

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_0^\ominus (FSO-F) 362 ± 19 , D_0^\ominus (SO-F) 337 ± 106 , D_0^\ominus (FSO₂-F) 379 ± 18 , and D_0^\ominus (SO₂-F) 229 ± 20 kJ mol⁻¹

THIONYL FLUORIDE (SOF₂) and sulphuryl fluoride (SO₂F₂) are examples of 'hypervalent' compounds¹ 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.² 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 SOF₂ or SO₂F₂ at a pressure so low (typically 2×10^{-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_{int}) in the other reaction products as well as in the final relative translational energy ($E_{\text{trans}}^{\text{f}}$) of the two collision partners can be neglected. Then detailed energy balance yields equation (1), where $n = 1$ or 2. Using the known² dissociation

$$D_0^\ominus (\text{FSO}_n\text{-F}) = D_0^\ominus (\text{SrF}) - E_{\text{int}}(\text{SrF}) + E_{\text{int}}(\text{Sr}) + E_{\text{int}}(\text{SO}_n\text{F}_2) + E_{\text{trans}}^{\text{f}} \quad (1)$$

energy, D_0^\ominus (SrF), of strontium monofluoride, the value of the internal energy of the SrF* product, E_{int} (SrF), found from the Figure, and estimated^{2,3} values of the initial translational and internal energies of the reactants, we find that D_0^\ominus (FSO-F) = 362 ± 19 kJ mol⁻¹ and D_0^\ominus (FSO₂-F) = 379 ± 18 kJ mol⁻¹. Combining these data with the known⁴ heats of formation of SO, SO₂, F₂, SOF₂, and SO₂F₂ permits the second S-F bond energy to be determined. D_0^\ominus (SO-F) = 337 ± 106 kJ mol⁻¹ and D_0^\ominus (SO₂-F) = 229 ± 20 kJ mol⁻¹. The large uncertainty in D_0^\ominus (SO-F) reflects the corresponding uncertainty in ΔH_0^\ominus (SOF₂).

For thionyl fluoride, there appear to be no measurements of D_0^\ominus (FSO-F) and D_0^\ominus (SO-F). For sulphuryl fluoride the only other value reported for D_0^\ominus (FSO₂-F) is an indirect measurement based on the shock tube study of

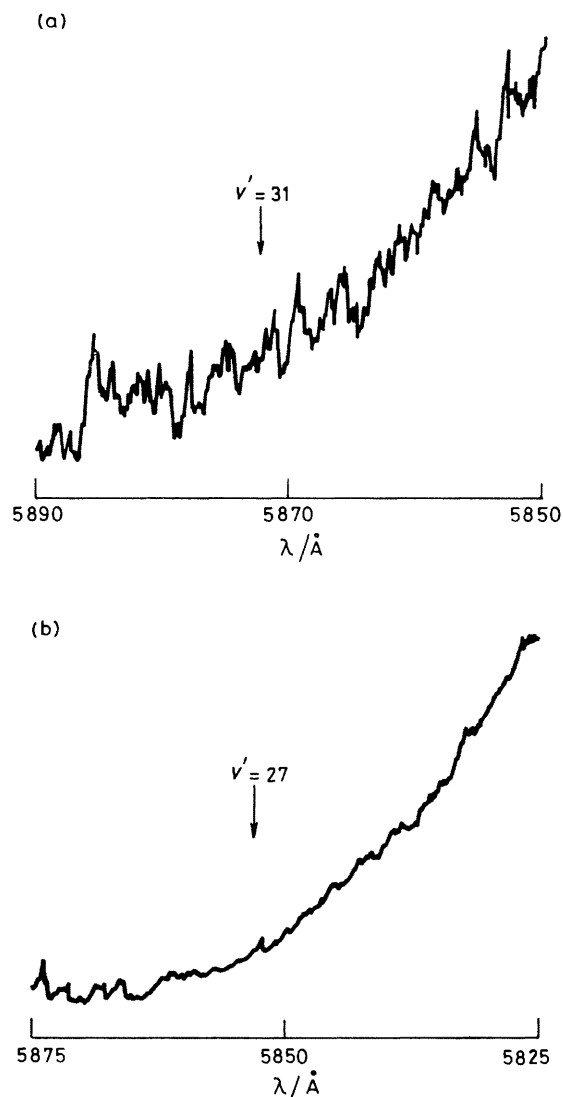


FIGURE Short wavelength portion of the SrF B-X chemiluminescent spectrum for the reactions (a) Sr(³P) + SOF₂ and (b) Sr(³P) + SO₂F₂. Arrows mark the highest vibrational level populated.

SO₂F₂ decomposition, made by Wray and Feldman⁵. 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 kJ mol⁻¹ for the FSO₂-F bond energy. Wray and Feldman rejected the latter value because the fit was poorer. However, Benson⁶ suggested that the pre-

exponential factor was too small for either fit and estimated instead a value of 418 kJ mol^{-1} . Our value of $D_0^\ominus(\text{FSO}_2\text{-F}) = 379 \pm 18 \text{ kJ mol}^{-1}$ also argues against the interpretation offered by Wray and Feldman.

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¹ J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 54.

² T. Kiang and R. N. Zare, *J. Am. Chem. Soc.*, 1980, **102**, 4024.

³ T. Kiang, Ph.D. thesis, Stanford University, Stanford, California, 1980.

⁴ 'JANAF Thermochemical Tables,' ed. D. R. Stull, Dow Chemical Co., Midland, Michigan, 1965.

⁵ K. L. Wray and E. V. Feldman, *J. Chem. Phys.*, 1971, **54**, 3445.

⁶ S. W. Benson, *Chem. Rev.*, 1976, **78**, 25.