The Mechanism of the Chemiluminescent Reaction between Nitric Oxide and Ozone

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MOST chemiluminescent reactions have complex mechanisms which are not fully understood. One of the very few systems having simple kinetics is the bimolecular reaction between nitric oxide and ozone which yields electronically excited and ground state NO_2 by separate paths

$$NO + O_3 = NO_2{}^* + O_2 \qquad (1a)$$

$$NO + O_3 = NO_2 + O_2 \qquad (1b)$$

$$NO_2{}^* = NO_2 + h\nu \qquad (2)$$

$$M + NO_2{}^* = NO_2 + M \qquad (3)$$

Previous investigation[1] established that reaction (1a) had an activation energy of 4180 ± 300 cal./mole., whereas the overall reaction in which reaction (1b) predominates has $k_{1a} + k_{1b} = 5{\cdot}7 \times 10^{11} \exp(-2460 \pm 150/\boldsymbol{R}T)$ cm.^{3} mole^{-1} sec.$^{-1}$.

In that work neither the total extent of infrared radiation by $NO_2{}^*$ nor the relative importance of radiation and quenching (k_2/k_3) could be determined. These quantities, which are needed to obtain the absolute value of k_{1a}, have recently been measured by us using a large capacity flow reactor fitted with multiple reflection mirrors to study the reaction at pressures between 5 and 60 microns Hg. Prism monochromators were used with a cooled PbS cell or a 9558B photomultiplier as detector.

At moderate resolution and chemiluminescence is pseudo-continuous, with an intensity distribution given in the Table. Above $2{\cdot}5\mu$, the electronic emission is overlapped by overtone vibration–rotation emission of NO_2. This distribution resembles the NO_2 emission in the air afterglow, but is shifted to longer wavelengths by about 8000 cm.$^{-1}$ which is close to the difference between the energies available from the $O + NO$ and $O_3 + NO$ reactions.

TABLE *Relative intensity distribution of* $NO + O_3$ *chemiluminescence.*

I(in quanta/unit wavelength/sec.) λ (in microns)

λ	I	λ	I	λ	I
0·58	0	0·95	84	1·7	78
0·6	0·7	1·0	100	1·8	67
0·65	3	1·1	121	1·9	58
0·7	9	1·2	126	2·0	49
0·75	21	1·3	118	2·2	33
0·8	36	1·4	109	2·4	20
0·85	52	1·5	101	2·6	10
0·9	70	1·6	88	2·9	0

The absolute intensity was found by comparison with the intensity of the air afterglow[2] using a conventional flow tube. At high pressures ($k_2 \ll k_3$[M]), the emission intensity is found to be

$$I = 0{\cdot}26 \pm 0{\cdot}04\ [NO][O_3]/[M]\text{sec.}^{-1}$$

at 293°K for $M = O_2$.

At lower pressures, the emission intensity can be expressed in the Stern–Volmer form

$$k_{1a}\frac{[NO][O_3]}{I} = 1 + \sum_{m} \frac{k_{3m}[M]}{k_2}$$

Plots of $[NO][O_3]/I$ against [M] for various added gases are good straight lines confirming the proposed mechanism, and yielding the following half-quenching pressures, which are independent of the wavelength of emission:—

NO_2, 3·7μ; NO, 5·2μ; O_2, 8·3μ; Ar, 13μ Hg

The relative values agree with those[3] for the NO_2 fluorescence excited by the Hg 4358 Å line; the lower absolute values found here are consistent with the lower probability of radiating quanta of lower frequency.

The above data, when combined, yield, a value of $k_{1a} = 5{\cdot}7 \times 10^8$cm.^{3}mole^{-1}sec.$^{-1}$ at 293°K. Using the previously determined activation energy for the emission,[1] and making the very reasonable assumption that the ratio k_2/k_3 is independent of temperature, this yields

$k_{1a} =$

$7{\cdot}6 \times 10^{11} \exp(-4180/\boldsymbol{R}T)$ cm.^{3}mole^{-1}sec.$^{-1}$

the overall rate expression then gives

$k_{1b} =$

$4{\cdot}3 \times 10^{11} \exp(-2330/\boldsymbol{R}T)$cm.^{3}mole,$^{-1}$sec.$^{-1}$

both for the range 216 to 322°K.

Thus the pre-exponential factors of reactions (1a) and (1b) which yield respectively electronically excited and ground state NO_2 are the same within experimental error. There was no evidence of the formation of electronically excited molecular oxygen in our work. The excited state of NO_2 populated in this work is almost certainly the linear or near-linear $^2B_1$ state which correlates with the same $^2\Pi$ state of NO_2 in a linear configuration as does the $^2A_1$ ground state.[4] The degeneracy associated with electronic orbital angular momentum in ground state NO means that $NO(^2\Pi) + O_3(^1A_1)$ yields two doublet potential surfaces, one of which correlates with $NO_2(^2A_1) + O_2(^3\Sigma_g^-)$ and the other with $NO_2(^2B_1) + O_2(^3\Sigma_g^-)$. The difference in barrier heights presumably arises from the two possible orientations of the singly occupied π-orbital to the O–N · · · O plane in the transition state, just as this determines the relative energies of the lowest states of NO_2.

Herschbach *et al.*,[5] have calculated a pre-pre-exponential factor of $4{\cdot}4 \times 10^{11}$cm.^{3}mole^{-1} sec.$^{-1}$ for this reaction assuming all the bond angles in the transition state to be 120°. We find that this value would be virtually unchanged with an O–N · · · O bond angle of 180°. Thus similar pre-exponential factors are accurately predicted for the formation of NO_2 in its bent $^2A_1$ ground state and its linear or near linear $^2B_1$ first excited state.

Unexpected results have been obtained in attempts to determine oxygen atom profiles in the upper atmosphere using the air afterglow produced when nitric oxide is released from rockets. The $NO + O_3$ chemiluminescence should be easily observed in such experiments at slightly lower altitudes where ozone predominates. This would provide a useful test of the nitric oxide release method, since unlike the air afterglow from O + NO, the behaviour of the $NO + O_3$ reaction at low pressures is well understood.

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