and Jaffe (*4*). The average temperature of reaction was 24.4° C. and the heat of dilution was corrected to this temperature using the heat capacity data cited previously. The following reaction sequence could then be set up:

	ΔH, kcal.
$Be(c) + [8.381\ HCl + 67.982\ H_2O] \rightarrow BeCl_2[\text{in aq. } HCl] + H_2(g)$	−89.62
$BeCl_2[\text{in aq. } HCl] \rightarrow BeCl_2(c) + [6.381\ HCl + 67.982\ H_2O] + 2HCl(g)$	+45.92
$[6.381\ HCl + 67.982\ H_2O] + 2HCl(g) \rightarrow [8.381\ HCl + 67.982\ H_2O]$	−30.43
Combining algebraically	ΔH, kcal.
$Be(c) + 2HCl(g) \rightarrow BeCl_2(c) + H_2(g)$	−74.13

A very small correction of 4 cal. mole^{-1} deg.$^{-1}$ was applied to bring this result to 25° C., which was then combined with −22.063 kcal. mole^{-1} for the heat of formation of HCl(g) to derive for $BeCl_2(c)$

$$\Delta H_{f298}(c) = -118.25 \text{ kcal. mole}^{-1}$$

The over-all uncertainty is estimated as ±0.50 kcal. mole^{-1}. Johnson and Gilliland found −118.03 ± 0.56 by direct reaction of beryllium and chlorine. The agreement of the two methods is very satisfactory and establishes the heat of formation of beryllium chloride within considerably narrower limits than the older literature values allowed.

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RECEIVED for review October 6, 1961. Accepted January 15, 1962.

Heats of Reaction of Halogenated Ethanes on Graphite

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LOW PRESSURE reactions between graphite and dichloro derivatives of ethane with chlorine atoms in the 1,2 positions have been the subject of a recent investigation (*1*). It has been proposed that the reaction involves the transfer of chlorine atoms from the gaseous reactants to the graphite,

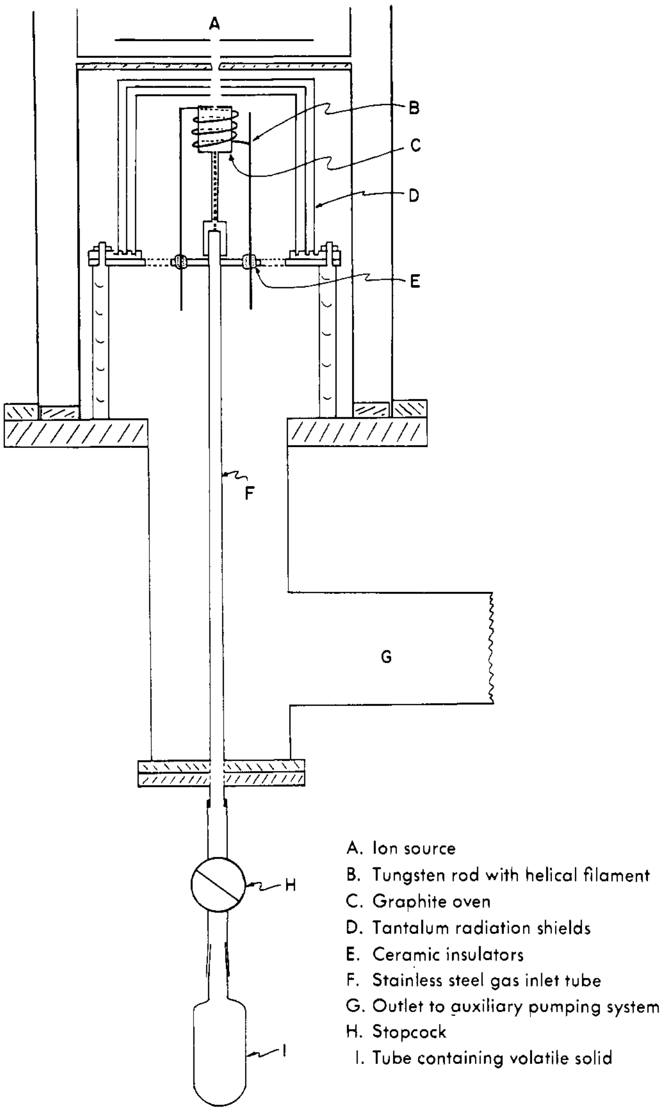
$$CR_2Cl{-}CR_2Cl + \text{graphite} = CR_2{=}CR_2 + 2Cl\ (\text{Graphite})$$

where R can be H, Cl, or F. The main experimental features of this reaction are the first order pressure dependence of product on reactant and the appearance of HCl(g) as the only other observable product.

This article is an extension of work described previously and includes an examination of the reaction of $CF_2Br{-}CF_2Br$ on graphite. An attempt to arrive at a more quantitative interpretation of the results has also been made.

EXPERIMENTAL

The mass spectrometer and high temperature assembly for vaporization studies and recent modifications to the original apparatus have been described (*1*, *7*). A further modification of the apparatus was introduced to allow investigations of solids with low vapor pressures (C_2Cl_6) in a method similar to that previously used only in gases and volatile liquids (Figure 1). For reactions of the dichloro compounds, reaction vessels constructed from an electrolytic grade of graphite were employed. For reactions with $CF_2Br{-}CF_2Br$ an oven made of pyrolytic-grade graphite was also used. With the present apparatus it is possible to control the leak rate and reaction pressure and temperature independently. Some care had to be taken in selecting a



A. Ion source
B. Tungsten rod with helical filament
C. Graphite oven
D. Tantalum radiation shields
E. Ceramic insulators
F. Stainless steel gas inlet tube
G. Outlet to auxiliary pumping system
H. Stopcock
I. Tube containing volatile solid

Figure 1. Mass spectrometer furance assembly and gas inlet system

mass fragment from the reactant that did not overlap with a peak from an isomeric impurity. Thus, for example, for $CF_2Cl—CFCl_2$ the $CFCl_2^+$ peak was observed rather than the $C_2F_3Cl_2^+$, which would also have a contribution from any $CF_3—CCl_3$ that was present as an impurity. In several cases it was necessary to subtract from the intensity of the ion used as a measure of the product pressure a contribution due to ion fragmentation from the reactant molecule.

As in previous work, the experimental technique involved introducing the gas or vapor into a graphite oven by a stainless steel delivery tube connected through a long graphite stem to the reaction chamber. Only the oven was heated directly. The stem connection to the inlet line was several hundred degrees cooler than the reactant vessel. The products were observed as ions produced by electron bombardment in a mass spectrometer. The oven was constructed in such a way that the ratio of the area of its exit orifice to the geometrical surface area was about 10^{-3}; the true area available for reaction is probably several times the apparent geometrical area. A Hoke valve was used to regulate the gas flow to provide pressures of between about 10^{-3} and 10^{-1} mm Hg. Under these conditions, molecular flow or Knudsen conditions prevail, so that we observe primarily the ineraction of the gases with the graphite surface, and the number of collisions between gas molecules is small. Since the compounds investigated will also react extensively on metal surfaces at high temperatures, the reactants aid in the removal of small traces of metallic impurities as volatile halides, especially at temperatures in excess of 1000° C.

RESULTS

In Figure 2, data for the pressure dependence of $CF_2Br—CF_2Br$ are given. The $C_2F_4^+$ peak was followed for the product, while for the reactant, CF_2Br^+ was observed. The experimental slope of the pressure dependence was found to be 1.15. This is taken as indicative of a first order pressure dependence. The data thus suggest that a reaction similar to that proposed for the dechlorination of 1,2-dichloroethane derivatives will also be true for the 1,2-dibromoethanes. HBr was observed among the products while Br_2 was not present. To interpret these results, we consider the following processes: The primary reaction

$$CF_2Br—CF_2Br(g) + \text{graphite} = CF_2{=}CF_2(g) + 2Br\ (\text{graphite}) \qquad (1)$$

is assumed to be close to equilibrium. This is accompanied by a secondary reaction, which is probably not reversible:

$$Br\ (\text{graphite}) + H\ (\text{graphite}) \rightarrow HBr(g) \qquad (2)$$

The temperature dependence of $C_2F_4/C_2F_4Br_2$ was also determined as indicated in Figure 3, where the observed ion current ratio is proportional to $P_{C_2F_4}/P_{C_2F_4Br_2}$. The temperature coefficients were found to be nonreproducible unless the oven was heated to 1100°-1200° C. to remove HBr or other surface contaminants prior to experimental measurements. When the oven was rapidly cooled, Reaction 1 gave a very high yield of $C_2F_4(g)$ and slowly recovered to its reproducible value; this indicated that the cleaned surface was temporarily very active.

Examining the process from a kinetic viewpoint, using Reactions 1 and 2, we can write for the steady-state condition for bromine on the surface:

$$R_{\text{appearance}}[Br\ (\text{graphite})] = 2k_1P_{C_2F_4Br_2}\theta_C^2 \qquad (3)$$

and

$$R_{\text{disappearance}}[Br\ (\text{graphite})] = 2k_2P_{C_2F_4}\theta_C^2\theta_{Br}^2 + k_3\theta_{Br}\theta_H \qquad (4)$$

where θ_C is the fraction of unoccupied C sites available for bromine and θ_{Br} and θ_H are the fraction of surface sites occupied by bromine and hydrogen, respectively. In the

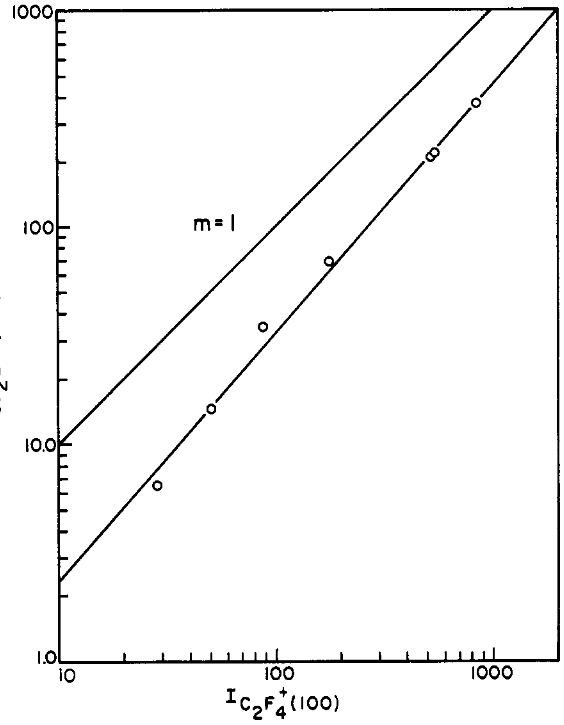


Figure 2. Pressure dependence data for the reaction of $CF_2Br—CF_2Br$ (CF_2Br^+) on graphite to yield $C_2F_4(g)$ ($C_2F_4^+$)

Numbers in parenthesis refer to m/e observed; ionizing electron energy = 75 volts; T = 680° K.

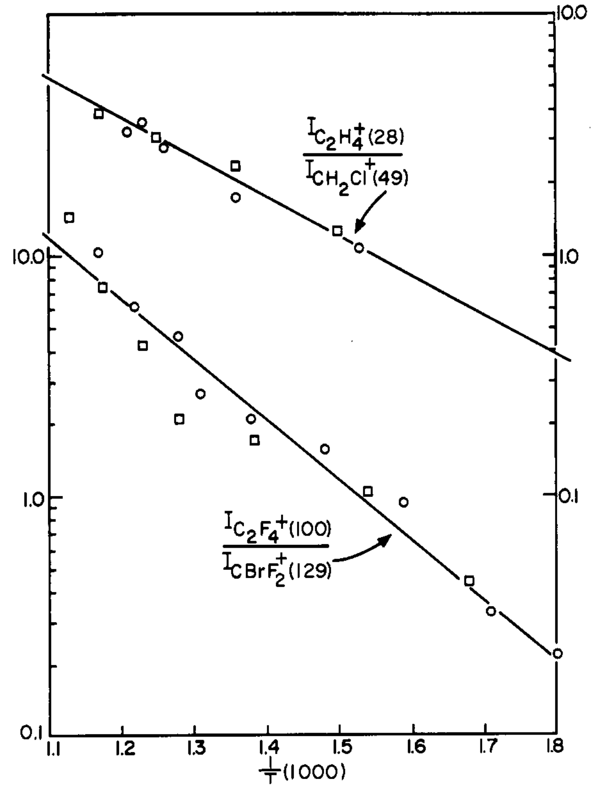


Figure 3. Temperature dependence data for the reactions of $CF_2Br—CF_2Br(g)$ (CF_2Br^+) and $CH_2Cl—CH_2Cl$ (CH_2Cl^+) on graphite to yield $C_2F_4(g)$ ($C_2F_4^+$) and C_2H_4 ($C_2H_4^+$), respectively

Squares and circles indicate independent sets of data; ionizing electron energy = 75 volts; numbers in parentheses refer to m/e observed above equations, it is assumed that two surface sites must enter the forward reactions and two carbon and two bromine sites into the reverse reactions. Other possible mechanisms may require modification of the surface dependence terms. For the steady state condition

$$2k_1P_{C_2F_4Br_2}\theta^2_C = 2k_2P_{C_2F_4}\theta^2_C\theta^2_{Br} + k_3\theta_{Br}\theta_H \tag{5}$$

The following expressions are for C_2F_4:

$$R_{appearance}[C_2F_4(g)] = k_1P_{C_2F_4Br_2}\theta^2_C \tag{6}$$

and

$$R_{disappearance}[C_2F_4(g)] = k_2P_{C_2F_4}\theta^2_C\theta^2_{Br} +$$

$$+ k_4P_{C_2F_4}a/(MT)^{1/2} \tag{7}$$

where the last term in the last expression takes into consideration the effusion of $C_2F_4(g)$ through the orifice of area a. For the steady state condition of $C_2F_4(g)$ with graphite

$$k_1P_{C_2F_4Br_2}\theta^2_C = k_2P_{C_2F_4}\theta^2_C\theta^2_{Br} + k_4P_{C_2F_4}a/(MT)^{1/2} \tag{8}$$

From Equations 3 and 6

$$k_4P_{C_2F_4}a/(MT)^{1/2} = \tfrac{1}{2}k_3\theta_{Br}\theta_H \tag{9}$$

where k_4 is a known constant. This implies that, for a true steady-state condition, the pressure of C_2F_4 should be proportional to that of HBr and that, when the steady state is reached, Br disappears from the surface at twice the rate that C_2F_4 disappears from the crucible. This is consistent with the initial experimental observations that the HBr^+ peak from HBr and the $C_2F_4^+$ peak from C_2F_4 were of comparable intensities and showed parallel behavior.

In one series of experiments, the area of the exit orifice was increased from 4.0×10^{-3} sq. cm. to 1.4×10^{-2} sq. cm. to investigate the effect of the orifice area on the reaction. The data obtained (Figure 4) indicate that the increased rate of effusion is not sufficient to seriously affect the equilibrium condition for Reaction 1. The departure of the temperature dependence plot from the straight line at low temperatures indicates that perhaps some new surface condition has been generated after prolonged heating of the cell; an adequate explanation of this behavior is not yet available.

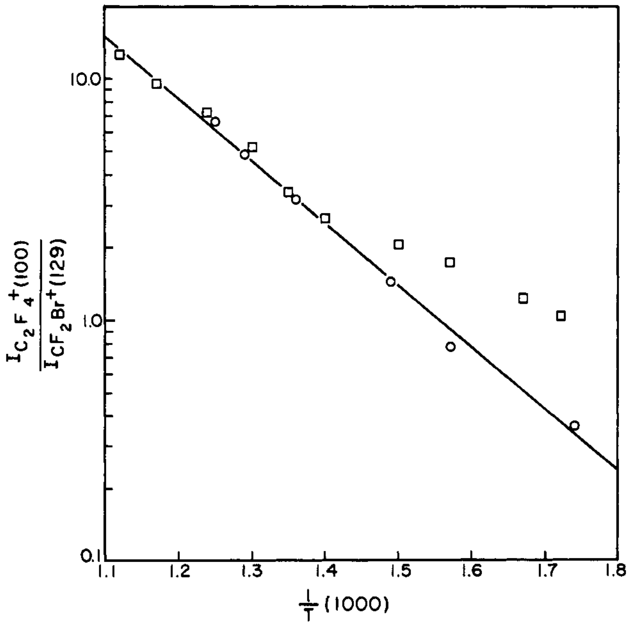


Figure 4. Temperature dependence data for the reaction of $CF_2Br—CF_2Br(g)$ (CF_2Br^+) on pyrolytic graphite to yield $C_2F_4(g)$ $(C_2F_4^+)$ for two orifice areas in reaction vessel.

Circles indicate data obtained with $a = 4.0 \times 10^{-3}$ sq. cm.; squares indicate data obtained with $a = 1.4 \times 10^{-2}$ sq. cm.

Thermodynamically, for Reaction 1

$$k_{eq} = P_{C_2F_4}(a_{Br})^2/P_{C_2F_4Br_2} \tag{10}$$

where a_{Br} refers to the activity of absorbed bromine. The invariance of the pressure ratio of product to reactant as a function of leak rate at constant temperature shows that during the initial experiments, a_{Br} was not a strong function of flow rate of reactant gas. Temperature dependence curves obtained from early sets of data were also found to be linear. Temperature coefficients were used to evaluate $\Delta H°$ for the reaction. Slopes of the curves for reactions with the two grades of graphite give essentially the same heat of reaction. The second law heat of reaction is not affected by the chemical nature of the absorbed bromine so long as its activity is not changing appreciably. Assuming that absorbed bromine is present as Br_2 molecules would give the same formal results.

The ΔH°_1 values thus obtained were combined with literature values (Table I) for the heat of reaction (ΔH°_{11}) for

$$CF_2Br—CF_2Br(g) = CF_2 = CF_2 + Br_2(g) \tag{11}$$

to yield the heat of reaction (ΔH°_{12}) for

$$Br_2 + \text{graphite} = 2Br\ (\text{graphite}) \tag{12}$$

Thus

$$\Delta H^\circ_{12} = \Delta H^\circ_{11} + \Delta H^\circ_1$$

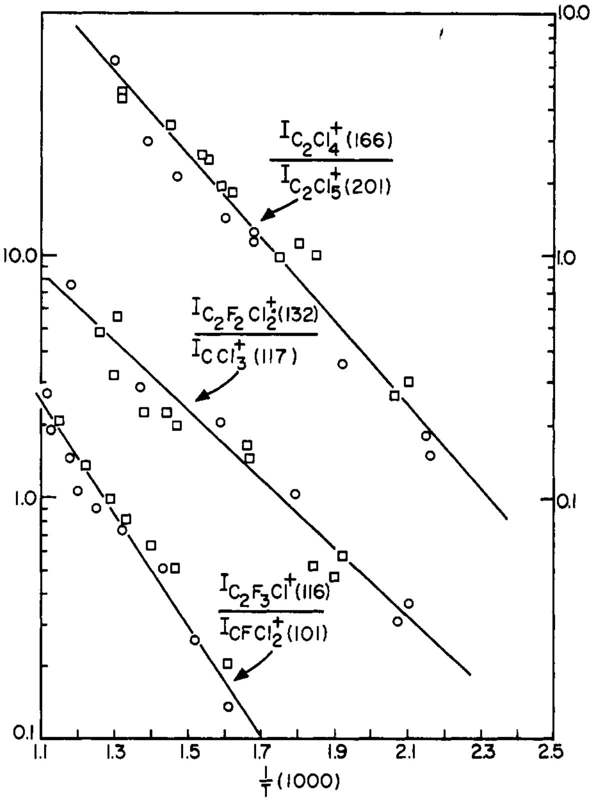


Figure 5. Temperature dependence data for reactions of three chloroethane derivatives on graphite

Left scale refers to reactions of $CF_2Cl—CCl_3(g)$ (CCl_3^+) and $CF_2Cl—CFCl_2$ $(CFCl_2^+)$ to yield $CF_2{=}CCl_2(C_2F_2Cl_2^+)$ and $CF_2{=}CFCl$ $(C_2F_3Cl^-)$, respectively; right scale refers to reaction $C_2Cl_6(g)$ $(C_2Cl_5^+)$ to yield C_2Cl_4 $(C_2Cl_4^+)$; squares and circles indicate independent sets of data. Ionizing electron energy = 75 volts; numbers in parentheses refer to mass over charge ratio observed

Table I. Data Used to Compute Heats of Reaction of Cl_2(g) and Br_2(g) with Graphite

Reactant	Product	Temp., ° K.	$\Delta H^{\circ a}$ (Kcals./Mole)	$-\Delta H^{\circ b}$ (Kcal./Mole)	$-\Delta H^{\circ c}$ (Kcal./Mole)
$CF_2Br—CF_2Br$	$CF_2=CF_2$	557-861	11.5	38.5(*5*)	27.0
$CCl_3—CCl_3$	$CCl_2=CCl_2$	464-772	7.9	41.0(*8*)	33.1
$CH_2Cl—CH_2Cl$	$CH_2=CH_2$	653-857	7.0	43.3(*6*)	36.3
$CF_2Cl—CFCl_2$	$CF_2=CFCl$	620-897	10.0	48.0(*6*)	38.2
$CCl_3—CF_2Cl$	$CCl_2=CF_2$	477-845	6.6	41.1(*6*)	34.5

[a] Reaction $CR_1R_2X—CR_3R_4X(g)$ + graphite → $CR_1R_2 = CR_3R_4(g) + 2X$ (graphite).

[b] Reaction $CR_1R_2 = CR_3R_4(g) + X_2(g) \rightarrow CR_1R_2X—CR_3R_4X(g)$.

[c] Reaction $X_2(g)$ + graphite → 2X (graphite).

To arrive at a value for the heat of reaction of chlorine with graphite, four reactions of the following type were studied:

$$CR_1R_2Cl—CR_3R_4Cl(g) + \text{graphite} = CR_1R_2=CR_3R_4(g) + 2Cl\ (\text{graphite}) \qquad (13)$$

Temperature dependence curves obtained at constant flow rate are given in Figures 3 and 5. Results of these data are summarized in Table I. The thermodynamic cycle is identical with that described above except that Br is replaced by Cl. The value for the heat of reaction of Cl_2 on graphite in the temperature range studied, deduced from the four sets of data, is -35.5 ± 2.5 kcal./mole Cl_2. The experimental heats of reaction for all the reactants with graphite are believed to be accurate to $\pm 10\%$.

DISCUSSION

Thermochemical data for the dissociation reaction:

$$CF_2Br—CF_2Br(g) = C_2F_4(g) + Br_2(g)$$

indicate that for temperatures between 800° and 1000° K., the equilibrium decomposition of $C_2F_4Br_2(g)$ at pressures employed in this work should be appreciable. Using the published value of 38.5 kcal./mole for the heat of reaction (used in Table I) and an estimated entropy change of 40 e.u. per mole, an equilibrium constant of about 0.1 is calculated at 800° K. Thus, if a purely homogeneous decomposition reaction occurred, we should observe a high product pressure of Br_2 comparable to that of $C_2F_4(g)$. Under our experimental conditions, it is therefore evident that a path for the homogeneous reactions is not provided through the surface reaction. The failure to obtain Br_2 saturation presumably must result from the competing reaction that removes bromine from the surface or may indicate that for kinetic reasons the bromine atoms on the surface cannnot combine rapidly. The tendency for graphite to retain some bromine at high temperatures in residual bromine-graphite compounds has also been observed by Henning (*2*). After several hours of surface exposure to the $CF_2Br—CF_2Br$, the ratio of $C_2F_4^+/CFBr_2^+$ was observed to decrease somewhat as the total reactant pressure was increased. This suggested that the surface was becoming deactivated due to an increasing concentration of absorbed bromine. The temperature dependence curves obtained under these conditions also exhibited a noticeable curvature. Furthermore, the $HBr^+/C_2F_4^+$ ratio eventually diminished. This suggested that the steady state condition as implied by Reactions 1 and 2 could not be maintained indefinitely due to the continued loss of H atoms as HBr(g).

The data do not allow us to infer which type of site in graphite is the most active for bromine absorption. The magnitude of the heat of reaction for Br_2 with graphite suggests that the bromine is chemically absorbed as Br atoms. This is also expected when the concentration of bromine on the surface is very dilute (*10*). The bromine-graphite compounds as described by Rüdorff (*9*) and Herold (*3*) are believed to involve bromine molecules at relatively low temperatures. Under the present experimental conditions, the value obtained for the heat of reaction of $Br_2(g)$ with graphite is assumed to be close to the limiting values for low surface coverage. Although the heat of reaction probably depends on the surface coverage by bromine, the concentration of bromine in the graphite was apparently not changing sufficiently during the initial measurements of temperature coefficients to exhibit a trend.

The reactions of 1,2-dichloroethane derivatives on graphite are apparently analogous to that for $C_2Br—CF_2Br$. A limiting value of −31.9 kcals per mole Cl_2 for the reaction of Cl_2 on charcoal at 0° C. has been obtained by a calorimetric procedure (*4*). The reasonable agreement with the present measured value of −35.5 kcal. per mole Cl_2 and graphite is perhaps noteworthy.

ACKNOWLEDGMENT

We thank D.R. Bidinosti for assistance with some of the initial experiments and William T. Miller for providing a number of fluorinated compounds.

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RECEIVED for review December 26, 1961. Accepted April 5, 1962. Work supported by the Advanced Research Projects Agency and the Alfred P. Sloan Foundation.