

## The Energy of the O-F Bond in Trifluoromethyl Hypofluorite

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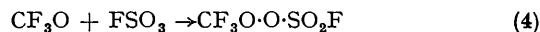
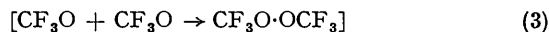
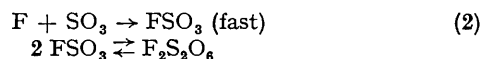
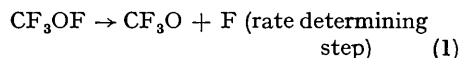
CADY,<sup>1</sup> by using the heat of formation of  $\text{CF}_3\text{OF}$  from its gaseous atoms and making certain assumptions for the C-F and C-O bond energies, obtained for the O-F bond-energy an estimated value of 47 kcal. By studying the kinetics of the thermal decomposition of  $\text{CF}_3\text{OF}$  in the presence of  $\text{SO}_3$ , we were able to determine this value exactly.

No direct reaction occurred between the two molecules. The  $\text{CF}_3\text{OF}$  decomposes in a unimolecular reaction, forming  $\text{CF}_3\text{O}$  radicals and F atoms. The F atoms reacted rapidly with  $\text{SO}_3$ , giving  $\text{FSO}_3$  (in equilibrium with its dimer,  $\text{F}_2\text{S}_2\text{O}_6$ ); the  $\text{CF}_3\text{O}$  radicals reacted with  $\text{FSO}_3$ , forming  $\text{CF}_3\text{O}\cdot\text{O}\cdot\text{SO}_2\text{F}$ , or with another  $\text{CF}_3\text{O}$  radical, forming the peroxide  $(\text{CF}_3\text{O})_2$ .

At temperatures above  $250^\circ$ , decomposition reactions, which led to the formation of  $\text{SO}_2\text{F}_2$ ,  $\text{O}_2$ , and  $\text{COF}_2$ , could be observed. However, at lower temperatures these reactions were too slow to affect the results.

With sufficiently high concentrations of  $\text{FSO}_3$ , which could be obtained by adding a certain amount of  $\text{F}_2\text{S}_2\text{O}_6$  before the reaction, the formation of  $(\text{CF}_3\text{O})_2$  could be almost completely suppressed. At  $200$ – $230^\circ$ , with  $\text{SO}_3$  pressures from 10 to 70 torr and  $\text{CF}_3\text{OF}$  pressures from 50 to 600 torr, 20–40 torr of  $\text{F}_2\text{S}_2\text{O}_6$  were needed. The only product formed under these conditions was  $\text{CF}_3\text{O}\cdot\text{O}\cdot\text{SO}_2\text{F}$  (>97%).

We were therefore able to determine the specific rate constants for the unimolecular decomposition of  $\text{CF}_3\text{OF}$  with high accuracy by simple pressure measurements.



$$\begin{aligned} \text{for } [\text{FSO}_3] \gg [\text{CF}_3\text{O}]: \\ -d[\text{CF}_3\text{OF}]/dt = d[\text{CF}_3\text{O}\cdot\text{O}\cdot\text{SO}_2\text{F}]/dt \\ = k_1[\text{CF}_3\text{OF}] \end{aligned}$$

In this pressure range the rate constants are weakly pressure dependent. By extrapolation to infinite pressure the values of  $k_{1\infty}$  at  $200$ ,  $220$ , and  $230^\circ$  were obtained. From the temperature coefficient of  $k_{1\infty}$ , the heat of activation, that is, the energy of dissociation of the O-F bond was calculated:

$$\begin{aligned} k_{1\infty} &= 2.5 \times 10^{14} \exp \left( - \frac{43,500 \pm 500}{RT} \right) \text{sec.}^{-1} \\ D_{\text{CF}_3\text{O-F}} &= 43.5 \pm 0.5 \text{ kcal.} \end{aligned}$$

(Received, August 5th, 1968; Com. 1083.)

<sup>1</sup> R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 5628.