Kinetics of the Chemiluminescent Reaction between Sulphur Monoxide and Ozone

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FEW gaseous transfer reactions yielding electronically excited molecules are known.[1] The simple bimolecular reaction (1) has recently[2] been

$$NO + O_3 = NO_2 + O_2 + 48 \text{ kcal./mole} \quad (1)$$

shown to have an activation energy of 2·4 kcal.-mole^{-1} to yield ground-state NO_2 and 4·2 kcal.-mole^{-1} to yield electronically excited NO_2.

The reaction between sulphur monoxide and ozone yields electronically excited SO_2 in the ^3B and ^1B states.[3] SO was generated in a weak r.f. discharge through SO_2 in an argon carrier and its concentration determined by gas-phase titration with NO_2.[4] It was found to undergo a simple bimolecular reaction with ozone, with higher activation energies to yield electronically excited SO_2 than to yield SO_2 in its electronic ground state.

$$\begin{array}{lll} & & E_a \\ SO + O_3 & = SO_2(X^1A_1) + O_2 + 106 \text{ kcal.mole}^{-1} & 2{\cdot}1 \text{ kcal.mole}^{-1} \\ & = SO_2(^3B) + O_2 + 32 \text{ kcal.mole}^{-1} & 3{\cdot}9 \text{ kcal.mole}^{-1} \\ & = SO_2(^1B) + O_2 + 21 \text{ kcal.mole}^{-1} & 4{\cdot}2 \text{ kcal.mole}^{-1} \end{array}$$

Even at the lowest pressures used (0·3 mm.Hg), electronically excited SO_2 is removed mainly by collisional quenching. Data on this process are limited,[5] but we estimate the pre-exponential factor of the reaction yielding electronically excited SO_2 in the ^1B state to be *ca.* 4×10^{11} cm.^{3} mole^{-1}sec.$^{-1}$ as compared with 2×10^{12}cm.^{3} mole^{-1} sec.$^{-1}$ for the formation of ground-state SO_2. For the $NO + O_3$ reaction the corresponding factors are *ca.* 3×10^{11} and 6×10^{11} 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 $SO + O_3$ 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 emission should not show more than a $T^{\frac{1}{2}}$ dependence since at least one of the species present (SO_2) quenches the ^1B state at almost every collision.[5]

(*Received, April 28th*, 1965.)

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