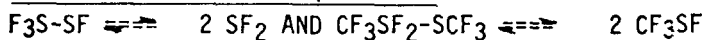


THE UNUSUAL CHEMICAL EQUILIBRIA



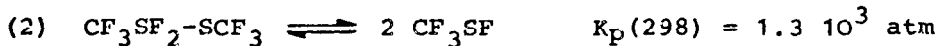
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In order to understand more about the instability of sulfur difluoride, we have investigated the chemical interrelations between each of the monomers SF_2 and CF_3SF and the corresponding dimers F_3SSF and $CF_3SF_2SCF_3$. Thus we have found that SF_2 and CF_3SF exist in chemical equilibria with their dimers. These equilibria are unusual because they involve two different bonds (S-F and S-S). The equilibrium constants and dissociation enthalpies have been determined by i.r. and mass spectroscopic measurements.



$$\Delta H_{298}^{\circ} = 68.5 \text{ kJ/mol}$$



$$\Delta H_{298}^{\circ} = 42.5 \text{ kJ/mol}$$

The equilibrium between F_3SSF and SF_2 is disturbed by a decomposition reaction of these compounds yielding SF_4 and SSF_2 . In both systems (1) and (2) the achievement of the

equilibrium is comparatively slow at -30 to 30 °C. The rates for dissociation and decomposition are strongly surface-dependent and the kinetics of the two processes have been studied separately. Under favorable conditions the half-lives at 298 K for the dissociation of F_3SSF and $CF_3SF_2SCF_3$ are found to be ca. 8.h and ca. 2 h, respectively, and for the decomposition of SF_2 to SF_4 and SSF_2 and CF_3SF to CF_3SF_3 and CF_3SSCF_3 ($p \approx 13$ mbar) the values are ca. 10 h and 1 year respectively.