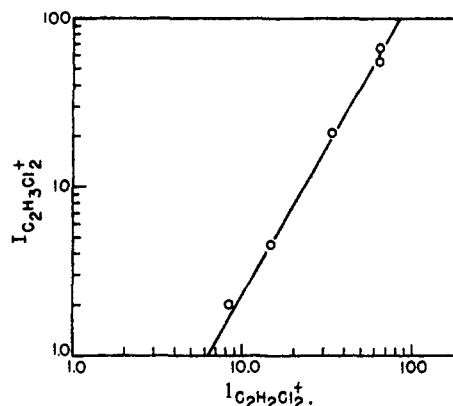
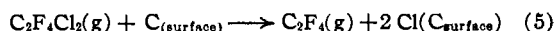


Fig. 10.—Pressure dependence of $CH=CCl_2(C_2H_2Cl_2^+)$ on $CH_3-CCl_3(C_2H_3Cl_3^+)$; $T = 740^\circ K.$, electron energy = 20 volts; pressure range 0.10 to 0.70 mm.

Taking I_{HCl^+} proportional to $I_{C_2H_3Cl_3^+}$, a plot of $\log T(I_{C_2H_3Cl_3^+})^2/(I_{C_2H_2Cl_2^+})$ vs. $1/T$ may be used to evaluate the enthalpy of reaction for the elimination of one mole of $HCl(g)$. A plot of this (Fig. 9) shows a reasonable linear relationship. Omitting the point of maximum deviation, we obtain for the reaction $\Delta H = +23.6 \pm 2.5$ kcal./mole.

Chloro-fluoroethanes: CF_2Cl-CF_2Cl .—It was of interest to examine the pyrolysis behavior of some of the fluorine-chlorine analogs of the chlorinated hydrocarbons discussed above. The mass spectrum of cold CF_2Cl-CF_2Cl gave major peaks in the intensity ratio $CF_2Cl^+ : C_2F_4Cl^+ : C_2F_4^+ = 100:49:1$ for 20 volt electrons. The intensity of the mass 100 peak ($C_2F_4^+$) was observed to increase at high temperatures relative to $C_2F_4Cl^+$ which is the ion fragment whose intensity is proportional to the pressure of CF_2Cl-CF_2Cl . The Cl_2^+ current was very small compared to $C_2F_4^+$. The enhancement of the $C_2F_4^+$ intensity is assumed to arise from the surface reaction



Identification of C_2F_4 as the reaction product was verified by observing the increase in the $C_2F_3^+$ which is the major ion fragment from $C_2F_4(g)$. A small ion current of $C_2F_4^+$ arises from fragmentation of the reactant compound. A correction for this effect has been subtracted from the observed $C_2F_4^+$ current in computing the $C_2F_4Cl^+/C_2F_4^+$ ratios

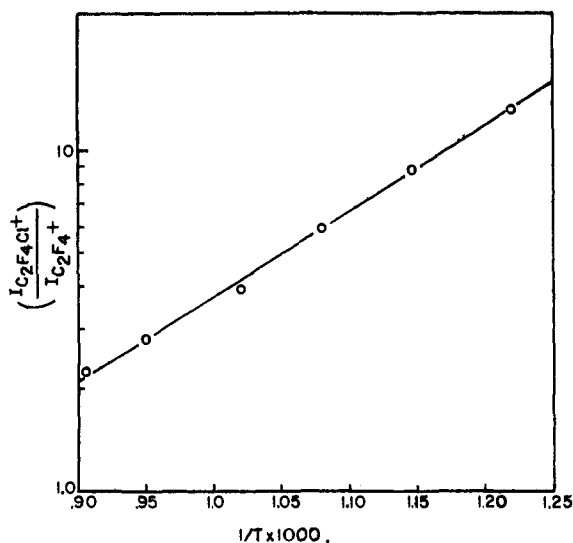


Fig. 11.—Temperature dependence of $C_2F_4(C_2F_4^+)$ on $CF_2Cl-CF_2Cl(C_2F_4Cl^+)$; electron energy = 20 volts; pressure range 0.08 to 0.60 mm.

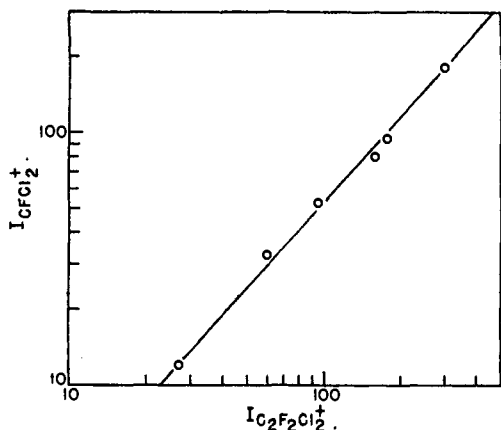
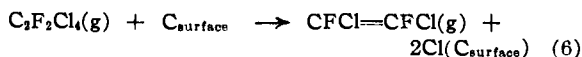


Fig. 12.—Pressure dependence of $CFC1=CFC1(C_2F_2Cl_2^+)$ on $CFCl_2-CFCl_2(CFC1_2^+)$; electron energy = 20 volts; $T = 780^\circ K.$, pressure range 0.04 to 0.25 mm.

which are indicative of the true $C_2F_4Cl_2(g)/C_2F_4(g)$ ratios. The correlation of the relative yield with temperature is shown in Fig. 11. From this a value of $\Delta H = 11.5 \pm 2.0$ kcal. is obtained.

$CFCl_2-CFCl_2$.—The major ion currents obtained in the mass spectrum of $CFCl_2-CFCl_2$ were in the ratios $CFCl_2^+ : C_2F_2Cl_2^+ : C_2F_2Cl_2^+ = 100:17:6$ for 20 volt electrons. At high temperatures the $C_2F_2Cl_2^+$ current became the major peak in the spectrum. Figure 12 shows the dependence of $C_2F_2Cl_2$ on $CFCl_2-CFCl_2$ here represented by $C_2F_2Cl_2^+$ and $CFCl_2^+$, respectively. Again fairly clear evidence was obtained for a first-order pressure relationship. This observation and the absence of Cl_2^+ suggests the surface reaction



The temperature dependence for the reaction is shown in Fig. 13, from which $\Delta H = 24.5 \pm 3.0$ kcal./mole is obtained. At high temperatures where the reaction is far to the right, the mass spectrum shows the intensity ratio $C_2F_2Cl_2^+ : CCl_2^+ : CFC1_2^+ = 100:33:8$ for 15 volt electrons. The CCl_2^+ observed here must be formed almost entirely from the $C_2F_2Cl_2$ since the contribution to this peak from the reactant is negligible. An independent check confirming that the product was $CFC1=CFC1$ was obtained by running the mass spectrum of $CFC1=CFC1$ prepared by standard procedures.⁹ The spectrum of the compound gave

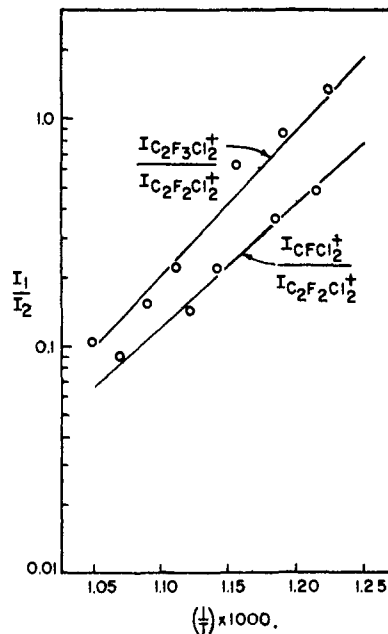
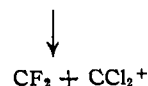


Fig. 13.—Temperature dependence of $CF_2=CCl_2(C_2F_2Cl_2^+)$ on $CF_2-CCl_2(C_2F_2Cl_2^+)$, upper curve, and $CFC1=CFC1(C_2F_2Cl_2^+)$ on $CFCl_2-CFCl_2(CFC1_2^+)$, lower curve; electron energy = 20 volts; pressure range 0.02 to 0.09 mm., upper curve, and 0.10 to 0.14 mm., lower curve.

intensities in the ratio $C_2F_2Cl_2^+ : CCl_2^+ : CFC1_2^+ = 100:56:3$, while the pyrolysis product gave 100:64:4, respectively, with 20 volt electrons. In contrast the 20 volt fragmentation of $CF_2=CCl_2$ yielded $C_2F_2Cl_2^+ : CCl_2^+ : CFC1_2^+ = 100:21:0$. The observation of a high CCl_2^+ peak from $CFC1=CFC1$ molecule implies a substantial rearrangement of the ion when it is formed. This is most probably a consequence of the stability of CF_2 in the process



The fragmentation of the two isomers with 100 volt electrons also has been determined. Under these conditions the ratios $C_2F_2Cl_2^+ : CCl_2^+ : CFC1_2^+$ are 100:88:13 and 100:37:0, for $CFC1=CFC1$ and $CF_2=CCl_2$, respectively. The CCl_2^+ ion is thus a more abundant fragment from $CFC1=CFC1$ than from $CF_2=CCl_2$.

The splitting of the double bond on ionization is apparently a characteristic of ethylenic fluorine compounds as the analogous split in $CCl_2=CCl_2$ is not a major fragmentation process. No evidence was found for the dechlorination of $CFC1=CFC1$.

CF_2-CCl_2 .—The mass spectrum of CF_2-CCl_2 shows that the fragmentation currents are in the ratios $C_2F_2Cl_2^+ : CCl_2^+ : C_2F_2Cl_2^+ = 100:71:0$ for 20 volt electrons. At temperatures above 650° $C_2F_2Cl_2^+$ became the most abundant ionic species. The pressure dependence of $C_2F_2Cl_2^+$ on CF_2-CCl_2 , i.e., product $C_2F_2Cl_2$ on reactant CF_2-CCl_2 , is shown in Fig. 14. The behavior in this case was more complex than for most of the previous systems because of the extraction of fluorine from the molecule. At low leak rates the current is essentially first order but departs toward a higher order at higher pressures. No evidence was found for $Cl_2(g)$ or $ClF(g)$ in the reaction. The only additional product of significant intensity was $HCl(g)$. This gas is assumed to arise by the reaction of adsorbed chlorine with other sources of hydrogen. The low pressure behavior is readily understood in terms of the simple reaction

(9) E. G. Locke, W. R. Brode and A. L. Henne, *J. Am. Chem. Soc.* **56**, 1727 (1934).

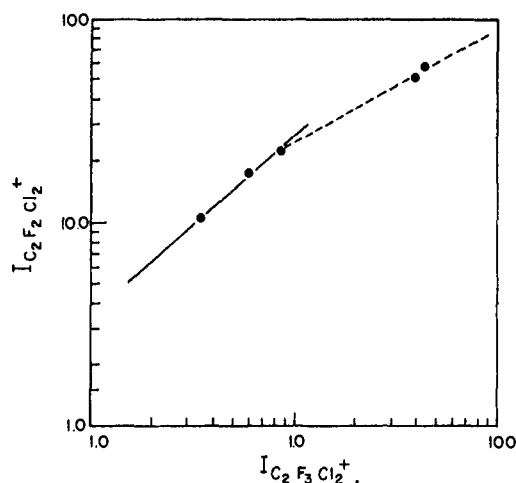
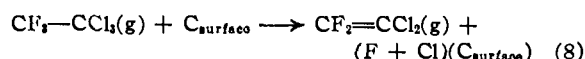


Fig. 14.—Pressure dependence of $CF_2=CCl_2(C_2F_2Cl_2^+)$ on $CF_2=CCl_2(C_2F_3Cl_2^+)$; electron energy = 20 volts; $T = 840^\circ K$.; pressure range 0.02 to 0.40 mm.



Verification that the product was the unsymmetrical $CF_2=CCl_2$ was obtained by comparing the 20 volt high temperature mass spectrum with that from the commercially prepared material. One obviously distinguishing feature between the mass spectra of $CF_2=CCl_2$ and $CFCl=CFCl$ is the presence of a relatively large $CFCl^+$ peak in the spectrum of the latter. This peak was absent in the pyrolysis of $CF_2=CCl_2$.

The temperature dependence of the yield obtained at low pressures is shown in Fig. 13 where $C_2F_2Cl_2^+$ and $C_2F_3Cl_2^+$ currents are proportional to the partial pressures of product and reactant, respectively. From the slope we have $\Delta H = 29.3 \pm 3.0$ kcal.

TABLE I

DATA FOR LOW PRESSURE PYROLYSIS OF SEVERAL HALOGENATED COMPOUNDS IN GRAPHITE OVENS

Reactant	Temp. ($^\circ K$) range studied	Products	ΔH° (kcal./mole)
CCl_4	633-1050	C_2Cl_4 , C_2Cl_2 , Cl_2	
C_2Cl_4	450-1300	C_2Cl_2	16.0 ± 3.0^a
$CHCl_2-CCl_2$	450-900	$CHCl=CCl_2$	21.0 ± 3.0^a
$CHCl_2-CHCl_2$	500-1000	$CHCl=CHCl$ $CHCl=CCl_2$	14.2 ± 3.0^a
CH_2Cl-CH_2Cl	450-1170	$CH_2=CH_2$ $CH_2=CHCl$	
$CH_2=CCl_2$	600-975	$CH_2=CCl_2$	
CF_2Cl-CF_2Cl	640-1190	$CF_2=CF_2$	11.5 ± 2.0^a
$CFCl_2-CFCl_2$	620-960	$CFCl=CFCl$	24.5 ± 3.0^a
$CF_2=CCl_2$	680-1000	$CF_2=CCl_2$	29.3 ± 3.0^b
$CFCl_2$	850-1160	$CFCl=CFCl$ $CFCl=CCl_2$ CF_2Cl , CF_2Cl_2	

^a Refers to removal of two chlorine atoms from adjacent C atoms. ^b Refers to removal of one F and one Cl atom from adjacent C atoms.

CCl_2F .—The pyrolysis behavior of several chlorofluoromethane compounds also was examined. Several reaction products were observed and identified for $CFCl_2$. The major ion fragment observed for cold $CFCl_2$ was $CFCl_2^+$. The ionic species present in the high temperature mass spectrum were $C_2F_2Cl_2^+$ and $C_2FCl_3^+$ which are attributed to $CFCl=CFCl$ and $CFCl=CCl_2$, respectively. No evidence was found for $CFCl_2-CFCl_2$ or $CFCl_2-CCl_2$ which are the logical precursors of the observed ethylenic products. Single carbon fragments CF_2^+ and CF_2Cl^+ were present. Under these conditions Cl_2^+ was also observed. A typical

TABLE II

TYPICAL MASS SPECTRUM OF PYROLYSIS PRODUCTS OF $CFCl_2$ THROUGH A GRAPHITE LEAK AT $1113^\circ K$.

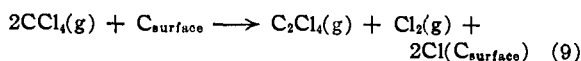
Ionizing electron energy = 16 volts

Ion	CF_2^+	Cl_2^+	CCl_2^+	$CFCl_2^+$	$C_2F_2Cl_2^+$	$C_2FCl_3^+$
Intensity	33	17	23	49	100	88

mass spectrum of the reaction products is included in Table II. Both CCl_2F_2 and $CClF_2$ were found to be very much less reactive than $CFCl_2$. No ethylene type derivatives were found at temperatures up to 1000° . No reaction was found for CF_4 at temperatures up to 1200° .

Discussion

We are now in a position to consider the pyrolysis behavior of CCl_4 . Since our observations for the chlorinated ethanes indicate that chlorine atoms from adjacent carbon atoms are removed by a surface reaction to yield an ethylenic product, it would seem reasonable to expect C_2Cl_4 to be the precursor in the formation of C_2Cl_2 . The ion peak, $C_2Cl_4^+$, however, that could be attributed to C_2Cl_4 exclusively was not observed. No direct evidence can therefore be offered for such an intermediate. The observation of Cl_2^+ from $Cl_2(g)$ suggests, on the other hand, that Cl_2 molecules are split out when two CCl_4 molecules react. The following reaction is consistent with the observed behavior.



For this reaction we have

$$K_{eq.} = \frac{(P_{C_2Cl_4})(P_{Cl_2})}{(P_{CCl_4})^2} = \frac{C(I_{C_2Cl_4})(I_{Cl_2})}{(I_{CCl_4})^2} = \frac{C'(I_{C_2Cl_4})^2}{(I_{CCl_4})^2}$$

where C and C' are constants which are independent of the cell temperature. The observed pressure dependence in Fig. 3 is consistent with this relationship.

At the low cell pressures of about 10^{-1} mm. for CCl_4 , it is unlikely that Cl_2 is split out in a bimolecular gas phase reaction. A more tenable explanation is that two adjacent CCl_4 molecules adsorbed on the graphite surface split out one Cl_2 molecule. Two Cl atoms from adjacent C atoms in the adsorbed C_2Cl_4 may then be transferred to the graphite surface. Of equal plausibility is the reverse time sequence where a chlorine atom is extracted from a CCl_4 molecule by the surface. Adjacent adsorbed CCl_3 groups then combine by eliminating a chlorine molecule. At higher temperatures where C_2Cl_2 becomes a major product we would assume that two additional chlorine atoms are extracted by the surface. The products present in the gas phase should then be in the approximate ratio of $C_2Cl_2:Cl_2 = 1:1$.

The situation with respect to CCl_2F is somewhat similar to that for CCl_4 . Here we can account for the behavior by assuming that a Cl_2 molecule is split out between two reactant molecules with a subsequent transfer of chlorine or fluorine atoms to the surface to yield $CFCl=CFCl$ and $CFCl=CCl_2$. The question of an ethane intermediate again arises. At the highest temperatures this problem is minimized since our previous observations indicate that the most probable intermediate, $CFCl_2-CFCl_2$, is almost totally pyrolyzed.

Schmeisser and Schröter¹⁰ report that CCl_2 is a major product from the pyrolysis of CCl_4 in a graphite tube at temperatures around 1300° . No evidence for this product was obtained in the present work. Extrapolation of our data to temperatures of 1300° suggests $\text{C}_2\text{Cl}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ to be the only major products. The only explanation that we can offer for the results of Schmeisser and Schröter is that the condensed product they obtained was a 1:1 mixture of C_2Cl_2 and Cl_2 . On the basis of the limited knowledge of the explosive nature of C_2Cl_2 , it would be surprising if a stable mixture could be prepared.

The hexachlorobenzene and hexachloroethane reported in the earlier literature as products from the pyrolysis of CCl_4 are not formed under the conditions of this present work. It would thus seem that the formation of these two materials is due to subsequent recombination of the primary pyrolysis products outside of the pyrolysis zone. No evidence was obtained for the formation of compounds containing three or more carbon atoms.

Our observations that the pyrolysis of CCl_4 goes through C_2Cl_4 and C_2Cl_2 is consistent with the early suggestion of Lüb.⁷

Although we have evidence that the removal of chlorine atoms from adjacent carbon atoms involves a surface reaction with graphite, we are not in a position to discuss in detail the nature of the chlorine absorbed on the surface. There is some general concern as to which type of lattice site the chlorine is bound. It is known that halogen atoms combine with graphite to give compounds with approximate formulas C_4F , C_8Cl and C_8Br . Ubbelohde¹¹ recently has discussed the bonding properties in this type of system.

For reactions of the form

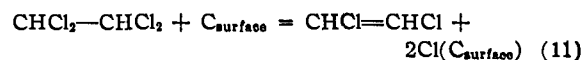


the available thermochemical data indicate values of ΔH_0 between +40 and +50 kcal. for the cases where R is H or Cl. This is also the range in ΔH

(10) M. Schmeisser and H. Schröter, *Z. angew. Chem.*, **72**, 349 (1960).

(11) A. R. Ubbelohde, *J. chim. phys.*, **58**, 107 (1961).

to be expected from simple bond additivity considerations.¹² For the reaction

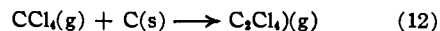


we have determined $\Delta H = +14.2 \pm 3.0$ kcal. This implies that an additional 25 to 35 kcal. are required to remove 2 Cl atoms from the surface as Cl_2 molecules. The reported value¹⁸ of -31.9 kcal. for the heat of absorption of $\text{Cl}_2(\text{g})$ on charcoal is in qualitative agreement with these considerations. This is consistent with the supposition that chlorine atoms from the chloroethanes are chemisorbed on graphite and/or are intercalated between graphite planes as Cl atoms. The ultimate fate of an absorbed chlorine atom is apparently determined to some degree by the presence of hydrogen or other surface contaminants which react to form $\text{HCl}(\text{g})$.

The mechanism of the removal of an H and a Cl atom from adjacent carbon atoms is apparently a more complicated process as indicated by the pressure data for CH_3-CCl_3 (Fig. 10). On the basis of the high HCl pressure, it appears that HCl is not strongly absorbed on the graphite surface. When $\text{H}_2(\text{g})$ was passed in at 600 to 1000° after the completion of a C_2Cl_4 pyrolysis, a 75% conversion of the $\text{H}_2(\text{g})$ to $\text{HCl}(\text{g})$ was observed.

When $\text{H}_2(\text{g})$ and $\text{C}_2\text{Cl}_4(\text{g})$ were run together through the hot oven, the $\text{C}_2\text{Cl}_2/\text{C}_2\text{Cl}_4$ ratio was the same as that observed in the absence of $\text{H}_2(\text{g})$. The presence of $\text{H}_2(\text{g})$ in the crucible does not therefore enter into the surface dechlorination of C_2Cl_4 directly.

Examination of the crucibles after pyrolysis of CCl_4 gave no evidence for the uptake of carbon by CCl_4 . We can therefore eliminate the reaction



This is also supported by the fact that Cl_2 is evolved and that the pyrolysis of C_2Cl_4 did not give the reverse reaction.

(12) T. L. Cottrell, "Strengths of Chemical Bonds," 2nd Ed., Butterworths, London, 1958.

(13) F. G. Keyes and M. J. Marshall, *J. Am. Chem. Soc.*, **49**, 156 (1927).

[CONTRIBUTION FROM THE NATIONAL INSTITUTES OF HEALTH, BETHESDA, MARYLAND, AND THE MEDICAL SCHOOL, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Proton Magnetic Resonance Studies of Porphyrins

BY EDWIN D. BECKER,^{1a} ROBERT B. BRADLEY^{1a} AND C. J. WATSON^{1b}

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High resolution proton nuclear magnetic resonance spectra are reported for eight porphyrins: the methyl esters of coproporphyrin-1 and -3, uroporphyrin-1, protoporphyrin-9, mesoporphyrin-9, hematoporphyrin-9 and phyloerythrin; and the di-cation form of tetra-benz-tetra-aza-porphin. The spectra are interpreted in terms of ring currents in the π -electron system. The equivalence of the four pyrrole rings in coproporphyrin-1 is demonstrated, and the proposal made that this equivalence results from a tautomerism of the NH protons at a rate much greater than 200 sec.⁻¹. Detailed assignments of the spectral lines to functional groups in the molecules are presented and analytical applications of the n.m.r. technique discussed.

High resolution proton nuclear magnetic resonance (n.m.r.) is being applied increasingly to the study of the structure of complex organic molecules, but thus far there has been only limited

application to porphyrins.^{2,3} The present work reports n.m.r. spectra of eight molecules containing

(2) E. D. Becker and R. B. Bradley, *J. Chem. Phys.*, **31**, 1413 (1959).

(3) J. Ellis, A. H. Jackson, G. W. Kenner and J. Lee, *Tetrahedron Letters*, No. 2, 23 (1960).

(1) (a) National Institutes of Health. (b) University of Minnesota.