that is, the larger the electron affinity, the larger the stability of anion radicals produced, and the esr spectra are detected at room temperature by the present technique.

But there are some exceptional cases; for example, $E_{1/2}$'s and ϵ_{LV}'s of isoquinoline N-oxide, phenanthridine N-oxide, and phthalazine mono-N-oxide are almost the same magnitude as those of quinoline N-oxide, pyrazine mono-N-oxide, and pyridazine mono-N-oxide. The esr spectra of the former compounds, however, could not be observed, and this was attributed to the relative instability of any radicals formed. In addition we may suppose that these unstable radicals are very reactive as a result of their irregular spin density distribution (Figure 7). For example, the N→O bond in isoquinoline N-oxide and phthalazine mono-N-oxide has a very small spin density compared with that of the other compounds. In the case of phenanthridine N-oxide the positions 11–14, which are in the same ring as the N→O group, have very small spin density.

Last, a linear relation between $E_{1/2}$ and Hammett's σ value (Figure 14) was obtained: $-E_{1/2} = 1.08\sigma - 2.19$ with a root mean square deviation equal to ± 0.06. Here Hammett's σ values used are the same as reported for the case[49] where the polarographic reduction mechanisms and $E_{1/2}$–σ relations were studied in aqueous solution for a series of substituted pyridine N-oxides.[7,15a] The slope (Hammett's ρ value) obtained here in DMF solvent may be compared with that obtained from the aqueous solution study. From Figure 14 we deduce that the former ρ values are much larger than the latter. The main reason for this may be due to the following facts. In the present case there is no protonation effect on the reduction mechanism of N-oxide bond, but in aqueous solvent the protonation of the oxygen atom of N→O bond plays an important role during the reduction.[7,15a,27] It is now well known[2] that the mutual interaction between substituent and N-oxide group is larger in nonaqueous solvents than that of the hydrated or protonated species in aqueous solvents; thus the ρ value of the former case appears to be larger than in the latter case.

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Mass Spectrometric Study of the High-Temperature Equilibrium $C_2F_4 \rightleftarrows 2CF_2$ and the Heat of Formation of the CF_2 Radical

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Abstract: A mass spectrometric study of the thermal decomposition of C_2F_4 in a graphite Knudsen cell showed that C_2F_4 can be maintained in thermal equilibrium with the CF_2 radical. The equilibrium reaction $C_2F_4 \rightleftarrows 2CF_2$ was studied over the temperature interval 1127–1244°K, and, from the measured heat of reaction, $\Delta H_r{}^\circ{}_{298} = 76.3 \pm 3$ kcal mole^{-1}, the heat of formation of CF_2 was calculated to be -39.3 ± 3 kcal mole^{-1}.

There has been a continued interest over the past 15 years in the experimental determination of the heat of formation of the CF_2 radical. However, the values obtained by appearance potential measurements[1–4] or from predissociation in the spectra[5] are widely scattered, varying from -17 to -45 kcal mole^{-1}. A value for $\Delta H_f{}^\circ(CF_2)$ of -43 ± 5 kcal mole^{-1} was calculated[6] on the basis of the measurements of Farlow,[7] who prepared C_2F_4 by reaction of CF_4 with graphite.

Pottie[8] recently calculated $\Delta H_f{}^\circ(CF_2) = -36.8 \pm 3.0$ kcal mole^{-1} from the ionization potential of CF_2 (11.86 ± 0.1 eV) and the appearance potential of $CF_2{}^+$ from C_2F_4 (15.26 ± 0.05 eV) by using the value -152 kcal mole^{-1} [9] for the heat of formation of C_2F_4. With the value $\Delta H_f{}^\circ{}_{298}(C_2F_4) = -155.0 \pm 2.0$ kcal mole^{-1} recommended in the JANAF Tables,[6] one obtains $\Delta H_f{}^\circ{}_{298}(CF_2) = -38.3 \pm 3$ kcal mole^{-1} from Pottie's data.

The most direct estimate of the heat of formation of CF_2 was made recently by Modica and LaGraff.[10] From the shock-tube studies of the C_2F_4–CF_2 thermal equilibrium, these authors obtained $\Delta H_f{}^\circ{}_{298}(CF_2) =$

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-39.7 ± 3.0 kcal mole^{-1}. The same authors[11] reported -40.2 ± 4.0 kcal mole^{-1} for the heat of formation of CF_2 from shock-tube studies of the decomposition of CHF_3.

Although the values for the heat of formation of CF_2 based on shock-tube measurements agree with each other, there are many assumptions involved in the interpretation of these experiments. In addition, one should note that only second-law calculations have been reported. With the equilibrium constants[10] for the reaction $C_2F_4 \rightleftarrows 2CF_2$ and free-energy functions[6] for C_2F_4 and CF_2, one finds $\Delta H_f{}^\circ{}_{298} = 67.5 \pm 0.3$ kcal mole^{-1} for the third-law heat of the reaction, almost 10 kcal mole^{-1} lower than the second-law heat. With this value, the heat of formation of CF_2 becomes -43.5 kcal mole^{-1}. The reason for such a discrepancy between the third- and second-law heats of reactions in the shock-tube experiments might be due to nonequilibrium conditions under which the reaction proceeded.

Because of the importance of the CF_2 radical, it seemed desirable to undertake a thermodynamic study of the reaction $C_2F_4 \rightleftarrows 2CF_2$ under true equilibrium conditions and determine the heat of formation of CF_2. This was the purpose of the present work.

Experimental Section

Perfluoroethylene, C_2F_4, was produced by the pyrolysis of polytetrafluoroethylene (Teflon) in a small graphite crucible at about 400°. A 10-cm long, 2-mm i.d. graphite tube connected the crucible with a Knudsen cell machined from a high-density graphite rod. The Knudsen cell was 3.0 cm long, 1.9 cm o.d., and 1.4 cm i.d., with an orifice diameter of 0.7 mm and thus had a ratio of the flat evaporating surface to orifice area of at least 400. Also, the Knudsen cell was filled with loose graphite pieces in order to increase its inner surface area.

The gases effusing from the Knudsen cell were ionized in an electron-impact ion source and ions were analyzed by a 12-in., 60° sector, single-focusing mass spectrometer.[12]

With the Knudsen cell at room temperature, the main gaseous products from the pyrolysis of Teflon were C_2F_4 and CF_4 as well as small amounts of C_2F_6 and C_3F_6. The appearance potentials of $C_2F_4^+$ (9.1 ± 0.3 eV), CF_2^+ (15.0 ± 0.3 eV), CF_3^+ (16.0 ± 0.5 eV), and CF^+ (15.8 ± 0.5 eV) were measured by the vanishing-current method, using the ionization potential of mercury, 10.4 eV,[13] as a standard for calibration of the electron-energy scale. The value AP ($C_2F_4^+$) = 9.1 ± 0.3 eV agrees well with the reported value for the ionization potential of C_2F_4;[14] the appearance potential of CF_2^+ is close to that measured previously for AP(CF_2^+) from C_2F_4.[14,15]

When the temperature of the Knudsen cell was increased above 900°, the decomposition of C_2F_4 occurred, leading to the formation of CF_2 radicals, as indicated by the appearance potential of the CF_2^+ ion of 11.8 ± 0.3 eV, close to the value of the ionization potential of CF_2 reported by Pottie[8] and Fisher and Lossing.[16] The stationary partial pressure of C_2F_4(g) at 900° was around 2×10^{-5} atm.

The intensities of CF_2^+ and $C_2F_4^+$ ions were measured at different temperatures at electron voltages 2 eV above the corresponding ionization potentials. The ion intensities were converted into partial pressures by use of the relation

$$P = \frac{I^+T}{S\sigma\gamma}$$

where P is the partial pressure in atmospheres, I^+ is the ion intensity in arbitrary units, σ is the relative cross section, γ is the secondary electron multiplier efficiency, T is the absolute temperature, and S is the instrumental sensitivity. The σ values were taken from Otvos and Stevenson,[17] while the secondary electron multiplier efficiency was estimated from the calibration data for a similar type of multiplier.[18] The instrumental sensitivity was measured by evaporating silver at a fixed temperature.

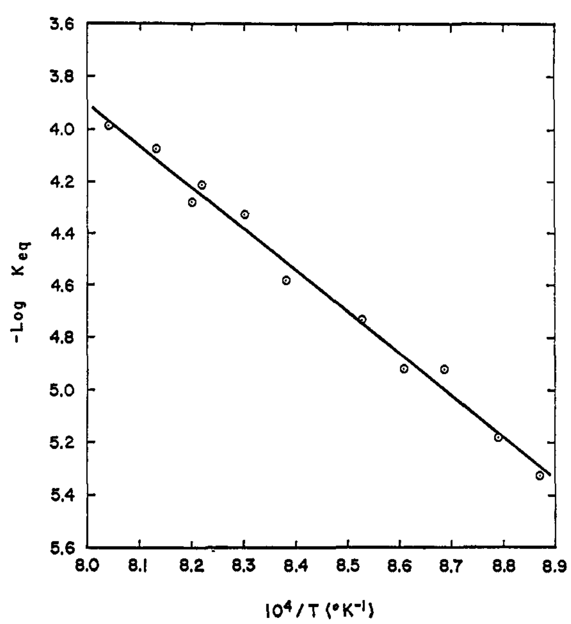

Figure 1. Second-law plot of the equilibrium constant for the reaction $C_2F_4 = 2CF_2$.

Results and Discussion

The enthalpy change, $\Delta H_r{}^\circ$, for the reaction $C_2F_4 \rightleftarrows 2CF_2$ was derived both by second- and third-law methods.

In the second-law procedure, the logarithm of the equilibrium constant $K_{eq} = P(CF_2)^2/P(C_2F_4)$ was plotted *vs.* reciprocal temperature, and $\Delta H_r{}^\circ$ was calculated from the slope of this plot by using the Clausius–Clapeyron equation. The second-law plot is shown in Figure 1. A least-squares treatment of the data yielded $\Delta H_r{}^\circ{}_{1178} = 73.2 \pm 3.3$ kcal mole^{-1}. With the heat-capacity data for C_2F_4 and CF_2,[19] one calculates $\Delta H_r{}^\circ{}_{298} = 76.1 \pm 3.0$ kcal mole^{-1}.

The equation employed in the third-law calculation is

$$\Delta H^\circ_{298} = \left[-RT\ln K_{eq} - \frac{T\Delta(G^\circ_T - H^\circ_{298})}{T}\right]$$

Free-energy functions for C_2F_4 are tabulated in the "JANAF Thermochemical Tables,"[6] and those for CF_2 were calculated on the basis of new spectroscopic results[19-21] for use in the third-law calculations. The results are shown in Table I. The average value $\Delta H^\circ_{298} = 76.5 \pm 0.2$ kcal mole^{-1} is in excellent agreement with the second-law heat of reaction.

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Table I. Equilibrium Constants and Heat for the Reaction $C_2F_4(g) = 2CF_2(g)$

Temp, °K	$-\text{Log } K_{eq}$	$-\Delta[(G^\circ - H^\circ_{298})/T]$, cal deg^{-1} mole^{-1}	ΔH°_{298}, kcal mole^{-1}
1220	4.28	43.42	76.9
1230	4.07	43.46	77.6
1244	3.98	43.56	76.8
1217	4.21	43.40	76.3
1205	4.33	43.33	76.1
1193	4.58	43.26	76.6
1173	4.74	43.17	76.1
1162	4.92	43.12	76.3
1151	5.02	43.06	76.0
1138	5.18	43.02	75.9
1127	5.33	42.94	75.9
$\Delta H^\circ_{298}(\text{av}) = 76.5 \pm 0.2$ kcal mole^{-1}			

Discussion

By using the mean value of the second- and third-law heats of reaction, $\Delta H^\circ_{298} = 76.3 \pm 3.0$ kcal mole^{-1}, together with the heat of formation of C_2F_4, $\Delta H_f{}^\circ{}_{298} = -155.0 \pm 2.0$ kcal mole^{-1},[6] one obtains -39.3 ± 3 kcal mole^{-1} for $\Delta H_f{}^\circ{}_{298}(CF_2)$. This value is very close to second-law values obtained in the shock-tube experiments[10,11] and also agrees, within the limits of experimental error, with Pottie's results.[8] Thus, on the basis of existing data, one confidently chooses $\Delta H_f{}^\circ{}_{298}[CF_2(g)] = -39 \pm 3$ kcal mole^{-1} and notes that the agreement of various experimental approaches validates the assumption of equilibrium in the various systems.

Table II gives currently accepted heats of formation of various fluorocarbon species, and Table III summarizes the dissociation energies of different carbon-fluorine bonds.

Table II. Heats of Formation of CF_n Species ($n = 1, 2, 3, 4$)

Species	$\Delta H_f{}^\circ{}_{298}$, kcal mole^{-1}	Species	$\Delta H_f{}^\circ{}_{298}$, kcal mole^{-1}
CF_4	-223.0 ± 1.0[a]	CF_2	-39 ± 3[d]
	-222.87 ± 0.38[b]	CF	49.2 ± 8.7[e]
CF_3	-115.9 ± 2.5[c]		

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Table III. Carbon–Fluorine Bond Strengths

Bond	D°_{298}, kcal mole^{-1}	Bond	D°_{298}, kcal mole^{-1}
CF_3–F	126.0[a]	CF–F	107.4,[a] 120[b]
CF_2–F	95.5[a]	C–F	140.6,[a] 132[b]

[a] Calculated from the respective heats of formation listed in Table II and by using values $\Delta H_f{}^\circ{}_{298}(F) = 18.86$ kcal mole^{-1} and $\Delta H_f{}^\circ[C(g)] = 170.9 \pm 0.5$ kcal mole^{-1} (ref 6). [b] Data reported by Thrush and Zwolenik[5] from predissociation in the spectra of CF_2 and CF.

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Chemistry of ^{38g}Cl Recoils in Neutron-Irradiated Crystalline $KClO_2$, $KClO_3$, and $KClO_4$

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Abstract: The distribution of recoil 37.5-min ^{38g}Cl among the chlorine valence states following the $^{37}Cl(n,\gamma)^{38}Cl$ reaction at 35° in crystalline $KClO_2$, $KClO_3$, and $KClO_4$ was measured. Anion-exchange column separations performed on aqueous solutions of the irradiated solids showed that radiochloride was the principal species formed. The production of $^{38}ClO_2{}^-$ and of $^{38}ClO_2$ was observed for the first time, as was the formation of $^{38}ClO_3{}^-$ in $KClO_2$ and of $^{38}ClO_4{}^-$ in $KClO_3$. The generation of small amounts of radioperchlorate ion in irradiated $KClO_4$ was confirmed. Radiohypochlorite appeared to be formed in very small yield, if at all. Comparisons of the relative yields of the chlorine valence states produced by ^{60}Co γ-radiation with those for recoil radiochlorine indicated that the rupture of all the Cl–O bonds in the target anion is much more probable in the "hot-atom" than in the radiation chemical process.

The chemistry of ^{38g}Cl recoil atoms formed by neutron irradiation of chlorine oxyanions in crystals has been the subject of recent investigations[1,2] which have generally confirmed and extended the findings of early research.[3,4] The valence states in which radiochlorine has been observed are chloride, chlorate, and perchlorate. However, few generalizations about yields can be made, and significant discrepancies between these reports are evident. It has seemed worthwhile, therefore, to conduct additional research to determine states of chemical combination of recoil radiochlorine generated by neutron irradiation of crystalline $KClO_2$, $KClO_3$, and $KClO_4$. The possibility that ^{38}Cl might be found in oxidation states other than those reported was

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