the Hokkaido University Computing Center and Miss K. Ushiki for their help in data analysis.

* Contribution Number 1246 from the Chemical Laboratories of Indiana University.

† We wish to thank the U. S. Air Force Office of Scientific Research, the U. S. Atomic Energy Commission, and the U. S. Educational Commission in Japan for their support of this work.

[1] F. Momany, T. Iijima, M. Williams, and R. A. Bonham (to be published).

[2] D. Kohl and M. Williams (to be published).

[3] One of us (RAB) wishes to thank the students in his Advanced Quantum Mechanics class for calculating the analytical functions for the elastic and inelastic scattering factors used in this analysis.

[4] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1949), p. 221.

[5] T. Iijima, R. A. Bonham, and T. Ando, J. Phys. Chem. **67**, 1472 (1963).

[6] R. A. Bonham and T. Iijima, J. Phys. Chem. **67**, 2266 (1963).

[7] T. Iijima and R. A. Bonham, Acta Cryst. **16**, 1061 (1963).

[8] T. Iijima and R. A. Bonham, J. Phys. Chem. **67**, 2769 (1963).

Reconsideration of the Rate Constants from the Thermal Decomposition of Ozone

SIDNEY W. BENSON

Stanford Research Institute, Menlo Park, California

AND

ARTHUR E. AXWORTHY

Rocketdyne Division, North American Aviation Inc. Canoga Park, California

(Received 20 November 1964)

FROM our investigation of the thermal decomposition of ozone,[1,2] we were able to determine the first quantitative values for the rate constants in the atomic mechanism

$$M+O_3 \underset{2}{\overset{1}{\rightleftarrows}} M+O_2+O, \qquad (1, 2)$$

$$O+O_3 \xrightarrow{3} 2O_2, \qquad (3)$$

where $(M)=(O_3)+A_{O_2}(O_2)+A_{N_2}(N_2)+$etc. Other investigators have since obtained independent values for these rate constants and, in some cases, the measurements were obtained by more direct methods (see Ref. 3 for a review). The fair agreement of these values with ours strongly supports our contention that this simple atomic mechanism includes all of the important processes in the thermal decomposition of purified ozone.

It has been shown[2,4-6] that the results of Kistiakowsky[7,8] on the photolysis of ozone by red light are in disagreement with this mechanism. Evidence was found for energy chains (quantum yields Φ, greater than 2), and the value obtained for k_2/k_3 at 25°C was higher by a factor of 2.2. However, Castellano and Schumacher[9] have recently reinvestigated the red-light photolysis and their results are now in excellent agreement with the pyrolysis mechanism. Their data give linear plots for $1/(\Phi)$ vs $(M)(O_2)/(O_3)$ with intercepts of 0.5 (corresponding to a maximum value of $\Phi=2.0$). The values of k_2/k_3 at 25°C obtained from the slopes differ from those obtained from the extrapolated pyrolysis constants by only 25%. The temperature coefficient of k_2/k_3 gives $E_3-E_2=5.4$ kcal/mole, in fair agreement with the thermal value of 6.6. Remarkably enough, Castellano and Schumacher obtained values for the efficiencies of various third bodies in Reaction (2) which are in almost exact agreement with the values which we calculated[2] from the pyrolysis data (of Glissmann and Schumacher[10]). These efficiencies obtained from the photolysis are for O_3, He, N_2, O_2, and CO_2 in the ratio 1.0: 0.34: 0.39: 0.44: 0.96, respectively, compared with our values of 1.0: 0.34: 0.41: 0.44: 1.06. They also report a value for argon of 0.25 which compares favorably with the value of 0.29 which we derived[2] from the pyrolysis results of Riesenfeld and Wassmuth[11] and with the value of 0.27 which one obtains from the recent work of Jones and Davidson[12] using our value of 0.41 for A_{N_2}. It thus appears that the mechanisms of the pyrolysis and long-wavelength photolysis of ozone are definitely established.

Only two rate constants can be measured in the thermal decomposition of ozone, k_1 and k_1k_3/k_2 (or k_3/k_2). We believe our limits of error on these at 90°C are not greater than 5% and 12%, respectively.[2] However, the values which we reported for k_2 and k_3 are derived from these measured constants using literature values[13] for the equilibrium constant for Reaction (1, 2) and, therefore, their accuracies will be dependent upon the accuracy of the thermodynamic data.

Kaufman[3] has suggested that our value for k_1 should be changed to reflect the newer value[14] for $H_f°(298)$ of $O(^3P)$ which is 59.56 kcal/mole, but this correction would apply only to the derived constants k_2 and k_3. Using this value (even though there is still considerable uncertainty in the enthalpy of formation of ozone[15]), the expressions for $K_{equil}=k_1/k_2$ (evaluated at 363°K) and $k_2[M=O_2]$ become $6.8\times10^4\exp(-24\,890/RT)$ mole/liter and $2.96\times10^7\exp(+890/RT)$ liter^2/mole^2·sec, respectively. This gives a value for k_2 at 25°C of 1.33×10^8 which is in fair agreement with the values obtained in more recent investigations of the pyrolysis of ozone.[15] We find $k_3=3.37\times10^{10}\exp(-5700/RT)$ liter/mole·sec.

Kaufman and Kelso[15] have measured a value for k_2 of 2.7×10^8 liter/mole·sec by reacting O atoms and oxygen directly. They believe this value is not in error by more than 30%. This value of k_2 is compatible with our measured value of k_1 even though it is larger than our derived value of k_2 by a factor of 2 since (1) the uncertainty in K_{equil} is a factor of 2.0 (+0.4 kcal/mole), (2) the uncertainty in E_1 introduces an uncertainty factor of 1.13, and (3) the value of A_{O_2} which is used in deriving k_2 is uncertain by a factor of 1.20. It is possible, however, that Kaufman and Kelso's value is

Downloaded 16 Oct 2008 to 169.232.48.36. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp

too high since they must subtract a fairly large amount of wall reaction and they assume the wall reaction is independent of oxygen. This really must be demonstrated independently.

Some investigators[16,17] prefer a value of A_{O_2} of about 0.33 rather than our value of 0.44. Both values have been calculated from the same experimental data.[10] It would appear that our weighted-average technique[2] should lead to the more reliable value. However, the observation of Zaslowsky *et al.*[17] that the decomposition of concentrated ozone [where Reaction (2) is negligible] is almost exactly second-order over the first 35% decomposition favors the lower value. The higher value would predict measurable deviation beyond about 20% reaction. The recent photolysis results,[9] of course, verify the value of 0.44. The difference between these two sets of values of A_{O_2} is not particularly significant since it has been shown[2] that it is inherently impossible to obtain a value for A_{O_2} with an uncertainty of less than $\pm 20\%$ from pyrolysis data.

[1] S. W. Benson and A. E. Axworthy, J. Chem. Phys. **26**, 1718 (1957).
[2] A. E. Axworthy, Ph.D. dissertation, University of Southern California, 1959 (University Microfilm, Ann Arbor, Michigan-L.C. Card No. M.C. 59–1837).
[3] F. Kaufman, Progr. Reaction Kinetics, **1**, 1 (1961).
[4] A. E. Axworthy and S. W. Benson, Advan. Chem. Ser. **21**, 308 (1959).
[5] H. J. Schumacker, J. Chem. Phys. **33**, 938 (1960).
[6] S. W. Benson, J. Chem. Phys. **33**, 939 (1960).
[7] G. B. Kistiakowsky, Z. Physik. Chem. **117**, 337 (1925).
[8] H. J. Schumacker, J. Am. Chem. Soc. **52**, 2377 (1930).
[9] E. Castellano and H. J. Schumacker, Z. Physik. Chem. **34**, 198 (1962).
[10] A. Glissmann and H. J. Schumacker, Z. Physik. Chem. **21B**, 323 (1933).
[11] F. H. Riesenfeld and E. Wassmuch, Z. Physik. Chem. **A143**, 397 (1929).
[12] W. M. Jones and N. Davidson, J. Am. Chem. Soc. **84**, 2868 (1962).
[13] "Selected Values of Chemical Thermodynamic Properties" Natl. Bur. Std. (U.S.) Circ. No. 500. Values presented below are from JANAF Interim Thermochemical Tables.
[14] P. Brix and G. Herzberg, J. Chem. Phys. **21**, 2240 (1953).
[15] F. Kaufman and J. R. Kelso, J. Chem. Phys. **40**, 1162 (1964).
[16] E. S. Campbell and C. Nudelman, AFOSR TN-60-502, NYU.
[17] J. A. Zaslowsky, H. B. Urbach, F. Leighton, and R. J. Wnuk, J. Am. Chem. Soc. **82**, 2682 (1960).

Vibraluminescence of CO_2 and N_2O in Active Nitrogen

E. L. MILNE AND M. STEINBERG
G. M. Defense Research Laboratories, Santa Barbara, California
AND
H. P. BROIDA*
Department of Physics, University of California Santa Barbara, California

(Received 17 November 1964)

THE addition of CO_2 and N_2O to active nitrogen produces a considerable heat release which has been attributed to an enhanced degradation of vibrationally excited N_2 ($X\ ^1\Sigma_g^+$) molecules.[1] On mixing CO_2 or N_2O in a stream of active nitrogen, Legay and Barchewitz observed emission in the corresponding 4.3- or 4.5-μ bands of the added gases.[2] Since the vibrational fundamental of ground-state N_2 at 2331 cm^{-1} is in near resonance with the modes of CO_2 and N_2O with vibrational fundamentals at 2349 and 2224 cm^{-1}, respectively, it was suggested that the excitation was a result of vibration–vibration exchange. In the present investigation (1) the excitation of the infrared-active gases was studied in the Lewis–Rayleigh, orange, and pink afterglows of N_2, and (2) a series of experiments was carried out to identify the source of the excitation of CO_2 and N_2O in the active nitrogen.

In the initial experiments prepurified N_2 was used in a fast-flow system in which an electrodeless discharge was maintained in a de Laval nozzle (1-mm orifice) in a 13-mm-o.d. Pyrex tube. The discharge was powered by a 2450-Mc/sec 125-W magnetron supply coupled to a $\frac{1}{4}$ wave coaxial cavity.[3] Twelve centimeters from the nozzle the flow tube opened into the side (near the upstream end) of a 30-mm-o.d. reaction chamber. Added gases could be mixed in the chamber or a few centimeters ahead of the chamber. Radiation was collected through a CaF_2 window, sealed to the upstream end of the reaction chamber, and focused on the entrance slit of a monochromator equipped with a CaF_2 prism and an InSb or Au:Ge detector.

Addition of small amounts of CO_2 caused strong quenching of the N_2 pink afterglow[4] and produced strong emission in the CO_2 4.3-μ band. The CO_2 4.3-μ radiation also was produced strongly in the N_2 orange afterglow which precedes the pink region, and less strongly in the Lewis–Rayleigh afterglow. The peak of the CO_2 emission was shifted toward the long-wavelength side of the 4.3-μ atmospheric absorption bands, as was noted in Ref. 2.

Since the products of a nitrogen discharge include a mixture[5] of N atoms, vibrationally and electronically excited molecules, and ions, a series of experiments was designed to distinguish between these possibilities as the source of the CO_2 excitation. High-purity He and Ar were pumped through a discharge in the nozzle. The addition of CO_2 to these gases failed to produce any detectable infrared excitation. By adding N_2 after the discharge, we excited N_2 molecules to the $N_2^+(B\ ^2\Sigma_u^+)$ and $N_2^+(X\ ^2\Sigma_g^+)$ electronic states by metastable He[6] and to the $N_2(C\ ^3\Pi_u)$, $N_2(B\ ^3\Pi_g)$, and $N_2(A\ ^3\Sigma_u^+)$ electronic states by discharged Ar[7]. Adding CO_2 to nitrogen excited to these electronic states failed to produce any detectable CO_2 4.3-μ radiation.

In a second experimental arrangement, discharged N_2 and mixtures of N_2 in He or Ar (designed to increase the $[N]/[N_2]$ concentration ratios) were passed through a glass-wool plug to deplete the concentration of vibrationally excited $N_2(X\ ^1\Sigma_g^+)$ molecules (i.e., $N_2^\dagger$).[8] NO was added to these gases just upstream of

Downloaded 16 Oct 2008 to 169.232.48.36. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/jcp/copyright.jsp