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The Thermal Decomposition of Ozone in a Shock Tube[1]

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The thermal decomposition of ozone in argon and nitrogen inert gases has been studied in a shock tube. The important reactions are R1 and R3.

R1, R2 $M + O_3 \leftrightharpoons M + O_2 + O$

R3 $O + O_3 \longrightarrow O_2 + O_2$

In the concentration and temperature range studied—argon 0.00334 to 0.0264 mole/l., 769 to 910°K.; nitrogen 0.00902 to 0.01285 mole/l., 689 to 863°K.—R1 is a unimolecular reaction at its low pressure second order limit with $k_{1N_2}/k_{1A} = k_{2N_2}/k_{2A} = 1.54 \pm 0.17$. Combining the shock tube data for $M = N_2$ with data in the range 303 to 383°K., due to Glissman and Schumacher and reinterpreted by Benson and Axworthy, gives $k_{1N_2} = (5.8 \pm 0.6) \times 10^{11} \exp(-23{,}150 \pm 300/RT)$(mole/l.)$^{-1}$ sec.$^{-1}$ and $k_{2N_2} = (9.4 \pm 1) \times 10^6 \exp(+1700 \pm 300/RT) = 2.0 \times 10^7 (1000/T)^{1.66}$(mole/l.)$^{-2}$ sec.$^{-1}$. The k_1 data are discussed in terms of the Slater and Hinshelwood–Rice–Ramsperger–Kassel (HRRK) theories. Interpretation of the data by the classical HRRK theory gives $2.8_3 \pm 0.2$ effective oscillators and a collision efficiency of 0.039. The values of k_3 obtained are consistent with an extrapolation of previous low temperature data. Vibrationally excited oxygen molecules with from 10 to 17 vibrational quanta, produced by the strongly exothermic R3 involving O(^{3}P) atoms, were detected by flash absorption spectra.

Introduction

Several investigations have been made of the thermal decomposition of ozone, from slightly above room temperature to 565°K. Without attempting a discussion of all this work[3] and of the evolution of thought regarding the mechanism, we follow Benson and Axworthy[4] in accepting reactions R1, R2 and R3 as providing a satisfactory explanation of the homogeneous thermal decomposition. Reaction R4 is included, although it is unimportant in all previous work and in the present work.

R1, R2 $O_3 + M \leftrightharpoons O_2 + O + M$ $\Delta E_0^0 = 24.35$ kcal.

R3 $O + O_3 \longrightarrow O_2 + O_2$ $\Delta E_0^0 = -93.6$ kcal.

R4 $O + O + M \longrightarrow O_2 + M$

With the steady state assumption for O atoms, eqs. R1, R2 and R3 yield the rate law E1

$$\text{(E1)} \qquad -\frac{d(O_3)}{dt} = \frac{2k_1(M)(O_3)}{1 + \frac{k_2}{k_3}\frac{(M)(O_2)}{(O_3)}}$$

An important contribution has been made by BA in reviewing earlier work, in studying the thermal decomposition of ozone at 99.8° and particularly in reanalyzing the extensive data of Glissman and Schumacher[5] in the range 70 to 110° on the decomposition of ozone and on the effect of inert gases. Under the conditions of that work,[4,5] extending up to pressures of almost one atmosphere, BA have concluded that R1 is a unimolecular reaction at its low pressure limit. The data give k_1 and k_1k_3/k_2. Equilibrium data give k_1/k_2, so that all three rate constants are determined. BA fitted k_1, k_2 and k_3 to Arrhenius equations and gave the efficiencies of O_2, N_2, CO_2 and He relative to O_3 for reactions R1 and R2. Some recent data[6] on k_1 for pure ozone are in general agreement with the conclusions of BA.

Garvin[7] studied the decomposition of ozone in excess nitrogen from 430 to 565°K. using a flow technique. His measurements yield values of k_1k_3/k_2.

It was of interest for several reasons to extend information on this system to the temperatures available with the shock tube. R1 is interesting as a unimolecular reaction involving a polyatomic molecule with a minimum number of vibrational degrees of freedom. The magnitude and temperature coefficients of rate constants of recombination reactions such as R2 have been of considerable recent interest. Moreover, renewed interest attaches to R3 as a result of the important work of McGrath and Norrish[8-10] (hereafter referred to as MN). They have observed oxygen molecules with from 12 to 17 vibrational quanta in the flash photolysis of ozone in ozone–nitrogen mixtures at room temperature. These molecules are presumably the products of the strongly exothermic R3. Since some ^{1}D oxygen atoms were almost certainly present in their system,[9,10] it was desirable to search for such excited molecules in a system where the O atoms, produced by R1, would be in their ^{3}P ground state. MN have again raised the question as to whether excited products of R3 might destroy further ozone, perhaps through short energy chains. This possibility has previously been considered in the thermal[5] and especially in the photochemical decomposition of ozone.[11]

The relationship among R1, R2 and R3 in the shock tube work is somewhat different from that in previous work. The oxygen atom concentration in the previous work is determined by a steady state involving R1 and, in general, both R2 and R3.

(1) This paper was presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959.

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(3) For earlier work on dilute solutions of ozone in oxygen see (a) S. Jahn, *Z. anorg. Chem.*, **48**, 260 (1906), and (b) R. C. Tolman and O. R. Wulf, *J. Am. Chem. Soc.*, **49**, 1650 (1927).

(4) S. W. Benson and A. E. Axworthy, Jr., *J. Chem. Phys.*, **26**, 1718 (1957). Hereafter referred to as BA.

(5) A. Glissman and H. J. Schumacher, *Z. physik. Chem.*, **21B**, 323 (1933).

(6) J. A. Zaslowsky, H. B. Urbach, F. Leighton, R. J. Wnuk and J. Wojtowicz, *J. Am. Chem. Soc.*, **82**, 2682 (1960).

(7) D. Garvin, *ibid.*, **76**, 1523 (1954).

(8) W. D. McGrath and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **242A**, 265 (1957).

(9) W. D. McGrath and R. G. W. Norrish, *Nature*, **182**, 235 (1958).

(10) W. D. McGrath and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **254A**, 235 (1960).

(11) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941.

This gives rise to the rate law E1. In the shock tube work R1 and R3 are the most important reactions in the experimentally available time. The atom concentration is not in a steady state, so that E1 is not applicable, and one can observe as a function of time the transition from a situation in which essentially only R1 is occurring to one in which R1 and R3 are proceeding at approximately equal rates.

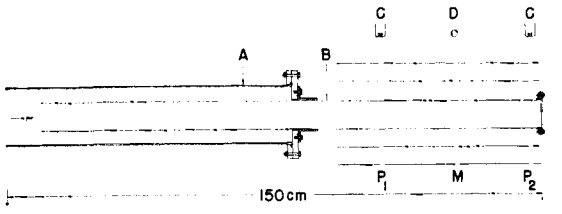
Experimental

General.—General characteristics of the shock wave method of studying reactions have been described elsewhere.[12,13] Dilute mixtures of ozone in argon or nitrogen were shocked to the desired temperature using H_2 or He driver gases. The initial ozone mole fraction in shocks evaluated for kinetic data varied from 4.83×10^{-4} to 1.87×10^{-2} for ozone–argon and from 1.38×10^{-3} to 1.93×10^{-3} for ozone–nitrogen. Total concentrations of shocked gas varied from 3.34×10^{-3} to 2.64×10^{-2} moles liter^{-1} for ozone–argon and from 9.02×10^{-3} to 1.285×10^{-2} moles liter^{-1} for ozone–nitrogen. Temperatures of shocked gas varied from 769 to 910°K. for ozone–argon and from 689 to 863°K. for ozone–nitrogen. Ozone concentration was observed spectrophotometrically as a function of time. The temperature and density of the shocked but unreacted gas were calculated from the measured shock velocity and the known state of the gas before arrival of the shock wave. This calculation was facilitated by tables obtained with an IBM-704 computing code made available to us by Dr. R. E. Duff of Los Alamos. Correction was made for departure of the initial temperature of the gas from that on which the tables were based. Thermodynamic data were taken from the NBS tables,[14] but corrections were made for the new dissociation energy of oxygen.[15] The N_2 was taken to be vibrationally unrelaxed. The vibrational relaxation of pure nitrogen[16] is long compared to the reaction time.

Instrumentation.—The 6" i.d. driver section was 9 feet long and was separated by a cellulose acetate membrane from a 10 foot long, 6" i.d. low pressure section of aluminum pipe and Pyrex pipe. The Pyrex was joined by an O-ring seal to a section of 3" i.d. fused quartz (Fig. 1), which permitted the measurement of ozone concentration by ultraviolet spectrophotometry. The various distances in Fig. 1 gave adequate time for observation of the once-shocked gas. Dural collars at the center and right hand end of the quartz piece fitted closely, were stabilized symmetrically with shim stock, and then cemented to the quartz with Epibond No. 202 resin (Furane Plastics, Los Angeles 39, Calif.). The quartz wall thickness was about 2 mm. For aerodynamic purposes a taper was ground onto the outside of the wall of the quartz tube where it intercepted the shock wave.

The slit system has been previously described.[17] One mm. slits were used. The measured shock velocity was the average value over a 40 cm. interval. *Schlieren* optics and a trigger circuit were used to start and stop the 1.6 megacycle Potter time intervalometer and to start the delaying sweep of a 531 Tektronix oscilloscope. After a suitable delay the main sweep of the 531 started, and the associated plus gate signal was used to start the sweep of a Tektronix 512 oscilloscope on which a parallel spectrophotometric record was taken. In order to estimate attenuation, the shock velocity was also determined for the first 20 cm. of the 40 cm. interval by utilizing the known delay and the duration of the 531 trace before arrival of the shock wave.

The light source for ozone spectrophotometry was an Osram HBO-200 high pressure DC mercury arc, operated from batteries. Light passed through the shock tube into a 500 mm. focal length Bausch and Lomb grating monochromator with a 600 grooves per mm. grating and 33 Å. per mm. dispersion. Light which could not enter the monochromator was excluded from the shock tube as much as possible. For most runs the monochromator was set at 2485 Å., corresponding to a maximum output of the HBO-200-photomultiplier combination and close to the ozone absorption maximum around 2550 Å. In measurements at and above 0.4% ozone the monochromator was set at 2975 Å. The transmitted light had a triangular profile with a base of 66 Å. at 2975 Å. and a trapezoidal profile with bases of 66 and 132 Å. at 2485 Å. Calculations based on the room temperature absorption spectrum indicated negligible error in the rate constants due to the finite spectral width. The signal from a 1P28 photomultiplier at the output of the monochromator went to the Tektronix 531 and 512 oscilloscopes operated in parallel. The output load resistor of the photomultiplier was 5 K and the RC time of the signal input circuit was about 0.6 μs. In many shocks measurements of light emission from a defined section of the shock tube were made with a 1P28 photomultiplier and 512 oscilloscope.



A PYREX PIPE, 15cm I.D.
B FUSED SILICA TUBE, 7.5 cm I.D.
C TUNGSTEN LAMPS
D Hg ARC
M MONOCHROMATOR
P_1, P_2 PHOTOMULTIPLIERS

Fig. 1.—Measurement end of shock tube; the fused silica tube intercepts the shock wave coming from the left.

In the flash absorption spectrograms of decomposing ozone the light of an Edgerton, Germeshausen, and Grier FX-3 flash lamp passed through a defined section of the quartz shock tube and was focussed with a quartz lens on the slit of a Bausch and Lomb medium quartz spectrograph. A 1/2 μfd. condenser charged to 12 kv. was discharged through the lamp. The spread of the light beam corresponded to 3 μs laboratory time or 9 μs molecule time. Eastman III-O plates were used. The relative unfiltered light intensity of the FX-3 was measured with a 1P28 photomultiplier and 531 oscilloscope (with appropriately triggered and delayed sweep) and was known as a function of time following passage of the shock wave past the position of spectroscopic observation. The lamp intensity rose to a maximum in about one microsecond. The main portion of the light decayed approximately exponentially with a 4 μs half life. There may be a long duration tail with an intensity about 1% of the maximum intensity.

Reagents.—Ozone was prepared from Matheson research grade oxygen (stated maximum impurity limits: CO_2 0.1%, CO 0.01%, A 0.01%, N_2 0.01%, H_2 0.01%) in a high vacuum system from which mercury vapor was excluded with a liquid nitrogen trap. The oxygen was passed through Ascarite and P_2O_5, condensed in liquid nitrogen and then vaporized into the ozonizer system. Stopcocks were kept to a minimum and greased with Kel-F No. 90 with no evidence of reaction. Convective circulation in the ozonizer was maintained by passing one limb of the circulation loop through a styrofoam dewar containing liquid nitrogen. The circulation greatly increased the rate of ozone formation. Ozone was condensed at the exit of the ozonizer with liquid nitrogen. Oxygen was thoroughly pumped off and the ozone stored at liquid nitrogen temperature. No explosions occurred.

Linde argon (stated to be 99.99% pure, 20 p.p.m. O_2, 20 p.p.m. H_2, principal impurity N_2) and Linde high purity dry nitrogen (0.01% O_2, traces of rare gases and CO_2) were used.

O_3–A and O_3–N_2 mixtures were prepared and stored in a 22-liter Pyrex bulb which was protected from light by a black cloth. Mixtures were prepared as follows. Ozone was

(12) T. Carrington and N. Davidson, *J. Phys. Chem.*, **57**, 418 (1953).

(13) D. Britton, N. Davidson and G. Schott, *Discussions Faraday Soc.*, **17**, 58 (1954).

(14) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., Series III (1954).

(15) P. Brix and G. Herzberg, *J. Chem. Phys.*, **21**, 2240 (1953); *Can. J. Phys.*, **32**, 110 (1954).

(16) V. Blackman, *J. Fluid Mechanics*, 1, 61 (1956).

(17) D. Britton, N. Davidson, W. Gehman and G. Schott, *J. Chem. Phys.*, **25**, 810 (1958).

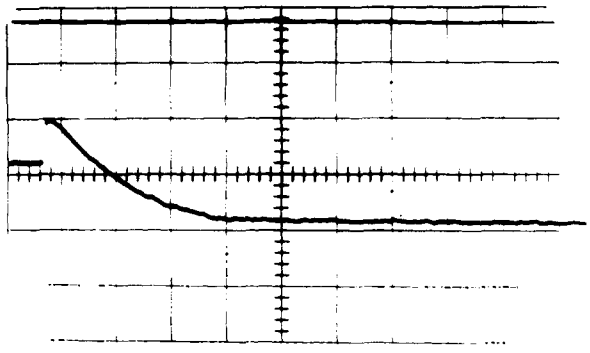


Fig. 2.—Oscilloscope trace of shock 15; writing rate 20 μs./cm. Downward deflection means increasing light intensity.

vaporized into a one-liter bulb. The pressure was measured on a sulfuric acid manometer. It was usually 100 to 400 mm. of acid. The stopcock to the one-liter bulb was then closed, the ozone was condensed with liquid nitrogen in a side arm of the bulb and the small line volume evacuated. A residual pressure in the 1-liter bulb, usually about 0.3 mm. of sulfuric acid, was then measured, and this gas was pumped off. The ozone was then condensed into a side arm on the 22-liter bulb. The inert gas was then bled into the 22-liter bulb, after slow passage through Ascarite, P_2O_5, and two Dry Ice–trichloroethylene traps. The liquid nitrogen was removed from the side arm and the ozone and inert gas were allowed to mix. The final total pressure, usually 130 cm., was measured on a mercury manometer. A cardboard cylinder was then placed on top of the bulb and Dry Ice added to it in order to promote convective mixing. One to two hr. were sufficient. Samples were withdrawn and analyzed for ozone on a Cary spectrophotometer at 2500 Å.

Procedure.—The shock tube was pumped down to a pressure of about 0.3 micron. Ozone-inert gas mixture was admitted to the shock tube, the pressure and the temperature were measured, H_2 or He was added to the driver section, and the stressed membrane was pierced to initiate the shock. The contact time of the ozone with the shock tube was about four minutes. The ozone mixture was analyzed on a Cary spectrophotometer shortly before a shock was to be run. This measurement, with the known pressure, the length of light path in the shock tube and the oscilloscope trace deflection before arrival of the shock wave, allowed prediction of I_0, the oscilloscope deflection after complete decomposition of the shocked ozone. Agreement was within experimental error. In a few cases where complete decomposition was not observed the calculated I_0 was used in data evaluation.

Results

Evaluation of k_1 in Dilute Mixtures.—Figure 2 shows an oscilloscope record of transmitted light intensity *versus* time. The usual procedure was to draw a smooth curve through a large scale plot of the record, evaluate d log $(OD)/dt_{scope}$ as a function of time and extrapolate this quantity to $t = 0$, which was taken to be the midpoint of the sharp rise in the trace which indicates arrival of the shock front. The quantity OD is the optical density, log (I_0/I). At ozone concentrations of 0.2% and less, E2 was then used to obtain k_1.

$$(E2) \quad k_1 = \frac{2.303}{\Delta^2 C_0} [\mathrm{d} \log (OD)/dt_{scope}]_0$$

For such mixtures corrections do not have to be made for changes in temperature, extinction coefficient and density, due to reaction. Strictly, the ozone concentration rather than the optical density should be used in E2, but there is no distinction if the extinction coefficient is constant. The total concentration before shock arrival is C_0 and

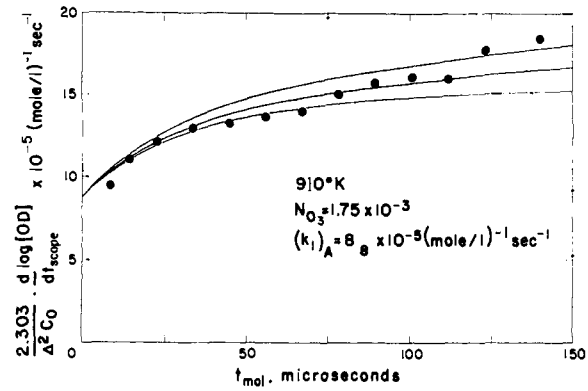


Fig. 3.—Data from shock 15. OD is the optical density. The intercept at zero time is k_1. The meaning of the three curves is discussed in the text.

Δ is the density compression ratio across the shock front. The time on the scope trace since the shock wave passed the observation slit is t_{scope}. Because the shocked gas is flowing, the gas being observed at time t_{scope} has been in the shocked state for a longer time, which we call molecule time, t_{mol} and which is equal to $\Delta \cdot t_{scope}$. Especially in the fastest reactions, a rounding of the trace in the immediate neighborhood of the shock front prevented utilization of this data. The rounding is due to some combination of electronics rise time, bow and tilt of the shock front, and vibrational relaxation. There is no evidence for a systematic difference between values of k_1 obtained from fast and slow reactions. No correction was made for scattered light (0.6% of I_0 at 2485 Å.), which had less than 1% effect on k_1.

Right behind the shock front ozone disappears only by R1. As the oxygen atom concentration rises, R3 sets in. If R1 and R3 are the only reactions, the atom concentration reaches an approximate steady state determined by them, and the fractional rate of disappearance of ozone, $\alpha = \mathrm{d} \ln(O_3)/dt$, approaches approximately twice the initial value. This situation is illustrated in Fig. 3, based on the trace of Fig. 2 (Shock 15). After practically all of the ozone has decomposed, first R4 and then R2 compete with R3 for O atoms. R2 and R4 are of negligible importance in our work.

Fig. 3 contains three calculated curves. The lowest curve was calculated (with the aid of a computing code[18] made available to us by Dr. R. E. Duff, Los Alamos) for an ideal non-attenuating shock wave for the k_1 obtained by extrapolation and k_2 obtained as discussed later. R2, R4 and R5 (discussed later) were included in the calculation, but they are not important. For this curve, the ratio of α to its initial value was calculated (see next section) to approach 1.7 rather than 2. The departure from 2 is almost entirely due to the inapplicability of the steady state approximation. At the end of the experimental period in Fig. 3, the calculated oxygen atom concentration is ap-

(18) R. E. Duff, *J. Chem. Phys.*, **28**, 1193 (1958). The Duff code, for use with an IBM 704 computer, integrates the differential equations of chemical kinetics subject to the conditions of a steady state shock wave. Concentrations of all species, temperature, density, etc. are calculated as a function of time when rate constants, initial conditions at the shock front, and shock velocity are specified.

preciable and amounts to about one-fifth of the initial ozone concentration in the shocked gas.

The middle curve in Fig. 3 is corrected for the effect on k_1 of the progressive increase in temperature of gas behind the shock front in an attenuating shock.[19] The top curve contains an additional and more uncertain correction to k_1 for a calculated temperature rise due to boundary layer interaction.[19,20] In Fig. 3 the attenuation was taken to be 0.34% decrease in shock velocity per 10 cm. length of 3'' i.d. shock tube, corresponding to the average for argon shocks with 0.2% O_3 or less. (This estimate of attenuation is reasonable, but it has an uncertainty almost equal to itself.) The attenuation averaged 1.0% for nitrogen shocks, and 1.7% for the E-series argon shocks. Considering the uncertainties in the experimental points in Fig. 3, especially at longer times, and the effects of shock wave non-ideality, there seems to be no reason to doubt that R1 and R3 are the principal reactions removing ozone. The values of k_1 in the dilute runs and of k_3 are not corrected for the non-ideal effects. The resulting error in k_1 is negligible, and the error in k_3 is probably not large compared to other sources.

Evaluation of k_1 above 0.2 Mole Per Cent. Ozone.—With argon as the inert gas several shocks were made with ozone mole fractions of 0.004 or greater (the E-series of Table I). At these higher ozone mole fractions the above extrapolation procedure becomes increasingly uncertain since the rate of R3 approaches that of R1 too rapidly. Although the steady state approximation for R1 and R3 becomes better, k_1 cannot be obtained in a simple way. Corrections must be made for changes in temperature and density and for vibrational relaxation, as discussed below.

As will be discussed later, it is likely that one of the O_2 products of R3 has high vibrational excitation, so that R3 can be written as R3'. The relaxation of O_2* to oxygen with an equilibrium vibrational distribution is written as R5. It is assumed

R3' $\quad O + O_3 = O_2^* + O_2$

R5 $\quad O_2^* + M = O_2 + M$

that the energy release of R3' which is not contained in O_2* is immediately utilized in raising the temperature of the gas, *i.e.* the second oxygen molecule product in R3' is effectively equilibrium oxygen.

The Duff code[18] was used to obtain k_1 in the E-series from data at appropriate times behind the shock front, as described below. Reactions R1, R3', R4, R5 and their reverses were considered in the code. α was obtained from the data at times sufficiently long that R1 and R3 were almost at a steady state, so that α was essentially independent of k_3. The times were not so long, however, that too great uncertainty was introduced, especially in the temperature, by the vibrational relaxation and by attenuation and boundary layer effects. It was found from the computing code that the observed α's at the above times should be divided by a factor f of approximately 2, the exact value depending on the experiment, in order to obtain the fractional rate of disappearance of O_3 at the shock front; k_1 was then calculated by E2. In the calculation of f a sufficiently accurate value of k_1 was known from the shocks on dilute mixtures; k_3 was known as discussed later; and k_4, to which the calculation of f is insensitive, was taken to be 2×10^9 (mole/l.)$^{-2}$ sec.$^{-1}$.[21]

In R5 it was sufficiently accurate to consider O_2* to have 16 vibrational quanta. If the vibrationally excited species relax stepwise such that $k_{v \to v-1} = vk_{10}$, then the internal energy relaxes in a simple exponential way with a time constant τ, even for an arbitrary initial distribution of O_2* among vibrational states.[22] Reaction 5 was used to simulate this relaxation of vibrational energy, and k_5 was derived from τ in a simple way. The values of τ for relaxation of oxygen by argon were taken to be one-third[23] of those for pure oxygen.[16] There is at present no experimental information on the deactivation rate of the high vibrational states. The indications are that anharmonicity would appreciably increase the rate.[24] The factor f was calculated for k_5 corresponding to τ and to $\tau/10$. The average f was used. Assuming that this procedure brackets the effect of the actual relaxation on the temperature, an average maximum uncertainty of 3% is introduced into the values of k_1 in the E-series. If the extreme assumption of instantaneous relaxation were made, the greatest resulting change would be for shock E-8, whose k_1 would become about two-thirds of that listed in Table I. A further correction, averaging about 10%, was made to f and thus to k_1 for the combined effects of attenuation and boundary layer interaction on the temperature of the gas. The values of k_{1A} in the E-series are in satisfactory agreement with the other values of k_{1A}, but they have a greater uncertainty.

Comparison with Other k_1 Data. Relative Efficiencies of Argon and Nitrogen.—Figure 5 gives plots of the shock tube and lower temperature data for N_2, according to E3 and E12. The low temperature values of k_{1N_2} were obtained by multiplying the values of k_1 for M = O_3 in BA's Fig. 4 by 0.41, the relative efficiency of N_2 compared to O_3 which was obtained by BA from their reanalysis of Glissman and Schumacher's data. The relative efficiency is believed by BA to be correct to 10%.[4] There are no published lower temperature data for ozone–argon. The line through the N_2 data in Fig. 4 corresponds to E12.

In general the quality of the nitrogen shocks was poorer than for the argon shocks, so that Figs. 4 and 5 may give a misleading impression as to the precision of k_{1N_2}. The fact that α increased from its value at the shock front to roughly three times this value by the end of the reaction, rather than by the expected factor of about two, as in argon, is further evidence for greater non-ideality of conditions well behind the shock front in nitrogen mix-

(19) M. Camac and A. Vaughan, Avco Research Report 84, December 1959, Avco Research Corporation, Everett, Mass.

(20) N. Rott and R. Hartunian, "On the Heat Transfer to the Walls of a Shock Tube," Cornell University Report, November, 1955.

(21) A. Vaughan and M. Camac, *Bull. Am. Phys. Soc.*, Series II, Vol. IV, 290 (1959).

(22) E. W. Montroll and K. E. Shuler, *J. Chem. Phys.*, **26**, 454 (1957).

(23) S. R. Byron, *ibid.*, **30**, 1380 (1959).

(24) (a) N. W. Bazley, E. W. Montroll, R. J. Rubin and K. E. Shuler, *ibid.*, **28**, 700 (1958); (b) **29**, 1185 (1958).

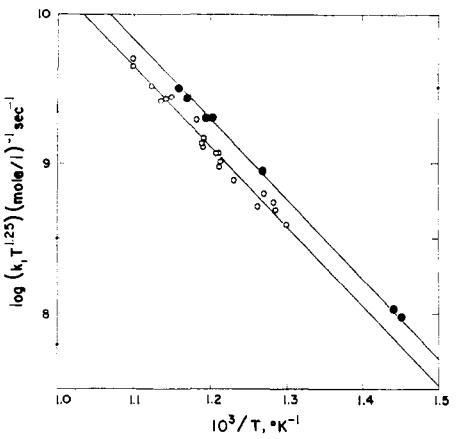


Fig. 4.—Plot of k_1 shock tube data. The line through the nitrogen points corresponds to E12. The line through the argon points is drawn parallel to the nitrogen line and is displaced from it by log 1.54 = 0.188; O, in ozone–argon; ●, in ozone–nitrogen.

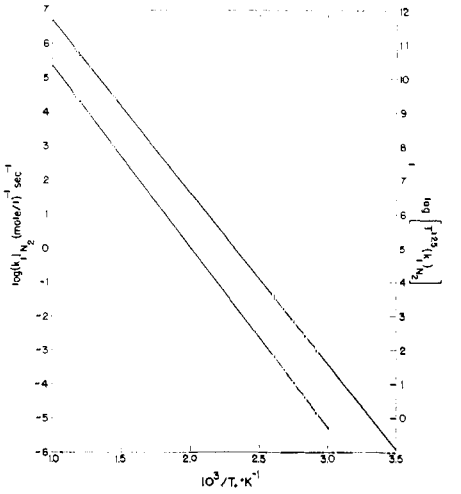


Fig. 5.—Shock tube and lower temperature[4,5] data on k_{1N_2}. The upper line and left hand ordinate correspond to E3. The lower line and right hand ordinate correspond to E12.

tures. However, the calculated effects of attenuation and boundary layer interaction are also larger and account, within the uncertainties, for the larger factor by which α increases in nitrogen shocks.

Each experimental value of k_{1A} was compared with k_{1N_2} calculated at the same temperature from E12 below. The average of the twenty values of k_{1N_2}/k_{1A} is 1.54 ± 0.17 (standard deviation of an individual value). The ratio of the relative velocities of approach is calculated from the masses to be 1.11. The experimental ratio may be compared with the value 1.49 ± 0.07 found by Volpe and Johnston[25] for the unimolecular decomposition of NO_2Cl at its low pressure limit at 203°, and the value 1.73 given by Johnston[26] for the decomposition of N_2O_5 at its low pressure limit at 50.5°.

The combined shock tube and lower temperature data are represented by E3, E4 and E5.

(25) M. Volpe and H. S. Johnston, *J. Am. Chem. Soc.*, **78**, 3903 (1956).

(26) H. S. Johnston, *ibid.*, **75**, 1567 (1953).

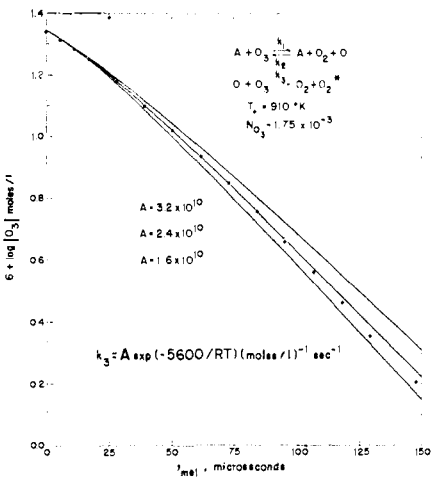


Fig. 6.—Plot of log O_3 *vs.* t for various k_3 in shock 15.

(E3) $k_{1N_2} = (5.8 \pm 0.6) \times 10^{11} \exp(-23{,}150 \pm 300/RT)$ (mole/l.)$^{-1}$ sec.$^{-1}$

(E4) $k_{2N_2} = (9.4 \pm 1) \times 10^6 \exp(+1700 \pm 300/RT) = 2.0 \times 10^7 (1000/T)^{1.63}$ (mole/l.)$^{-2}$ sec.$^{-1}$

(E5) $k_{1N_2}/k_{1A} = k_{2N_2}/k_{2A} = 1.54 \pm 0.17$

Other representations will be considered later. The temperature coefficient of k_{2N_2} is negative as is well established for the recombination of atoms. The shock tube values of k_{2N_2} would have to be increased by a factor of more than three in order to eliminate a negative temperature coefficient. E4 was obtained from E3 and the dissociation constants for the equilibrium R1, R2, corrected for the new dissociation energy of oxygen.[15] The uncertainty in the energy in the exponential term in E4 does not include an uncertainty of perhaps 250 calories in the heat of formation of ozone. Uncertainties in E3 and E4 include the effects of a 10% uncertainty in the relative efficiencies of nitrogen and ozone in R1 and R2.[4]

Determination of k_3.—Roughly speaking, k_3 determines the time dependence with which the rates of R1 and R3 tend to equality. Values of k_3 were determined by a curve fitting procedure.

Using k_1, determined for a given run as described, the Duff code was used to compute (O_3) as a function of time for various values of k_3. That k_3 was chosen which fit the experimental data best on a plot of $\log(O_3)$ *versus* time. This is illustrated in Fig. 6. R1, R3′, R4, R5 and their reverses were included in this calculation. R4 and R5 are unimportant, since the ozone mole fraction was always less than 0.002. The values of k_3 given in Table I were obtained from seven argon and four nitrogen shocks, selected for the quality of their oscilloscope traces. In the case of nitrogen k_3 was based on data pertaining to conditions closer to the shock front than in argon, because of the greater non-ideality of the nitrogen shocks.

The equation for k_3 given by BA, after correction for the new dissociation energy of oxygen,[15] is

(E6) $k_3 = (2.96 \pm 0.2) \times 10^{10} \exp(-5600 \pm 500/RT)$ (mole/l.)$^{-1}$ sec.$^{-1}$

The activation energy cannot be determined from our data. Taking the activation energy to be

TABLE I

RATE CONSTANTS FOR $M + O_3 \xrightarrow{k_1} M + O_2 + O$ AND $O + O_3 \xrightarrow{k_3} O_2 + O_2$

Shock	Temp., °K.	$N_{O_3} \times 10^3$ ozone mole fraction	$C_s \times 10^2$ total concn. shocked gas, M	log k_{1A} liter mole^{-1}	log k_3 sec.$^{-1}$
2	779	1.14	0.721	5.13	
3	841	1.58	1.230	5.48	
5	825	1.49	1.237	5.33	
6	840	1.42	1.227	5.51	
8	828	1.84	1.235	5.42	
10	827	2.06	0.778	5.42	8.89
11	871	1.57	2.145	5.77	
12	846	1.58	0.490	5.64	8.93
13	890	1.95	1.361	5.83	
14	778	1.80	2.640	5.09	
15	910	1.75	1.262	5.94	9.04
16	881	1.60	0.334	5.74	
17	769	0.503	2.480	4.99	8.80
18	840	.494	2.276	5.46	8.62
19	812	.534	2.183	5.25	8.59
20	876	.483	2.317	5.75	9.16
E 5	787	6.03	1.238	5.18	
E 8	910	18.7	1.445	6.00	
E11	792	4.87	1.873	5.09	
E13	824	4.97	2.350	5.37	
				log k_{1N_2}	
21	689	1.93	1.157	4.43	
22	788	1.64	1.285	5.33	8.88
23	831	1.64	0.910	5.66	8.98
24	837	1.49	.902	5.65	8.91
25	863	1.44	.942	5.83	8.96
26	855	1.43	1.074	5.77	
27	694	1.38	1.201	4.48	

5600 cal. and evaluating the pre-exponential factor from our values of k_3, we obtain

(E7) $k_3 = (2.4 \pm 0.5) \times 10^{10} \exp(-5600 \pm 500/RT)$ (mole/l.)$^{-1}$ sec.$^{-1}$

The uncertainty in the pre-exponential is the mean deviation. An uncertainty of $\pm 1 \times 10^{10}$ in the pre-exponential factor of E7 would be more conservative, since extreme values of 1.2×10^{10} and 3.6×10^{10} were obtained.

In the N_2 runs the rate of recombination of N_2 and O to give N_2O was considered, utilizing the work of Johnston[27] and of Harteck and Dondes,[28] and was estimated to be negligible compared to R3 except possibly at the end of the reaction. Since such a recombination might influence k_3, it is worth noting that values of k_3 for the four nitrogen shocks give an average pre-exponential of 2.6×10^{10} (mole/l.)$^{-1}$ sec.$^{-1}$ in E7, in agreement with the average value.

Garvin's[7] Fig. 1 would be essentially a plot of log $(2k_1k_3/k_2)$ *versus* $1/T$, if R1, R2 were in equilibrium. His values of k_1k_3/k_2 or of k_3 would then appear to be about a factor of two lower than those calculated from E6 or E7. However, Axworthy[29] has calculated that the oxygen atom concentration in Garvin's experiments averaged only about half the equilibrium value for R1, R2, so that Garvin's experiments are consistent with E6. The activation energy of k_3 obtained[14,15] from Garvin's data is 5600 ± 1300 cal.

The data on k_3 from the thermal decomposition thus seem to be in general agreement. Axworthy[29] has also shown that k_2/k_3 from the photolysis of ozone in red light at 17° (see ref. 40 below) is lower than calculated from the equations of BA by a factor of 2.2. This may represent agreement within the uncertainties.

A preliminary account has been given[30] of a determination of k_3 from low pressure flow experiments in the range 0 to 80°, involving oxygen atoms produced in an electric discharge. The data were represented by $k_3 = 4.26 \times 10^9 \exp(-3200/RT)$ (mole/l.)$^{-1}$ sec.$^{-1}$. At 850°K. this equation gives a value of k_3 which is 28% less than is given by E7. The shock wave experiments are not accurate enough to distinguish between these two values, and the extrapolation must in any case be uncertain. At 350°K., midway between the temperatures of Garvin's experiments and of those[4,5] from which E6 was deduced, the above equation[30] and E6 give $k_3 = 4.3 \times 10^7$ and 0.96×10^7 (mole/l.)$^{-1}$ sec.$^{-1}$, respectively. At 296°K. the corresponding values are 1.87×10^7 and 2.23×10^6 (mole/l.)$^{-1}$ sec.$^{-1}$. Eucken and Patat[31] photolyzed oxygen in a low pressure flow system with 1720 Å. light (which presumably gives one ^3P and one ^1D oxygen atom) and evaluated k_2/k_3 from the steady state ozone concentration. An extrapolation of Eucken and Patat's data to 850°K. gives a k_2/k_3 which is about 40% larger than obtained from E4 and E7. Their values of k_2/k_3 at 296°K. are about $1/8$ of those calculated from E4 and E6 and about twice those calculated from ref. 30. There are thus rather definite disagreements between the flow[30,31] and thermal experiments at the lower temperatures.

Extinction Coefficients.—Extinction coefficients of ozone in the shocked gas are shown in Fig. 7. The room temperature values were obtained by determination of the optical density of samples on a Cary spectrophotometer using a quartz absorption cell of 10 cm. length. The samples were taken from the storage bulb right after the mixing of the ozone–inert gas mixtures so that their composition was known. It was verified that there was no absorption by the argon or nitrogen due to possible impurities.

As expected from the effect of temperature on the population of vibrational levels, $d\epsilon/dT$ is slightly negative at 2485 Å., near the absorption maximum, and positive at 2975 Å., well away from the maximum. The decadic extinction coefficients at 25 ± 2° are 3060 ± 60 and 158 ± 3 (mole/l.)$^{-1}$ cm.$^{-1}$ at 2485 and 2975 Å., respectively. They agree with values of Inn and Tanaka[32] as well as can be determined from their graph. The extinction coefficients in argon and nitrogen at 2485 Å. are equal

(27) H. S. Johnston, *J. Chem. Phys.*, **19**, 663 (1951).

(28) P. Harteck and S. Dondes, *ibid.*, **22**, 758 (1954).

(29) A. E. Axworthy, Jr., Thesis, University of Southern California, Los Angeles, California, 1959.

(30) F. Leighton, H. B. Urbach, J. A. Wojtowicz and J. A. Zaslowsky, Paper 109, Division of Physical Chemistry, Abstracts of the 135th National Meeting of the American Chemical Society, Atlantic City, New Jersey, Sept. 13–18, 1959. See also Paper 110.

(31) A. Eucken and F. Patat, *Z. physik. Chem.*, **B33**, 459 (1936).

(32) E. C. Y. Inn and Y. Tanaka, *J. Opt. Soc. Am.*, **43**, 870 (1953).

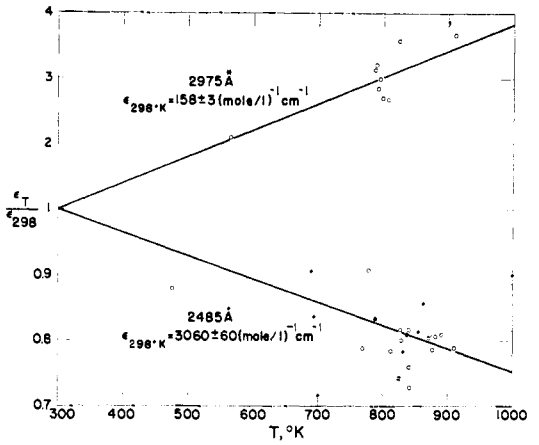


Fig. 7.—Extinction coefficients of ozone at 2485 and 2975 Å. O, in ozone–argon mixtures; ●, in ozone–nitrogen mixtures.

within experimental error, but the accuracy and magnitude of the temperature coefficient of ϵ are not sufficient to prove that the nitrogen was vibrationally unrelaxed at the shock front. The ϵ data were not used in the evaluation of rate constants. The largest correction (not actually made) would be to lower k_1 from shock E8 by about 2.5%, due to the variation of ϵ with temperature.

Vibrationally Excited Oxygen.—The strongly vibrationally excited oxygen molecules observed spectroscopically are probably produced by R3′, as suggested by MN.

Six flash absorption spectrograms were taken of ozone–argon mixtures decomposing in the shock tube. The ozone mole fraction varied from 0.015 to 0.020. In one spectrogram, F-4, the observed Schumann–Runge bands indicate the presence of oxygen molecules in the ground electronic state with vibrational quantum numbers v equal to 10, 11, 12, 13, 14, 15, and 16. Ozone absorption was not measured photoelectrically in the flash spectrogram shocks but calculations indicate that the average ozone concentration for the exposure of spectrogram F-4 was about 15% of the initial value. The maximum intensity (visual estimate) is at v = 12 or 13. Shock F-3 was similar to F-4.

In another shock, F-6, the average ozone concentration over the time of exposure was calculated to be 22% of the initial value. This plate showed the presence of v = 11, 12, 13, 14, 15, 16, and, very weakly, 17 (only the head of the (1,17) band was observed). The maximum intensity (visual estimate) is at v = 13 or 14. Comparison of F-6 with F-4 gives evidence of greater vibrational relaxation in F-4, as expected. Failure to observe v = 10 in F-6 might be partly due to the greater absorption by ozone in F-6 as compared to F-4. The effects of relaxation were much more strongly shown in F-1, F-2 and F-5, where spectra were taken when even more of the ozone had decomposed. F-1 and F-2 showed no bands, and F-5 showed only v = 10, 11, 12, and 13, with v = 12 strongest. The disappearance of the spectra when the ozone is gone also shows that the excited oxygen is not associated with recombination of oxygen atoms, which are at their highest concentration at the end of the reaction.

Table II gives a comparison of the wave lengths of observed band origins (or heads) with origins calculated from the equation of Curry and Herzberg.[33]

TABLE II

ORIGINS OF SCHUMANN-RUNGE BANDS[a]

(v', v'')	λ, Å. in air obsd.	λ, Å. in air calcd., C and H
(1, 10)	2813	2814.2
(0, 10)	2863	2869.7
(1, 11)	2925	2923.3
(0, 11)	2984	2983.4
(1, 12)	3040	3039.3
(0, 12)	3104.5	3104.2
(1, 13)	3165	3162.5
(0, 13)	3232.2	3232.9
(2, 14)	3224	3223.0
(2, 15)	3356	3356.8
(0, 14)	3369.7	3370.1
(0, 15)	3517.0	3516.6
(1, 16)	3583	3582.7
(0, 16)	3673	3673.2
(1, 17)	3759	3757.2

[a] Our measurements cannot distinguish heads from origins.

Several IBM calculations were made giving the concentrations of the vibrational states[34] to be expected as a function of time for various assumptions regarding the vibrational relaxation and the primary distribution of vibrationally excited species in R3′. These concentrations were then multiplied by relative optical transition probabilities for the Schumann-Runge (0,v″) sequence in order to permit comparison with visual estimates of the relative intensities in the spectrograms. The transition probabilities used were those calculated by Fraser, Jarmain and Nicholls,[35] but shifted towards lower quantum numbers by 1.5 numbers in order to be consistent with the measurements of Wurster and Treanor.[36] The maximum transition probability is around v = 13 or 14 and is important in determining the apparently most populous states. If a single vibrational state is produced by R3′, then this state is probably around v = 16. Production of relatively more species around v = 16 and 15 was not preferable to production of v = 16, 15, 14, 13 and 12 with equal probability. The calculations show that it would be necessary to take flash spectra of very short duration right behind the shock front in order for the spectra to be indicative of the primary distribution among vibrational states without complication by relaxation.

P and R branches of a given vibrational band were not resolved; a P branch line with rotational quantum number K of the lower rotational state is not resolved from the R branch line of quantum

(33) J. Curry and G. Herzberg, *Ann. der Physik, Series 5*, **19**, 800 (1934).

(34) Concentrations of vibrational states were calculated only down to v = 8; accumulation of v = 8 or rapid dumping to vibrationally equilibrated oxygen was shown to affect negligibly the concentrations of the higher vibrational states of interest.

(35) P. A. Fraser, W. R. Jarmain and W. Nicholls, *Astrophysical Journal*, **119**, 286 (1954).

(36) C. E. Treanor and W. H. Wurster, *J. Chem. Phys.*, **32**, 758 (1960).

number K + 4. The composite rotational intensity distribution in absorption was calculated[37] for 900° and 1000°K. The (0–13) band of the spectrogram of F-6 was microphotometered. Comparison with the calculations by the isointensity method gave a rotational temperature of 950 ± 50°K. An average temperature of 990 ± 20 degrees was estimated for the period of the exposure from the shock velocity and corrections for reaction and relaxation. The agreement, within the uncertainties, is to be expected, since the flash time is very long compared to the few collision times which are sufficient for equilibration between rotation and translation.

Our spectra are very similar to those of MN.[8–10] These workers give evidence[9,10] that their system contained at least some ^1D oxygen atoms. While recognizing that $O(^3P)$ could produce vibrationally excited oxygen, they preferred to attribute the excitation observed by them to $O(^1D)$. So far as we know the oxygen atoms in our system should be only those produced by R1 in the ^3P state.

Several reactions of the type R3′ are now known in which vibrationally excited products are produced. Smith[38] has used a relatively simple model to estimate the maximum fraction of the reaction energy which appears as vibrational excitation in these reactions. For reaction R3′ this fraction is in the range $^2/_3$ to $^3/_4$, and corresponds, for $\Delta E_0^0 = -93.6$ kcal., to from 16 to 17 quanta, about as observed (more recently very weak absorption due to molecules with $v = 18$, 19 and perhaps 20 has been reported[39]). The vibrationally excited O_2 molecule should be the one containing the original atom.

Decomposition of Ozone by Excited Oxygen Molecules.—It has frequently been suggested that one or both products of the strongly exothermic R3′ might destroy further ozone by R6.

R6 $O_2^* + O_3 = O_2 + O_2 + O$

The shock wave experiments can be interpreted without assuming that R6 occurs. Various reasonable trial calculations that we have made suggest that the vibrationally excited oxygen does not undergo R6 with a probability greater than 2.5×10^{-3} per collision.

BA concluded that the data on the thermal decomposition of ozone analyzed by them[4,5] do not require decomposition of ozone by excited products of R3′.

On the other hand the quantum yields for the photolysis of ozone with red light[40,41] (where the atom and molecule resulting from the light absorption are in their ground electronic states as in the thermal reaction R1) are under some conditions (high ozone mole fraction and low pressure) as high as 3.5. Possibly values greater than 2 are due to experimental uncertainty. However, Schumacher[41] has explained these data by assuming the reaction R6 and physical deactivation of O_2^* by O_3 and O_2. Thus there is some uncertainty regarding the occurrence of R6, involving one or both products of R3′, under particularly favorable conditions.[41a]

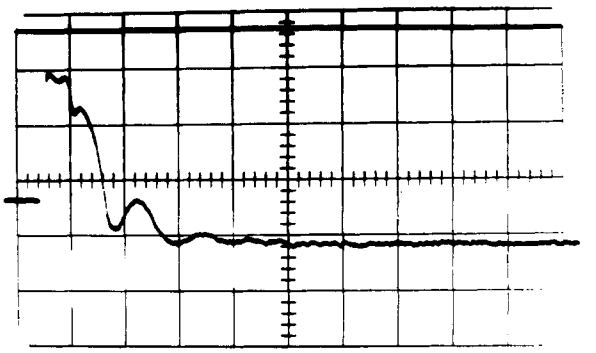


Fig. 8.—Oscilloscope trace showing shock wave irregularity in ozone–argon; helium driver gas; writing rate 50 μs./cm.; shock velocity 78.9$_1$ cm./msec.; T_s = 808°K.; ozone mole fraction 0.0189; total concentration in front of shock wave 0.004964 mole/l.; total concentration of gas right behind shock front 0.01353 mole/l.

Irregularities in Shock Waves.—When the kinetics measurements on A-O_3 were extended to mixtures of higher ozone content, it was found that mixtures with 2% ozone showed very irregular traces if they were not shocked sufficiently strongly. This behavior was observed for both He and H_2 driver gases. A particularly unstable trace is shown in Fig. 8. The irregularities disappeared when 2% O_3–98% A gas was shocked to, say, 900° K. or higher. Irregularities decreased at lower ozone mole fractions.

The shock velocities associated with the irregular traces do not seem to be anomalous when judged by plots of velocity *versus* bursting pressure ratio for all argon shocks with the same driver gas (H_2 or He). This is not a sensitive test, however. Attenuation does not correlate with the occurrence of the oscillations. The shock velocity was considerably greater than the detonation velocity of ozone (from the literature and as calculated for us by Dr. R. E. Duff).

A plot of ozone concentration against time derived from the trace of Fig. 8 was compared with a calculated curve, assuming the same reactions as in the dilute mixtures. The computed curve fits the general trend of the data satisfactorily, *i.e.* the oscillations are superimposed on the expected relationship. This suggests that the irregularities are hydrodynamic and not associated with a change of reaction mechanism.

Spinning detonations and unsteady shock waves are notoriously complex phenomena. In general, they are more frequent in low temperature shocks involving exothermic reactions with significant activation energies. The ozone results are in agreement with this qualitative generalization. The stability of a one-dimensional shock wave accompanied by heat release has been considered

(37) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950.

(38) F. T. Smith, *J. Chem. Phys.*, **31**, 1352 (1959).

(39) N. Basco and R. G. W. Norrish, *Can. J. Chem.*, **38**, 1769 (1960).

(40) G. B. Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925).

(41) H. J. Schumacher, *ibid.*, **17B**, 405 (1932).

(41a) NOTE ADDED IN PROOF.—In a recent note E. Castellano and H. J. Schumacher, *J. Chem. Phys.*, **36**, 2238 (1962), indicate that their new unpublished quantum yields in yellow-red light attain a maximum value of 2.0 and this in oxygen-free systems.

by Shchelkin,[42] and pertinent observations have recently been made by White.[43]

Unfortunately, the flash absorption measurements on 2% O_3–98% A mixtures were made without photoelectric records of (O_3) as a function of time, before these irregularities were discovered. However, the flash spectrum shocks were sufficiently strong that the erratic traces should not have occurred with them. This was verified in two shocks which duplicated the conditions of the spectroscopic shocks. Shock E-8, Table I, was also made under similar conditions.

Emission.—The emission of weak orange-yellow light was noted visually. For several shocks, time-resolved records were taken of the intensity of the unfiltered emission incident on a 1P28 photomultiplier. The light came from a defined section of the shock tube which corresponded to a resolution of 7 μs. laboratory time.

The following comments apply to incident shocks in A–O_3 mixtures. The signal was weak, corresponding very roughly to one quantum per 10^8 ozone molecules decomposing (this number is probably uncertain by at least a factor of ten and possibly by much more if there is light at undetected wave lengths). The intensity rose to a maximum and then decreased. This suggests a possible association of the light with R3 or its products. Comparison of the light intensity with the calculated rate of R3 as functions of time suggests that the light intensity reached its maximum a little later than the rate of R3 and persisted to longer times. Emission was much weaker for incident shocks in N_2–O_3 mixtures than in A–O_3 mixtures and may not have been definitely detected photoelectrically. The visually detected emission was also weaker for N_2–O_3 shocks. The difference in behavior might be due to quenching by nitrogen. We cannot assess the extent to which impurities may have affected or caused the emission.

The emission measurements were made primarily to verify that emission would not affect the spectrophotometry. Even neglecting wave length selection by the monochromator, it is estimated that the strongest emission observed corresponded to less than $^1/_2$% of I_0.

Very weak and apparently continuous emission during the thermal decomposition of ozonized oxygen was observed by Barbier, Chalonge and Masriera.[44] Broida, Schiff and Sugden[45] have reported emission which may be associated with the reaction of ozone with oxygen atoms generated in an electric discharge. Emission was noted by Huffman and Davidson[46] and by Steinberg and Lyon[47] in the decomposition of NO_2 in a shock tube.

(42) K. I. Shchelkin, *Soviet Phys.-JETP*, **9**, 416 (1959).

(43) D. R. White, *Phys. Fluids*, **4**, 465 (1961).

(44) D. Barbier, D. Chalonge and M. Masriera, *Compt. rend.*, **212**, 984 (1941).

(45) H. P. Broida, H. I. Schiff and T. M. Sugden, *Nature*, **185A**, 759 (1960).

(46) R. E. Huffman and N. Davidson, *J. Am. Chem. Soc.*, **81**, 2311 (1959).

(47) M. Steinberg and T. F. Lyon, abstract of paper presented before the Inorganic and Physical Chemistry Section, 131st National Meeting, American Chemical Society, Miami, Florida, April, 1957.

Discussion

Discussion of k_1 in Terms of HRRK and Slater Theories.—The low temperature data pertain to R1 as a unimolecular reaction at its low pressure second order limit.[4] The shock tube data also pertain to this limit, as is seen from the argon shock tube data in Table I and Fig. 4, which cover an eight-fold range in total concentration.

There are at present two theoretical approaches to unimolecular reactions. due to Hinshelwood–Rice–Ramsperger–Kassel (HRRK)[48] and to Slater.[49] In the HRRK theory a molecule is regarded as a collection of oscillators, essentially harmonic but sufficiently coupled to allow flow of energy among them. Dissociation occurs when a critical energy accumulates in a particular oscillator. The Slater Theory considers the contributions of *uncoupled* normal vibrational modes of the molecule to the extension of a specified distance, *e.g.*, the distance between two bonded atoms. Dissociation occurs when the extension reaches a critical value.

The classical harmonic oscillator equations for rate constants in the two theories at the low pressure limit are E8 and E9 (the right sides of E8 and E9 are actually the first and most important terms of expansions[48,49]); s is the number of oscillators: n is the number of normal modes contributing to extension of the reaction coördinate; Z is the collision number, including a factor $T^{1/2}$; E^0 is the crit-

$$k_1 = \frac{PZ}{(s-1)!}\left(\frac{E^0}{RT}\right)^{s-1} e^{-E^0/RT} \qquad \text{HRRK} \tag{E8}$$

$$k_1 = PZ\left(\frac{4\pi E^0}{RT}\right)^{1/2(n-1)}\left(\prod_k \mu_k\right) e^{-E^0/RT} \qquad \text{Slater} \tag{E9}$$

ical energy (HRRK) or the energy corresponding to the critical extension of the reaction coördinate (Slater); P may be called the collision efficiency (it is frequently, but somewhat arbitrarily, taken to be unity); μ_k is a fraction, related to the contribution to the reaction coördinate of the kth contributing normal mode. The RHS of E9 must be multiplied by the number of equivalent reaction coördinates, *e.g.* by 2 for ozone dissociation.

It can hardly be doubted that an unimolecular reaction is more complicated than presently available models must assume. Nevertheless, it is useful to evaluate the parameters of the theories from experimental data in order to note regularities. E10, which is of the form of E8 and E9, should ideally be regarded as having three parameters. Data of unattainably high accuracy would be needed in order to evaluate all three parameters with significant accuracy. An additional assumption regarding at least one of these parameters must then be made, as discussed below.

Gill and Laidler[50,51] treated the low temperature data summarized by BA[4] for R1 with M = O_3. They obtained E^0 by equating the experimental activation energy to that computed by

(48) L. Kassel, "The Kinetics of Homogeneous Gas Reactions," The Chemical Catalog Co., Inc., New York, N. Y., 1932.

(49) (a) N. B. Slater, *Phil. Trans. Roy. Soc.* (London), **246A**, 57 (1953); (b) "Theory of Unimolecular Reactions," Cornell University Press, Ithaca, New York, 1959.

(50) E. K. Gill and K. J. Laidler, *Proc. Roy. Soc.* (London), **250A**, 121 (1959).

(51) The details for ozone are in E. K. Gill and K. J. Laidler, *Trans. Faraday Soc.*, **55**, 753 (1959).

logarithmic differentiation of E8 or E9, assuming $n = s = 3$. The μ_k were calculated by means of a detailed vibrational analysis. Then, assuming $P = 1$ and a collision diameter of 3.35 Å., they calculated k_1 at 372.8°K. from E8 and E9. Both calculated values of k_1 agreed fairly well with experiment. We made a similar calculation at 600° K. for comparison with E3, representing the combined low temperature and shock tube data for M = N_2. Assuming a collision diameter of 4.02 Å. (see below), we found values of k_1 computed from E8 and E9 to be larger than that calculated from E3 by factors of 2.3 and 12, respectively. Considering the facts that E^0 is obtained from the data itself, that there are uncertainties in the collision diameter and that P cannot be assumed to be unity,[52,53] it appears that calculations of this type cannot be used, at least in the case of ozone, to indicate a superiority of E8 or E9.

We may discuss the combined low temperature[4] and shock tube data for k_{1N_2} in a different way. We take the critical energy E^0 to be ΔE_0^0 for R1 and use the data to evaluate s, n and P. E8 and E9 both have the form of E10. For the HRRK theory m is $s - 1$. For the Slater theory m is $^1/_2(n-1)$. For the purpose of obtaining m and P we put E10 in the form E11, writing $Z = AT^{1/2}$.

$$k_1 = \frac{PZ}{m!}\left(\frac{E^0}{RT}\right)^m e^{-E^0/RT} \quad \text{(E10)}$$

$$L \equiv \log k_1 + \frac{E^0}{2.303\,RT} = -(m - {}^1/_2)\log T + m \log E^0/R + \log PA - \log m! \quad \text{(E11)}$$

A plot of L against log T gives $m = 1.75 \pm 0.2$. According to E8, $s = m + 1 = 2.75 \pm 0.2$.[54] An absolute error of 20% in the shock tube or low temperature values of k_1 would change s by 0.15–0.20. An uncertainty of 250 cal. in the heat of formation of ozone causes an uncertainty of 0.08 in s. Taking $A = N\sigma^2(8\pi k/\mu)^{1/2}$ and $\sigma = 4.02$ Å (the mean of the collision diameters of N_2 and SO_2 from viscosity data[55]), we obtain $P = 0.052$. This leads to representation E12. If account is

$$k_1 = (0.052)(1.057 \times 10^{10})T^{1/2}\frac{(24350/RT)^{1.75}}{1.75!}\exp(-24350/RT) = 3.4 \times 10^8\, T^{1/2}(24350/RT)^{1.75}\exp(-24350/RT) \text{ liter mole}^{-1}\text{ sec.}^{-1} \quad \text{(E12)}$$

taken of the expansion neglected in E12 (*cf.* the previous comment in connection with E8 and E9), the values of s and P become 2.83 ± 0.2 and 0.039. This value of s is fairly close to the value of 3 expected if energy flows among all three vibrational modes (taken to be the "oscillators" of the HRRK theory). The parameter m is more consistent with the HRRK theory than with the harmonic oscillator version of the Slater theory, which requires $n = 3$, $m = 1$. The possibility of a movement toward Kassel-like rates at sufficiently low pressures, due to anharmonicity, was anticipated by Slater (ref. 49a, pg. 65; ref. 49b, pgs. 133, 185). Gill and Laidler[50] suggested that the effect would be most pronounced in small molecules, where there is a large amount of energy in each "normal mode." One must also recognize that the apparent value of s is influenced by various effects for which corrections cannot yet be made very satisfactorily (quantum corrections, anharmonicity, rotation, distortion of the vibrational distribution by reaction if the strong collision assumption implicit in E8 and E9 is not valid, etc.).

Recombination Rate Constants. Comparison with NO_2.—While the various data are not entirely concordant, the bulk of the evidence indicates that the temperature coefficient of k_2 is negative (*cf.* equation E4).[56]

The rate constant for the recombination reaction R8 has been measured by various workers. It too appears to have a negative temperature coefficient.[59]

R7, R8 $M + NO_2 \rightleftarrows M + NO + O$ $\Delta E_0^0 = 71.775$ kcal.[14,15]

The main fact to which we wish to draw attention is that $k_8/k_2 \approx 200$ from room temperature to 2000°K. Reactions R8 and R2 appear to be very similar recombination reactions and this large difference in rates is rather unexpected. If the rate constant of the dissociation, OXO + M → O

(52) D. J. Wilson and H. S. Johnston, *J. Am. Chem. Soc.*, **75**, 5673 (1953).

(53) H. S. Johnston, *Ann. Rev. Phys. Chem.*, **8**, 249 (1957); p. 260.

(54) s could also be obtained from $E_{expt1} = E^0 - \left(s - \frac{3}{2}\right)\bar{R}\bar{T}$, although the choice of $\bar{T}$ is a little uncertain. By this method the experimental activation energy from low temperature data alone[4] (24.0 ± 0.5 kcal.), together with $E^0 = \Delta E_0 = 24.35$ kcal. and $\bar{T} = 363$°K., gives $s = 2.0 \pm 0.7$, to be compared with $s = 2.75 \pm 0.2$ above from the combined data.

(55) J. H. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases," John Wiley and Sons, Inc., New York, N. Y., 1954.

(56) The values of k_2 deduced in references 4 and 6 are in essential agreement. Values of k_2 (M = O_2) have been obtained, using an electric discharge and low pressure flow systems, at 5 and −60°[57] and at room temperature.[58] These values[57,58] agree within a factor of about two with E4 (corrected[4] to M = O_2) or with BA's corrected[15] expression for k_2. This may be within the accuracy of the data and of the extrapolation. According to E4, the temperature dependence of k_2 (M = N_2) from the combined shock tube data and those treated by BA can be represented by a negative experimental activation energy of 1.7 kcal. The data treated by BA gave a negative activation energy of 0.6 ± 0.5 kcal. for the range 70–110°; the magnitude of this quantity should be increased to 1.0 ± 0.5 kcal. in view of the revision in the dissociation energy of O_2.[15] Elias, *et al.*,[57] interpreted their data at 5 and −60° to indicate a negative activation energy of 0.7 ± 0.2 kcal. A negative experimental activation energy, decreasing in magnitude at low temperatures, as the above data suggest, is consistent with E8 as a description of k_1 (with E^0 equal to ΔE_0^0 for R1) and the thermodynamics of R1, R2. From their measurements on k_1 (M = O_2) in the range 115 to 130°, Zaslowsky, *et al.*,[8] deduce that k_2 has a slightly positive activation energy (+0.3 kcal.), although they do not exclude a slightly negative value; correction[15] gives −0.1 kcal. This group's measurements[30] on k_3 and k_3/k_2 give values of k_2 (M = O_2) in the range −30 to −60° which correspond to a +0.3 kcal. activation energy.

(57) L. Elias, E. A. Ogryzlo and H. I. Schiff, *Can. J. Chem.*, **37** 1680 (1959).

(58) F. Kaufman, *Proc. Roy. Soc.* (London), **247A**, 123 (1958).

(59) Near room temperature k_8 (M = O_2, A, N_2, 300°K.) is approximately 2×10^{10} (mole/l.)$^{-2}$ sec.$^{-1}$.[58,60-62] Also reported[63] is k_8 (M = N_2O, 1000°K.) = 6×10^9 (mole/l.)$^{-2}$ sec.$^{-1}$. From the shock tube data[46] on k_7, we estimate k_8 (M = A, 2000°K.) = 9×10^8 (mole/l.)$^{-2}$ sec.$^{-1}$. These data suggest a negative temperature coefficient.

(60) H. W. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1156 (1957). These workers actually obtain $k_8/k_2 = 270$, which can then be combined with k_2 to give k_8.

(61) E. A. Ogryzlo and H. I. Schiff, *Can. J. Chem.*, **37**, 1690 (1959).

(62) P. Harteck, R. R. Reeves and G. Manella, *J. Chem. Phys.*, **29**, 1333 (1958).

(63) F. Kaufman, N. J. Gerri and R. E. Bowman, *ibid.*, **25**, 106 (1956).

+ XO + M, is given by an expression of the type E8

$$k_1 = \frac{PZ}{(s-1)!}\left(\frac{E^0}{RT}\right)^{s-1} e^{-E^0/RT} \quad \text{(E8)}$$

and if the equilibrium constant is given by an expression of the form

$$K = Ae^{-E^0/RT}$$

(which is approximately true), then the recombination constant will be given by

$$k_2 = k_1/K = \frac{1}{A}\cdot\frac{PZ}{(s-1)!}\left(\frac{E^0}{RT}\right)^{s-1}$$

with a similar expression for k_8. The factor A is about the same for the two reactions. From a simple viewpoint the PZ factors would also be about equal. With $s = 3$ the ratio of the $(E^0/RT)^{s-1}$ terms contributes a factor of about 9 to k_8/k_2. The rest of the difference in the rates of the O + NO + M and O + O_2 + M reactions remains unexplained.

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The Reactivity of Phenols toward Peroxy Radicals. I. Inhibition of the Oxidation and Polymerization of Methyl Methacrylate by Phenols in the Presence of Air[1]

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In an effort to elucidate the mechanism by which phenols retard vinyl polymerization in the presence of air, the action of twenty phenols upon the polymerization of methyl methacrylate has been studied. Induction periods and rates of polymerization have been measured dilatometrically. Addition of a phenol increases the length of the inhibition period over that due to oxygen alone. A kinetic scheme has been developed which accords well with the experimental results. On this basis it is concluded that phenols act as anti-oxidants, as is often found to be the case in other free-radical reactions. The phenol prevents oxygen from becoming depleted too rapidly, thus extending the inhibition period by maintaining a reasonably high oxygen concentration level for a longer time than would normally be the case. Relative efficiencies of several phenols have been determined and these results correlated with other kinetic studies of oxidation inhibition by phenols.

Introduction

While phenols have long been used as stabilizers for vinyl monomers, their mechanism of action is still not clear. It has usually been assumed that the phenols act by destroying peroxides that can initiate polymerization, or by being oxidized to quinoid products that can inhibit polymerization.[2-5] It has been found in the present work that these mechanisms of stabilization do not appear to be generally valid. An alternative mechanism which appears to be in better accord with the experimental facts has been set forth.

A defect common to the previous theories is the lack of attention given to the role of oxygen in the stabilization process. Oxygen itself is well-known as a polymerization inhibitor.[6] Schulz and Henrici[7] have recently studied the oxygen-inhibited polymerization of methyl methacrylate by a simple dilatometric technique in which the length of the well-defined inhibition periods were used to estimate the rate of oxidation of the monomer during the inhibition periods. They assumed an exactly alternating copolymerization of methyl methacrylate and oxygen during the inhibition period. The greatly decreased rate of polymerization during the inhibition period was found to be caused chiefly by a large decrease in the kinetic chain-length relative to the chain-length found in normal polymerization. Since essentially all of the oxygen is used up during the inhibition period, the rate of oxidation was taken to be equal to the initial concentration of oxygen divided by the length of the inhibition period. This is very convenient for studying inhibition-period rates since the length of this period is a quantity easily measured.

Mayo and Miller[8] have carried out a much more complete study of the same system. They used the complete copolymerization equations in their study and so obtained much more detailed information about the various steps as well as their change with time. For conditions corresponding to those of Schulz and Henrici, some expected differences were found. In spite of these differences, the assumptions of Schulz and Henrici are probably a fair approximation during the larger part of the inhibition period. It appears reasonable

(1) Taken from a portion of the Ph.D. thesis of R. G. C. Inquiries should be addressed to J. L. I. The financial support of the Research Corporation and of the University of Hawaii Research Committee is gratefully acknowledged.

(2) C. Walling and R. R. Briggs, *J. Am. Chem. Soc.*, **68**, 1141 (1946).

(3) B. A. Dolgoplosk and D. Sh. Korotkina, *Zhur. Obshchei Khim.*, **27**, 2226 (1957). Consultants Bureau (C. B.) Translation, p. 2285.

(4) B. A. Dolgoplosk and G. A. Parfenova, *ibid.*, **27**, 3083 (1957). C. B. Translation, p. 3122.

(5) G. P. Belonovskaya, Zh. D. Vasyutina and B. A. Dolgoplosk, *Zhur. Priklad. Khim.*, **32**, 1824 (1958). C. B. Translation, p. 1863.

(6) F. A. Bovey and I. M. Kolthoff, *Chem. Revs.*, **42**, 491 (1948).

(7) G. V. Schulz and G. Henrici, *Makromol. Chem.*, **18/19**, 437 (1956).

(8) F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2493 (1958).