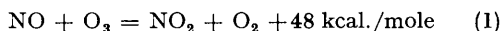


Kinetics of the Chemiluminescent Reaction between Sulphur Monoxide and Ozone

By C. J. HALSTEAD and B. A. THRUSH

(University of Cambridge, Department of Physical Chemistry)

FEW gaseous transfer reactions yielding electronically excited molecules are known.¹ The simple bimolecular reaction (1) has recently² been

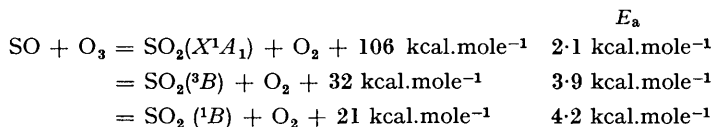


shown to have an activation energy of 2.4 kcal.mole⁻¹ to yield ground-state NO₂ and 4.2 kcal.mole⁻¹ to yield electronically excited NO₂.

The reaction between sulphur monoxide and ozone yields electronically excited SO₂ in the ³B and ¹B states.³ SO was generated in a weak r.f. discharge through SO₂ in an argon carrier and its concentration determined by gas-phase titration with NO₂.⁴ It was found to undergo a simple bimolecular reaction with ozone, with higher activation energies to yield electronically excited SO₂ than to yield SO₂ in its electronic ground state.

factor of the reaction yielding electronically excited SO₂ in the ¹B state to be *ca.* 4 × 10¹¹ cm.³ mole⁻¹sec.⁻¹ as compared with 2 × 10¹² cm.³ mole⁻¹ sec.⁻¹ for the formation of ground-state SO₂. For the NO + O₃ reaction the corresponding factors are *ca.* 3 × 10¹¹ and 6 × 10¹¹ cm.³ mole⁻¹ sec.⁻¹; it is clear that the formation of ground-state and electronically excited products in both these reactions occur by *separate potential surfaces* involving barriers with different heights.

Since the SO + O₃ reaction must proceed *via* triplet potential surfaces, the ³B and ¹B states may well be formed *via* the same potential surface. The small, but real, difference in the activation energies of the ³B and ¹B emissions is then attributed to a small positive temperature coefficient for quenching the ³B state. Quenching of the ¹B



Even at the lowest pressures used (0.3 mm.Hg), electronically excited SO₂ is removed mainly by collisional quenching. Data on this process are limited,⁵ but we estimate the pre-exponential

emission should not show more than a T¹ dependence since at least one of the species present (SO₂) quenches the ¹B state at almost every collision.⁵

(Received, April 28th, 1965.)

¹ D. W. Setser and B. A. Thrush, *Nature*, 1963, **200**, 864.

² M. A. A. Clyne, B. A. Thrush, and R. P. Wayne, *Trans. Faraday Soc.*, 1964, **60**, 359.

³ C. J. Halstead and B. A. Thrush, *Nature*, 1964, **204**, 992.

⁴ M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, in course of publication.

⁵ K. F. Greenough and A. B. F. Duncan, *J. Amer. Chem. Soc.*, 1961, **83**, 555.