The Energy of the O–F Bond in Trifluoromethyl Hypofluorite

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CADY,[1] by using the heat of formation of CF_3OF 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 CF_3OF in the presence of SO_3, we were able to determine this value exactly.

No direct reaction occurred between the two molecules. The CF_3OF decomposes in a unimolecular reaction, forming CF_3O radicals and F atoms. The F atoms reacted rapidly with SO_3, giving FSO_3 (in equilibrium with its dimer, $F_2S_2O_6$); the CF_3O radicals reacted with FSO_3, forming $CF_3O{\cdot}O{\cdot}SO_2F$, or with another CF_3O radical, forming the peroxide $(CF_3O)_2$.

At temperatures above 250°, decomposition reactions, which led to the formation of SO_2F_2, O_2, and COF_2, could be observed. However, at lower temperatures these reactions were too slow to affect the results.

With sufficiently high concentrations of FSO_3, which could be obtained by adding a certain amount of $F_2S_2O_6$ before the reaction, the formation of $(CF_3O)_2$ could be almost completely suppressed. At 200—230°, with SO_3 pressures from 10 to 70 torr and CF_3OF pressures from 50 to 600 torr, 20—40 torr of $F_2S_2O_6$ were needed. The only product formed under these conditions was $CF_3O{\cdot}O{\cdot}SO_2F$ (>97%).

We were therefore able to determine the specific rate constants for the unimolecular decomposition of CF_3OF with high accuracy by simple pressure measurements.

$$CF_3OF \rightarrow CF_3O + F \text{ (rate determining step)} \qquad (1)$$

$$F + SO_3 \rightarrow FSO_3 \text{ (fast)} \qquad (2)$$

$$2\,FSO_3 \rightleftarrows F_2S_2O_6$$

$$[CF_3O + CF_3O \rightarrow CF_3O{\cdot}OCF_3] \qquad (3)$$

$$CF_3O + FSO_3 \rightarrow CF_3O{\cdot}O{\cdot}SO_2F \qquad (4)$$

for $[FSO_3] >> [CF_3O]$:

$$-\,d[CF_3OF]/dt = d[CF_3O{\cdot}O{\cdot}SO_2F]/dt = k_1[CF_3OF]$$

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° 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:

$$k_{1\infty} = 2{\cdot}5 \times 10^{14} \exp\left(-\frac{43{,}500 \pm 500}{RT}\right) \text{sec.}^{-1}$$

$$D_{CF_3O-F} = 43{\cdot}5 \pm 0{\cdot}5 \text{ kcal.}$$

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[1] R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 5628.