Stepwise Bond Dissociation Energies for the Removal of Fluorine from Thionyl Fluoride and Sulphuryl Fluoride

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Summary Detailed energy balance studies of the single-collision chemiluminescent reactions of metastable strontium atoms with thionyl fluoride and sulphuryl fluoride yield the bond dissociation energies $D_o ^{(FSO-F)} = 362 \pm 19$, $D_o ^{(SO-F)} = 337 \pm 106$, $D_o ^{(FSO_2-F)} = 379 \pm 18$, and $D_o ^{(SO_2-F)} = 229 \pm 20 \text{kJ mol}^{-1}$.

Thionyl fluoride (SO\textsubscript{2}F\textsubscript{2}) and sulphuryl fluoride (SO\textsubscript{2}F\textsubscript{2}) are examples of 'hypervalent' compounds\textsuperscript{4} in which the central (sulphur) atom forms more bonds than the octet rule permits. As such, their stepwise bond dissociation energies are of more than just thermodynamic interest since such information can increase our understanding of the chemical bonding in these species. Recently, we have completed a determination of the stepwise bond dissociation energies for sulphur hexafluoride and sulphur tetrafluoride. We report here the results for thionyl fluoride and sulphuryl fluoride using the same technique.

A beam of metastable strontium atoms traverses a scattering chamber filled with SO\textsubscript{2}F\textsubscript{2} or SO\textsubscript{2}F\textsubscript{2} at a pressure so low (typically $2 \times 10^{-5}$ Torr) that the electronically excited SrF products make no collision before radiating. The chemiluminescence is collected and spectroscopically analysed using a 1-m spectrometer. By resolving the SrF$^*$ chemiluminescent spectrum (Figure), the highest populated internal state of the product is identified.

The assumption is made that in some collisions the maximum reaction exothermicity appears in the SrF$^*$ product. Moreover, when the SrF$^*$ is populated in its highest internal state, the internal energy ($E_{\text{int}}$) in the other reaction products as well as in the final relative translational energy ($E_{\text{trans}}$) of the two collision partners can be neglected. Then detailed energy balance yields equation (1), where $n = 1$ or 2.

$$D_o ^{(FSO_n-F)} = D_o ^{(SrF)} - E_{\text{int}}(SrF) + E_{\text{int}}(Sr) + E_{\text{trans}}(SO_nF_2) + E_{\text{trans}}(SO_2F_2)$$

Combining these data with the known\textsuperscript{4} heats of formation of SO, SO\textsubscript{2}, F\textsubscript{2}, SO\textsubscript{2}F\textsubscript{2}, and SO\textsubscript{2}F\textsubscript{2} permits the second S-F bond energy to be determined: $D_o ^{(SO-F)} = 337 \pm 106 \text{kJ mol}^{-1}$ and $D_o ^{(SO_2-F)} = 229 \pm 20 \text{kJ mol}^{-1}$. The large uncertainty in $D_o ^{(SO-F)}$ reflects the corresponding uncertainty in $\Delta H_{\text{f}}^{\circ}(SOF)$.

For thionyl fluoride, there appear to be no measurements of $D_o ^{(FSO-F)}$ and $D_o ^{(SO-F)}$. For sulphuryl fluoride the only other reported value for $D_o ^{(FSO_2-F)}$ is an indirect measurement based on the shock tube study of SO\textsubscript{2}F\textsubscript{2} decomposition, made by Wray and Feldman.\textsuperscript{5} Using Rice-Ramsperger-Kassel (RRK) theory to analyse their kinetic data, these authors found two possible fits, involving different pre-exponential factors and numbers of active oscillators. These two fits gave the values 339 and 397 \text{kJ mol}^{-1} for the FSO\textsubscript{2}-F bond energy. Wray and Feldman rejected the latter value because the fit was poorer.

However, Benson\textsuperscript{6} suggested that the pre-
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