slightly asymmetric although the overall spectrum retains a center of symmetry in each case. This suggests that the asymmetry could be the result of an axially symmetric phosphorus hfs tensor. However, the anisotropy is small and implies that the radicals must be tumbling almost freely in both matrices.

From the magnitude of the phosphorus splitting the orbital of the unpaired electron in the valence shell is deduced to have *ca.* 37% s character. This lies within the range found for other 33 valence electron radicals, as shown in Table II. It is therefore logical to conclude that the structure of $POCl_3 \cdot -$ is similar to that of these other radicals. The structure is most easily visualized as a distorted trigonal bipyramid, and in this representation,⁵ it is probable that the unpaired electron, the oxygen, and the chlorine giving the smaller splitting are in equatorial positions and the two remaining chlorines are axially placed.

 Table II: Central Atom Parameters for 33 Valence

 Electron Radicals

	POCl3 · ~ a	PCl4·a	PF₄· ^b	PO4 • 4 - c	SF4 · + d	AsO4 · 4- or As(OH)4·
$a_{iso}, G_{c_s^{2f}}$	$\begin{array}{c} 1367 \\ 0.37 \end{array}$	$\begin{array}{c} 1217 \\ 0.33 \end{array}$	$\begin{array}{c}1330\\0,37\end{array}$	$1156 \\ 0.32$	$\begin{array}{c} 310 \\ 0.32 \end{array}$	$\begin{array}{c} 1084 \\ 0.32 \end{array}$

^a This work. ^b Reference 4a. ^c References 7 and 8. ^d Reference 4c. ^e M. Hampton, F. G. Herring, W. C. Lin, and C. A. McDowell, *Mol. Phys.*, 10, 565 (1966). ^f Refers to 3s orbital for phosphorus and sulfur radicals and to 4s orbital for the arsenic radical.

The formation of $POCl_3 \cdot - by$ simple electron capture is in accord with the very recent suggestion by Symons⁷ that $PO_4 \cdot ^{4-}$ is produced from PO_4^{3-} in phenacite crystals⁸ and in inorganic phosphate glasses⁹ by γ irradiation. Since there is no esr evidence for the production of $POCl_2 \cdot$, it seems likely that radiation chemical mechanisms of P-Cl bond breakage by homolysis and dissociative electron capture are relatively unimportant in $POCl_3$. On the other hand, in the radiolysis of phosphorus trichloride, we observed only $PCl_2 \cdot$ and $PCl_4 \cdot$ with $PCl_2 \cdot$ present in large excess ($\sim 10:1$). These latter findings are qualitatively similar to those obtained by uv photolysis⁵ which indicates that in PCl_3 the predominant mechanism is the rupture of a P-Cl bond to give $PCl_2 \cdot$ and chlorine atoms.

Notes

An Investigation of the Reaction $2\text{COF}_2 \rightarrow \text{CO}_2 + \text{CF}_4$ and the Heat of Formation of Carbonyl Fluoride

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A study of the thermal decomposition of carbonyl fluoride, reaction 1, was originally reported by Ruff and

$$2\operatorname{COF}_2 \longrightarrow \operatorname{CF}_4 + \operatorname{CO}_2$$
 (1,-1)

Li.¹ The reaction was carried out in a flow system over a nickel catalyst between 300 and 650° and a platinum catalyst between 1000 and 1200°. An attempt was also made to approach the equilibrium position from the right-hand side with mixtures of CF_4 and CO_2 at 1000 and 1100°. In a subsequent paper Li² assumed that equilibrium had been established at 650° and reported $\Delta H_1 = +26 \,\mathrm{kcal \, mol^{-1}}$ over the temperature range 650-1200° from a conventional second-law plot; see the dashed line in Figure 1. This heat of reaction has been used to derive a value³ for $\Delta H_f^{\circ}(\text{COF}_2)$ in considerable excess to the value obtained from the heat of hydrolysis of COF_{2} .^{4,5} The use of the second-law method in the interpretation of the data of RL^1 on reaction 1, -1 has recently been severely criticized and it is concluded⁶ that a third-law treatment of the high-temperature data (obtained over the Pt catalyst) leads to the only valid thermodynamic interpretation of the system, with $\Delta H_1 = -12 \pm 3 \text{ kcal mol}^{-1}$. We report a reinvestigation of the reaction in a static system over a Pt catalyst.

The reaction vessel was a 1150-ml Pyrex glass cylinder, with a platinum wire running axially down the center, located *via* two Kovar seals at the ends. The reaction temperature was taken to be the temperature of the Pt wire, measured by means of its resistance. The exterior of the glass reactor was cooled with a stream of air to reduce any attack by COF_2 .

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Table I: Data on COF₂ Decomposition

Run	$\Delta P,~\%^a$	C	0F2	-Initial and fin	al pressures, m Fa	imC	02	<i>T</i> , °K	$- \log K_{eq}$	$\begin{array}{c} \Delta H_1^{\circ}(298^{\circ}\mathrm{K}),\\ \mathrm{kcal\ mol^{-1}} \end{array}$
6	2.9	33.1	29.6		1.23		1.26	545	2.754	+1.40
16	2.8	33.1	28.4		1.92		1.86	784	2.353	+0.735
15	2.6	33.1	28.2		2.05		2.03	854	2.280	+0.561
12	3.2	35.5	29.4		2.53		2.50	873	2.134	+0.004
14	3.7	32.9	26.5		2,60		2.56	905	2.025	-0.426
13	3.3	32.7	26.5		2.61		2.56	956	2.021	-0.433
11	2.6	28.2	27.4	4.03	3.94	3.91	3.84	992	1.697	-1.90
10	4.3	33.3	25.5		3.18		3.23	1017	1.802	-1.43
3	3.3	28.1	19.8		3.64		3.68	1053	1.467	-3.07
9	4.3	16.0	14.6	4.75	4.93	4.86	5.01	1066	0.935	-5.69
1	4.3	20.6	16.1		1.85		1.75	1075	1,904	-0.968
2	5.5	23.3	18.0		1.97		2.06	1126	1,901	-0.990
18	4.6	32.7	18.8		6.16		6.21	1168	0.967	-5.99
17	4.5	28.6	19.4	2.96	6.77	2.93	6.74	1202	0.918	-6.41
19	5.4	35.1	16.5		8.47		8.26	1215	0.589	-8.29
5	11	16.0	7.58	4.40	7.29	3.87	6.75	1314	-0.068	-12.8
4	9,3	24.6	6.24		7.55		7.53	1448	-0.166	-14.7
7	9.0			14.6	13.2	13.8	12.6	1036		
8	8.7			14.4	13.1	15.5	14.2	1173		

 $^{a} \Delta P$ is the percentage discrepancy in pressure between the initial and final total pressures. The run numbers indicate the sequence in which the experiments were carried out.



Figure 1. Log K_{eq} vs. $10^3/T$ °K for $2\text{COF}_2 \rightleftharpoons \text{CO}_2 + \text{CF}_4$: O, our data; \bigcirc , our data when CO₂ and CF₄ were also present initially; \Box , Ruff and Li's data, numbered as in ref 1. Runs 1-3, Ni catalyst, CO carrier gas. Runs 4-7, Pt catalyst. In all cases CO₂ was initially present. \blacksquare , runs 8 and 9, attempt to approach equilibrium from the reverse direction with CO₂ + CF₄ mixture. Run 9 was rejected.^{1,2} The dashed line corresponds to $\Delta H_1 = +26$ kcal mol⁻¹, and the solid line to $\Delta H_1 = +5$ kcal mol⁻¹.

 COF_2 , CF_4 , and CO_2 were Matheson Co. research grade. Their purity was checked mass spectrometrically, and in the case of COF_2 by the infrared spectrum;⁷ any CO_2 impurity in it was <1%. Products were analyzed by gas chromatography on a 125-cm silica gel column at 100°. COF_2 and CO_2 showed identical retention times and sensitivities due to the quantitative conversion of COF_2 to CO_2 on a silica gel column.⁸ The decrease in the number of moles of $(\text{COF}_2 + \text{CO}_2)$ because of reaction was equivalent to the number of moles of CF₄ formed, as required by the reaction stoichiometry. SiF₄ was detected as a minor product (<1%) mass spectrometrically.

There was reaction in 3 weeks at 545°K. At higher temperatures reaction was completed in about 1 week, and at the highest temperatures in about 1 day. Completion of reaction was established when there was no further change in the system with lapsed time. No apparent reaction was observed between CO₂ and CF₄ in 3 weeks. Our data are presented in Table I where K_{eq} is given by $[CO_2][CF_4]/[COF_2]^2$. All of the data are presented in Figure 1. The slope of the solid line corresponds to $\Delta H_1 = +5$ kcal mol⁻¹. The values of ΔH_1° given in Table I are obtained by the third-law method using the Gibbs energy functions.^{5,6} The corresponding values obtained from the RL data¹ are tabulated by SWS.⁶

There was a small loss in total pressure during reaction which increased at very high temperatures. A 3%discrepancy is within the range of our analytical procedures. RL¹ suggested that there is a significant reaction between COF₂ and Pt at high temperatures, which could account for the increasing loss in total pressure.

SWS⁶ concluded that true equilibrium may not have been reached at low temperatures, and our observations substantiate this. In high-temperature experiments

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Table II: The Thermochemical Data of Duus⁸

ΔH , ^{<i>a</i>} kcal mol ⁻¹	Fraction to COF ₂	ΔH_{i}° (fluorocarbon), ^b kcal mol ⁻¹	$\Delta H_{f}^{\circ}(\mathrm{COF}_{2}),$ keal mol ⁻¹
-160.3 ± 2.9	0.1178	$C_2F_4, -155 \pm 2^g$	-151 ± 23^{f}
-116.5 ± 4.6	0.202	$(1/n)(C_2F_4)_n, -199.16 \pm 1.07^c$	-155 ± 15
-209.9 ± 4.6	0.1163	C_3F_{6} , -263.4 ± 12.0^d	$-152 \pm 49'$
-271.8 ± 7.8	0.1156	$c-C_4F_8, -360.3 \pm 4(?)^e$	$-154 \pm 27(?)^{f}$

^a E.g., $\Delta H = -160.3 \pm 2.9 = 0.8822(\Delta H_2) + 0.1178(\Delta H_3)$. ^b $\Delta H_t^{\circ}(CF_4)$ and $\Delta H_t^{\circ}(CO_2)$ as in text. ^c Based on $\Delta H = -246.84 \pm 0.07$ kcal mol⁻¹ for C₂F₄(s, polymer) + 2F₂(g) $\rightarrow 2CF_4$ (g); see J. L. Wood, R. J. Lagow, and J. L. Margrave, J. Chem. Eng. Data, **12**, 255 (1967). Using $\Delta H = 247.92 \pm 0.07$ kcal mol⁻¹ for this reaction^{9a} lowers $\Delta H_t^{\circ}(COF_2)$ to -152 ± 15 kcal mol⁻¹. ^d From the heat of conversion³ $\Delta H = -20.6 \pm 6.0$ kcal mol⁻¹ for C₂F₄(g) $\rightarrow \frac{2}{3}C_3F_8$ (g). ^e Based upon $\Delta H = -25.15 \pm (?)$ for the conversion of C₂F₄(g) $\rightarrow \frac{1}{2}C_4F_8$ (g); see B. Atkinson and A. B. Trenwith, J. Chem. Soc., 2082 (1953). Duus³ gave $\Delta H = -24.7 \pm 6.8$ kcal mol⁻¹, which yields $\Delta H_t^{\circ}(cC_4F_8) = -359.4 \pm 17.6$ kcal mol⁻¹ and $\Delta H_t^{\circ}(COF_2) = -152 \pm 57$ kcal mol⁻¹. ^f Conversely, if $\Delta H_t^{\circ}(COF_2) = -153$ kcal mol⁻¹ is adopted, the data are consistent with $\Delta H_t^{\circ}(C_2F_4) = -155$ kcal mol⁻¹. ^f See ref 5.

when all three gases were present in the initial mixture, runs 17 (1202°K) and 5 (1314°K), the mass action ratio was observed to increase. It is probable that the catalytic reaction sites are effectively blocked at lower temperatures, so that the reaction is not able to move toward equilibrium. At 1273°K (run 8, Figure 1) RL¹ were able to approach the equilibrium position from the reverse direction with initial mixtures of CO₂ and CF₄, but at lower temperatures, runs 7 and 8 in Table I, we were not successful.

The third-law analysis of all the acceptable data at about 1200°K and above (RL's experiments¹ 4–8 and runs 4, 5, 17–19 in Table I) yields $\Delta H_1^{\circ}(298^{\circ}\text{K}) = -10.9 \pm 2.2$ (probable error) kcal mol⁻¹. We have

$$\Delta H_{f}^{\circ}(\text{COF}_{2}(\mathbf{g}), 298^{\circ}\text{K}) = -\frac{1}{2} \{ \Delta H_{1}^{\circ}(298^{\circ}\text{K}) - \Delta H_{f}^{\circ}(\text{CF}_{4}(\mathbf{g}), 298^{\circ}\text{K}) - \Delta H_{f}^{\circ}(\text{CO}_{2}(\mathbf{g}), 298^{\circ}\text{K}) \}$$

Taking⁹ $\Delta H_f^{\circ}(CF_4(g), 298^{\circ}K) = -223.0 \pm 0.5$ kcal mol⁻¹ and $\Delta H_f^{\circ}(CO_2(g), 298^{\circ}K)^5 = -94.054 \pm 0.011$ kcal mol⁻¹, a value for $\Delta H_f^{\circ}(COF_2(g), 298^{\circ}K) = -153.1 \pm 1.4$ kcal mol⁻¹ is obtained. The value derived from the heat of hydrolysis experiment is given in the JANAF tables⁵ as -151.7 ± 2 kcal mol⁻¹; this is subject to the uncertainty in $\Delta H_f^{\circ}(HF(aq))^{.9,10}$ Adjusting $\Delta H_f^{\circ}(HF(aq))^{.9,10}$ SWS⁶ gave $\Delta H_f^{\circ}(COF_2(g), 298^{\circ}K) = -153.2 \pm 0.20$ kcal mol⁻¹. These error limits are probably unrealistically small.

Duus³ reported thermochemical data on the reactions

$$C_2F_4 + O_2 \longrightarrow CO_2 + CF_4 \tag{2}$$

and

$$C_2F_4 + O_2 \longrightarrow 2COF_2 \tag{3}$$

and the corresponding reaction pairs with tetrafluoroethylene polymer, hexafluoropropylene, and perfluorocyclobutane. The fraction of fluorocarbon converted to COF_2 is $\sim 12\%$ in each case, except for the Teflon, where it is 20%. From the data we may obtain values for $\Delta H_t^{\circ}(\text{COF}_2)$. The computations are summarized in Table II. Due to the small percentage conversion to COF_2 the calculations are very sensitive to the heat terms involved, and the limits of error are large. Interestingly enough, however, the average value is -153 kcal mol⁻¹.

Although we have been unable significantly to improve upon the data of RL¹ obtained over 30 years ago, the results do substantiate the value for $\Delta H_f^{\circ}(\text{COF}_2)$ obtained from the hydrolysis experiment,⁴⁻⁶ and a value of $\Delta H_f^{\circ}(\text{COF}_2(\mathbf{g}), 298^{\circ}\text{K}) = -153 \text{ kcal mol}^{-1}$ is indicated, as recommended by SWS.¹¹

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Specific Rates in the Acid Dissociation-Ion Recombination Equilibrium of Dilute Aqueous Hydrazoic Acid at 25°

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Azide ion is often used in rate studies of both ligand substitution and redox reactions. For instance, a comparison of azide with thiocyanate as bridging groups in redox reactions of transition metal ions has shown