Atmospheric Chemistry Involving Electronically Excited Oxygen Atoms

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The presence of the ozone molecule in the Earth's atmosphere is of profound importance. Because of strong absorption by O_3 in the middle ultraviolet (peaking at ~250 nm), the flux of solar photons at the surface is attenuated by a factor of 10^5 at wavelengths where radiation induces significant damage to DNA in biological systems. Indeed, it has been hypothesized that the development of a shield of O_3, when the level of O_2 in the atmosphere reached ~10% of its present level about 400 million years ago, led to the emergence of life from the sea to land during the Silurian period.[1]

Stratospheric ozone is maintained in balance by a complex photochemical mechanism, the details of which have recently been reviewed.[2] Near the upper reaches of the stratosphere, molecular oxygen is dissociated[3]

$$O_2 + h\nu(\lambda < 244\ \text{nm}) \rightarrow 2O(^3P_J) \quad (1)$$

to form oxygen atoms. These then undergo reaction with O_2

$$O(^3P_J) + O_2 \xrightarrow{M} O_3 \quad (2)$$

to form O_3. In a pure oxygen atmosphere, the formation of ozone would be counterbalanced by

$$O_3 + h\nu(\text{visible, UV}) \rightarrow O_2 + O(^3P_J) \quad (3)$$

$$O(^3P_J) + O_3 \rightarrow 2O_2 \quad (4)$$

Note that (3) is effectively the reverse of 2. As ozone and atomic oxygen are effectively maintained in a photostationary state (at least above ~25 km), O and O_3 are often considered together as "odd" oxygen. Reaction 4 was initially proposed by Chapman[4] as the mechanism by which odd oxygen would be destroyed, although it subsequently became clear that (4) by itself could not account for the rate of odd oxygen destruction required in order to maintain ozone balance in the stratosphere.

Models of the stratosphere that include not only chemical processes but also the as yet ill-understood phenomena of vertical and horizontal transport are currently under active development.[5] Any account of ozone chemistry in the stratosphere must begin with its photodissociation in the intense Hartley continuum. Below 310 nm, this dissociation is dominated by the spin-allowed production of electronically excited oxygen atoms, $O(^1D_2)$, and molecules, $O_2(^1\Delta)$.

$$O_3 + h\nu(\lambda < 310\ \text{nm}) \rightarrow O(^1D_2) + O_2(^1\Delta) \quad (3a)$$

Below, I shall discuss the efficiency of $O(^1D_2)$ production in (3a) vs. other routes resulting in the formation of oxygen atoms in the ground, ^3P_J, state.

$$O_3 + h\nu \rightarrow O(^3P_J) + O_2(?) \quad (3b)$$

It is currently believed that $O_2(^1\Delta)$, in spite of its optical metastability, does not play a significant role in establishing the chemical composition of the stratosphere.

Several parallel destruction mechanisms account for the current stratospheric ozone balance. Two of these are initiated by oxidation reactions involving $O(^1D_2)$ produced in (3a). Reaction of $O(^1D_2)$ with N_2O (produced as a byproduct of denitrification) results in the formation of NO

$$O(^1D_2) + N_2O \rightarrow N_2 + O_2(^1\Delta) \quad (5a)$$

$$\rightarrow 2NO \quad (5b)$$

Subsequent catalytic destruction of odd oxygen proceeds via

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ O + NO_2 &\rightarrow O_2 + NO \\ \hline O + O_3 &\rightarrow 2O_2 \end{aligned}$$

Reaction of $O(^1D_2)$ with water and methane

$$O(^1D_2) + H_2O \rightarrow 2OH \quad (6)$$

$$O(^1D_2) + CH_4 \rightarrow CH_3 + OH \quad (7a)$$

leads to production of hydroxyl radicals that can further react to remove O_3 catalytically, e.g.,

$$\begin{aligned} OH + O_3 &\rightarrow HO_2 + O_2 \\ HO_2 + O_3 &\rightarrow OH + 2O_2 \\ \hline O + O_3 &\rightarrow 2O_2 \end{aligned}$$

In the troposphere, hydroxyl radicals produced in (6) are responsible for the oxidation of CO to CO_2 as well as the initiation of the free radical cycle leading to smog[6] via

$$OH + RH \rightarrow H_2O + R$$

$$R + O_2 \xrightarrow{M} RO_2 \rightarrow \ldots$$

All atmospheric reactions of $O(^1D_2)$ compete with quenching of the excited atoms to $O(^3P_J)$ following

(1) L. C. Berkner and L. L. Marshall, *Discuss. Faraday Soc.*, **37**, 122 (1964).
(2) B. A. Thrush, *Acc. Chem. Res.*, **14**, 116 (1981).
(3) Standard atomic ($^{2S+1}L_J$) and molecular term symbols are used throughout, e.g., $^1D_2$ represents the lowest excited singlet state of atomic oxygen while ^3P_J represents the ground state. For further details, see M. Karplus and R. N. Porter, "Atoms and Molecules: An Introduction for Students of Physical Chemistry", W. A. Benjamin: Menlo Park, CA, 1979, pp 157–158, 202–207, 338–344.
(4) S. Chapman, *Memoirs R. Met. Soc.*, **3**, 103 (1930).
(5) J. S. Chang and W. H. Duewer, *Annu. Rev. Phys. Chem.*, **30**, 433 (1979).
(6) B. J. Finlayson and J. N. Pitts, *Science (Washington, D.C.)*, **192**, 111 (1976).

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Table I
Threshold Wavelengths (in nm)
for Production of Specific Atomic and
Molecular States by Photodissociation of O_3 at 0 K

	O_2		
O	$X^3\Sigma_g^-$	$a^1\Delta_g$	$b^1\Sigma_g^+$
^3P_J	1180	611	463
$^1D_2$	411	310	266
$^1S_0$	237	200	180

collisions with N_2 and O_2. Because of the relative abundances of these major constituents compared to trace materials such as O_3, N_2O, etc., the preponderance of $O(^1D_2)$ deactivating collisions involve quenching and not chemical reaction. It should be noted, however, that the resulting ground-state ^3P_J atoms are translationally excited immediately following quenching and may, themselves, be implicated in as yet poorly characterized chemical reactions.[7]

Meaningful models of the atmosphere can be developed only if reliable photochemical and kinetic data are available over a broad range of temperature (200–300 K).[8] In the following sections, recent detailed studies of O_3 photodissociation and $O(^1D_2)$ reaction dynamics of interest to aeronomists will be discussed. Work reported prior to 1972 has been reviewed previously[9,10] and will not, in general, be considered in the present Account.

Ultraviolet Photodissociation of Ozone

The wavelength thresholds for photodissociation of O_3 into specific states of atomic and molecular oxygen are presented in Table I. A weak ($\sigma_{600} = 5.2 \times 10^{-21}$ cm^2 molecule^{-1}) absorption in the visible region, ~ 450–800 nm (Chappius band) leads to production of $O(^3P_J)$ and, apparently, $O_2(^3\Sigma^-)$, only. A far more intense ($\sigma_{255} = 1.1 \times 10^{-17}$ cm^2 molecule^{-1}) absorption feature in the region 200–300 nm (Hartley band) is known to correlate primarily with $O(^1D_2)$ and $O_2(^1\Delta)$.

Extensive calculations of the electronic structure of ozone in its electronically excited states have been reported.[11] Absorption in the Chappius band corresponds to a $^1B_1 \leftarrow {}^1A_1$ transition in which an electron is promoted from a pσ to a pπ orbital on either terminal oxygen atom. An intense $^1B_2 \leftarrow {}^1A_1$ transition is associated with absorption in the Hartley band. This involves a charge-transfer transition from the pπ orbital of the central oxygen to that of either terminal atom. A correlation diagram for the low-lying singlet states of O_3 is presented in Figure 1.

The theoretical assignments of O_3 photodissociation pathways have been elegantly confirmed under collision-free conditions by monitoring the angular distribution of atomic photofragments produced following excitation in the Hartley and Chappius bands.[12] Further investigations[13] using a more intense laser operating at 266 nm concentrated on measuring the velocity distribution of the molecular photofragments and,

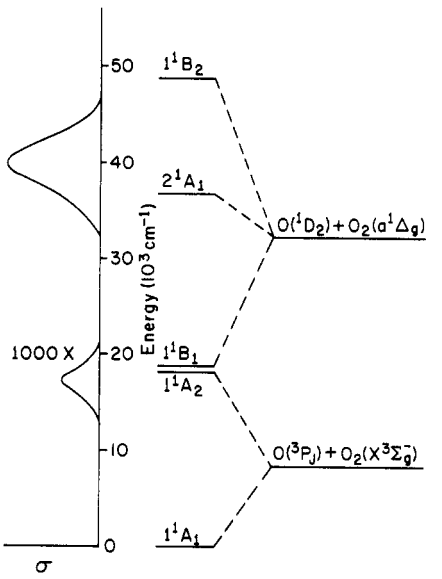

Figure 1. Correlation diagram for low-lying singlet states arising from $O + O_2 \rightarrow O_3$. Calculated vertical excitation energies are from ref 11. A schematic of the O_3 absorption spectrum is displayed at the left.

hence, their energies in the center-of-mass frame. These experiments revealed that, of the $O_2(^1\Delta)$ formed in (3a), 57% was produced in $v = 0$, 24% in $v = 1$, 12% in $v = 2$, and 7% in $v = 3$. About 17% of the remaining energy was deposited into rotation of $O_2(^1\Delta, v = 0)$. Both the angular dependence and energetics of the photofragments suggest that ozone dissociation in the Hartley band proceeds via a "vertical" $^1B_2 \leftarrow {}^1A_1$ transition. Impulsive energy release occurs from an excited-state configuration similar to that of the ground state. This is in reasonable accord with calculations[11] that suggest that the $^1B_2$ state displays a weak potential minimum at an elongated bond length but similar bond angle as the ground state, $^1A_1$.

Of considerable interest to atmospheric chemists is the yield of electronically excited oxygen atoms following ozone photodissociation in the Hartley band. Because stratospheric ozone so effectively filters solar radiation reaching the troposphere, photolysis of O_3 in this region occurs predominantly via absorption of photons with $\lambda > 300$ nm, i.e., within 1200 cm^{-1} of the threshold for production of $O(^1D_2) + O_2(^1\Delta)$. In this spectral region, ozone absorption is approximately 2 orders of magnitude weaker than at the peak of the Hartley continuum. The yield of $O(^1D_2)$ near the 310 nm threshold can be followed by analysis of products resulting from the reaction of $O(^1D_2)$ with various reagents, such as N_2O or hydrocarbons.[14] Alternatively, the luminescence of electronically excited NO_2 is monitored in O_3/N_2O mixtures following the sequence

$$O_3 + h\nu \rightarrow O(^1D_2) + O_2(^1\Delta) \quad (3a)$$

$$O(^1D_2) + N_2O \rightarrow 2NO \quad (5b)$$

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (8)$$

$$NO_2^* \rightarrow NO_2 + h\nu(\text{visible})$$

It should be noted that the production of electronically excited NO_2 in (8) proceeds in relatively inefficient competition with direct formation of ground-state NO_2.

(7) J. A. Logan and M. B. McElroy, *Planet. Space Sci.*, **25**, 117 (1977).
(8) NASA panel for data evaluation, "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling", J. P. L. Publication, 81-3 (1981).
(9) H. I. Schiff, *Ann. Geophys.*, **28**, 67 (1972).
(10) M. Nicolet, *Planet. Space Sci.*, **20**, 1671 (1972).
(11) P. J. Hay and T. H. Dunning, Jr., *J. Chem. Phys.*, **67**, 2290 (1977).
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(13) R. K. Sparks, L. R. Carlson, K. Shotatake, M. M. Kowalczyk, and Y. T. Lee, *J. Chem. Phys.*, **72**, 1401 (1980).
(14) G. K. Moortgat and E. Kudszus, *Geophys. Res. Lett.*, **5**, 191 (1978), and references therein.

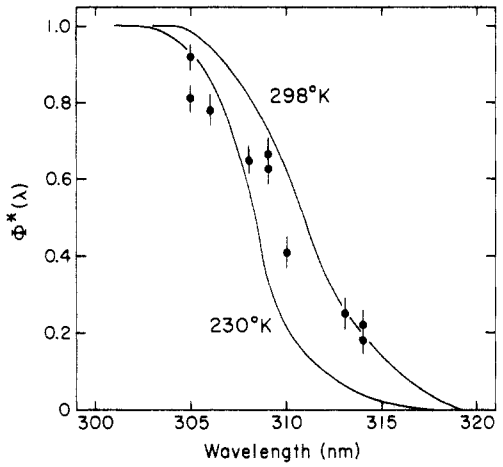

Figure 2. Relative yield of $O(^1D_2)$, normalized to unity at 300 nm as a function of wavelength at T = 230 and 298 K. Solid lines are a "best fit" to indirect studies.[14] The points were obtained in a direct measurement of $O(^1D_2)$ emission intensity following laser dissociation of O_3.[16]

The indirect methods for monitoring $O(^1D_2)$ production are potentially vulnerable to systematic errors arising from incompletely understood reaction mechanisms. For example, the reactive cross section for (8) appears to be sensitive[15] to the internal energy of NO produced in (5b). If the translational energy of $O(^1D_2)$ were to affect the vibrational population distribution of NO produced in (5b), significant variation of the O_3 photolysis wavelength might result in changes to the overall efficiency of the reaction sequence leading to NO_2*.

In Figure 2 are presented currently accepted values[14] of the yield of $O(^1D_2)$ relative to that at 300 nm,

$$\Phi^*(\lambda) = \Phi_{O(^1D_2)}(\lambda)/\Phi_{O(^1D_2)}(300)$$

near the threshold for production of $O(^1D_2) + O_2(^1\Delta)$. These curves are derived from chemical and luminescence studies. Also included are data reported in a recent study of $O(^1D_2)$ production following photolysis of O_3 by a tunable dye laser.[16] The yield of $O(^1D_2)$ was monitored directly by observation of the weak $O(^1D_2) \rightarrow O(^3P_{1,2})$ emission at 630 nm. Some residual disagreement between the direct studies and more classical experiments still remains.

The calculation of the rate coefficients for $O(^1D_2)$ production in the atmosphere requires the absolute yield of excited atoms to be known.

$$J_{O(^1D_2)} = \int \sigma(\lambda) I(\lambda) \Phi_{O(^1D_2)}(\lambda)\, d\lambda$$

Here $\sigma(\lambda)$ is the cross section for photodissociation of ozone and $I(\lambda)$ is the intensity of solar radiation. Experimental measurements of $J_{O(^1D_2)}$ are systematically somewhat lower than the values derived from calculations based on the spectroscopic and photochemical data.[17,18] The calculated values should represent an upper limit that does not fully account for aerosol scattering and variable surface albedo. In addition, absolute values of $\Phi_{O(^1D_2)}$, which have hitherto been assumed to be unity at and below 300 nm, must also be evaluated.

Table II
Relative Yield of Electronically Excited Oxygen Atoms in the Photolysis of O_3 (295 K)

λ, nm	$\phi(\lambda) = \frac{O(^1D_2)}{O(^1D_2) + O(^3P_J)}$	ref
248	0.85 ± 0.02	19
266	0.88 ± 0.02	23
270	0.92 ± 0.03	16
300	0.96 ± 0.03	16

Several measurements of the yields of $O(^1D_2)$ and $O(^3P_J)$ in the photolysis of O_3 have been reported in the last few years. All now agree with the initial observation[12,13] made in studies carried out under collision-free conditions, namely, that a discernible fraction of the oxygen atoms resulting from the ultraviolet photolysis of ozone are produced in the ground ^3P_J state. The spectroscopic studies of oxygen atom production all utilized laser sources for photolysis and vacuum ultraviolet resonance techniques (either absorption or fluorescence) to detect the presence of $O(^3P_J)$. One study,[19] carried out in this laboratory, directly compared the density of $O(^3P_J)$ produced immediately following photolysis with that observed after all of the $O(^1D_2)$ had been converted to $O(^3P_J)$ upon collision with O_3. This conversion is known to proceed with an efficiency of unity;[20,21] i.e., one $O(^3P_J)$ is produced for each $O(^1D_2)$ atom deactivated. The detailed mechanism of the deactivation process is still in some doubt.[22] The other direct studies of ozone photolysis[16,23] have depended upon comparison of the $O(^3P_J)$ yield observed in the presence of an excess of N_2 (a material known to quench $O(^1D_2)$ to $O(^3P_J)$) and that seen when a gas such as H_2 or CH_4 (both known to undergo reaction with $O(^1D_2)$) is added. The results of these studies are presented in Table II.

The yield of $O(^1D_2)$ is seen not to be unity across the Hartley band continuum below 300 nm. Indeed, there is an apparent trend to decreasing values of $\Phi_{O(^1D_2)}$ near the peak of the continuum. Clearly, the value of $\Phi_{O(^1D_2)}$ at 300 nm is less than unity, being perhaps 0.92–0.96. Under any circumstances, the results of the spectroscopic studies of O_3 photodissociation certainly suggest that previous estimates of $J_{O(^1D_2)}$ in the atmosphere, where $\Phi_{O(^1D_2)}$ in the intense portion of the Hartley continuum had previously been thought to be 1.0, are too high by 10–15%.

Finally, it should be noted that measurements of $\Phi_{O(^1D_2)}$ over a wide temperature range have only recently been undertaken.[16] Further experimental studies of this critical parameter are clearly needed in order to further refine models of atmospheric chemistry.

Collisional Deactivation of $O(^1D_2)$ by Atmospheric Gases

Because the magnetic dipole allowed emission

$$O(^1D_2) \rightarrow O(^3P_{1,2}) + h\nu(\lambda = 630\ \text{nm}) \qquad (9)$$

(15) J. C. Brock and R. T. Watson, *Chem. Phys.*, **46**, 477 (1980).
(16) J. E. Davenport, "Parameters for Ozone Photolysis as a Function of Temperature at 280-330 nm", FAA-EE-80-44 (1980).
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(22) I. Arnold and F. J. Comes, *J. Mol. Struct.*, **61**, 223 (1980).
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Table III
Overall Bimolecular Rate Constants for Deactivation of $O(^1D_2)$ by Atmospheric Gases (295 K)

	10^{-10} k cm^3 molecule^{-1} s^{-1}				
gas	$O(^1D_2)$ absorption[25,27]	$O(^1D_2)$ emission[28-30]	$O(^3P_J)$ absorption[21,31]	$O(^3P_J)$ resonance fluorescence[32]	recommended values
O_3	2.7 ± 0.2	2.4 ± 0.5	2.4 ± 0.11	2.3 ± 0.2	2.4
N_2	0.69 ± 0.06	0.28 ± 0.06	0.24 ± 0.01	0.25 ± 0.02	0.26
O_2	0.70 ± 0.05	0.37 ± 0.07	0.42 ± 0.02		0.40
N_2O	2.3 ± 0.2	1.1 ± 0.2	1.2 ± 0.1	1.2 ± 0.1	1.2
CO_2	2.1 ± 0.2	1.0 ± 0.2	1.28 ± 0.07	1.0 ± 0.1	1.1
H_2O	3.0 ± 0.3	2.3 ± 0.4	1.9 ± 0.3	1.9 ± 0.2	2.2

occurs infrequently (A_q = 0.007 s^{-1})[24] by comparison with collisions between $O(^1D_2)$ and molecules at ordinary atmospheric pressures, deactivation of electronically excited oxygen atoms is dominant throughout the troposphere and stratosphere. Such collisional deactivation may proceed either by physical quenching of $O(^1D_2)$ to $O(^3P_J)$ with possible concomitant excitation of the collision partner or through reaction to yield chemically distinct product species.

In order to assess the rate at which specific $O(^1D_2)$ reaction products will be formed under atmospheric conditions, it is necessary to know not only the rate of ozone photolysis to yield electronically excited oxygen atoms but also the rate at which these labile atoms react with ambient gases. In principle, it would be sufficient to measure the rate at which such reactions occur relative to the rate for $O(^1D_2)$ quenching by the major constituents of the atmosphere, N_2 and O_2,

$$O(^1D_2) + N_2 \rightarrow O(^3P_J) + N_2 \quad (10)$$

$$O(^1D_2) + O_2 \rightarrow O(^3P_J) + O_2 \quad (11)$$

Thus the atmospheric formation of, for example, NO in reaction 5b would be given by

$$\frac{d[NO]}{dt} = 2\frac{k_{5b}[N_2O]}{k_{10}[N_2] + k_{11}[O_2]} J_{O(^1D_2)}[O_3]$$

Such determinations of relative rates for $O(^1D_2)$ deactivation were reported in the late 1960s and early 1970s, but as noted earlier, the results of such classical experiments are prone to systematic error arising from incomplete understanding of complex reaction mechanisms involving highly labile intermediates.

Determination of absolute deactivation rates requires time-resolved measurement of $O(^1D_2)$ densities, $[O^*]_t$. Such studies were initiated in the laboratory of David Husain at the University of Cambridge where $[O^*]_t$ was monitored[25] by observing the attenuation of the resonance radiation, $O(^1P_1) \leftarrow O(^1D_2)$ (λ = 115 nm), following broad-band photolysis of O_3. In principle, $[O^*]_t$ could be directly related to the observed absorption via the Beer–Lambert law, but mismatched absorption and emission line shapes as well as self-reversal in the microwave powered source of resonance radiation must be taken into account. A modified form of the usual Beer–Lambert law

$$A_t^{1/\gamma} = \epsilon l[O^*]_t \quad (12)$$

was used in these early studies.[26] The parameter γ was empirically determined for the particular apparatus by measuring the dependence of the initial absorbance immediately following ozone photolysis upon the ozone pressure. Values of γ near 0.4 were obtained.

Rate constants were measured[27] for deactivation of $O(^1D_2)$ by a variety of atmospheric gases from the dependence of the observed pseudo-first-order rate coefficient, k', upon collision gas pressure. Substitution for $[O^*]_t$ in the integrated exponential rate law

$$[O^*]_t = [O^*]_{t=0} \exp(-k't)$$

yields

$$A_t^{1/\gamma} = A_{t=0}^{1/\gamma} \exp(-k'\gamma t) \quad (13)$$

Because of the form of (13), the kinetic behavior of $O(^1D_2)$ removal could not be determined independently of the absorption behavior characterizing the resonance line at 115 nm. All values of the apparent removal rate coefficient, $k'\gamma$, had to be divided by the experimental parameter γ in order to obtain the "true" rate coefficient for $O(^1D_2)$ removal (Table III).

With the advent of efficient pulsed laser sources operating in the ultraviolet, other experiments were developed to study $O(^1D_2)$ collisional deactivation. In the United States, the kinetics of $O(^1D_2)$ removal following photolysis of O_3 at 266 nm with a frequency-quadrupoled Nd/YAG laser were determined by monitoring the weak atomic emission at 630 nm.[28-30] Interferences by a variety of emitting species were experienced but overcome by careful choice of reaction mixtures. The values of the bimolecular rate constants determined in this way (over an extended range of temperature) were, in general, only half as large as those determined in the earlier studies of atomic resonance absorption.

More recent investigations of $O(^1D_2)$ deactivation have depended upon both absorption[31] and fluorescence[32] of atomic resonance radiation at the triplet $^3S_1 \leftarrow {}^3P_{0,1,2}$ lines near 130 nm. These studies, which follow the *growth* in $O(^3P_J)$ density following laser photolysis of O_3, confirm the slower rates measured in the emission experiments and strongly suggest that the absorption dependence of 115 nm resonance radiation by $O(^1D_2)$ was more closely linear upon atomic concentration than was determined experimentally. No simple explanation of this discrepancy has been forthcoming, although the

(24) R. H. Garstang, *Mon. Not. R. Astronom. Soc.*, 111, 115 (1951).
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(32) P. H. Wine and A. R. Ravishankara, *Chem. Phys. Lett.*, **77**, 103 (1981).

similar result obtained by all methods for the deactivation rate of $O(^1D_2)$ by O_3 suggests the possibility of systematic problems leading to compensating errors in the case of ozone deactivation. In any event the bimolecular rate constants for $O(^1D_2)$ deactivation by the atmospheric gases seem now to be well characterized. Variation in deactivation rates over the range of temperature required for atmospheric modeling is very small and the rates are also apparently determined with good (±10%) accuracy.

Although determination of overall deactivation efficiencies is of considerable importance in developing reliable chemical models of the atmosphere, more detailed information concerning branching ratios and product energetics is also required. Furthermore, the reactivity of a highly energetic species such as $O(^1D_2)$ is of interest to dynamicists who are concerned with energy flow during bimolecular collisions in the gas phase.[33] Presented below are brief descriptions of recent dynamical studies of $O(^1D_2)$ deactivation processes involving the atmospheric gases.

Nitrogen. Deactivation of $O(^1D_2)$ by N_2 proceeds via quenching

$$O(^1D_2) + N_2 \rightarrow O(^3P_J) + N_2 \qquad (14)$$

with approximately 30 ± 10% of the electronic energy associated with $O(^1D_2)$ being transferred to vibration in N_2.[34] This interaction apparently involves the formation of an N_2O intermediate that is sufficiently long-lived to permit multiple traversals of those portions of configuration space in which nonadiabatic crossings may occur.[35,36] The corresponding deactivation of $O(^1D_2)$ by CO has been studied in considerable detail by probing the small signal transmission of a continuous wave CO laser through a cell following flash photolysis of an O_3/CO mixture.[37] The results of this study are consistent with the formation of a long-lived CO_2 complex, although the efficiency of electronic–vibrational (E–V) energy transfer measured here, 21 ± 0.5%, is a factor of 2 lower than that reported previously.[34] Because the reported efficiency of (14) is based on the corresponding efficiency of E–V transfer involving $O(^1D_2)$ and CO, this discrepancy must be resolved in order to understand the role of $O(^1D_2)$ deactivation by N_2 in heating of the upper atmosphere.

Oxygen. Deactivation of $O(^1D_2)$ by O_2 is known to result in significant electronic–electronic (E–E) energy transfer to produce $O_2(^1\Sigma^+)$

$$O(^1D_2) + O_2(^3\Sigma^-) \rightarrow O(^3P_J) + O_2(^1\Sigma^+) \qquad (15a)$$

in competition with physical quenching

$$O(^1D_2) + O_2(^3\Sigma^-) \rightarrow O(^3P_J) + O_2(^3\Sigma^-) \qquad (15b)$$

The ratio k_{15a}/k_{15} has most recently been measured[38] as 0.77 ± 0.2. The presence of electronically excited $O_2(^1\Sigma^+)$ in the upper atmosphere is confirmed by observation of the $O_2(^1\Sigma^+ \rightarrow {}^3\Sigma^-)$ bands.[39,40] The *reactive* deactivation of $O_2(^1\Sigma^+)$ by O_3

$$O_2(^1\Sigma^+) + O_3 \rightarrow O(^3P_J) + 2O_2(^3\Sigma^-)$$

is known to proceed with an efficiency of 25–50% in the collisional quenching of excited oxygen with ozone and may affect the odd oxygen balance to some degree.[41,42]

Nitrous Oxide. As noted previously the reaction of $O(^1D_2)$ with N_2O

$$O(^1D_2) + N_2O \rightarrow N_2(^1\Sigma^+) + O_2(^1\Delta) \qquad (5a)$$

$$\rightarrow 2NO(^2\Pi_i) \qquad (5b)$$

is of singular importance to atmospheric chemistry. Production of $O_2(^1\Delta)$ in (5a) has been inferred indirectly.[43] Measurement of the ratio $b = k_{5b}/k_5$ has been widely attempted because of the sensitivity of any atmospheric model to this parameter. The most recent experiments[44-47] suggest that this critical parameter lies very close to $b = 0.60$. No significant difference in b has been observed at 296 and 177 K.[47] Still a matter of some controversy is the dependence of b upon the kinetic energy of $O(^1D_2)$ reacting with N_2O, the most recent studies suggesting that no such dependence exists.

The product NO molecules formed in (5b) have been analyzed by kinetic spectroscopy.[48] These studies suggest that the population of vibrational levels falls off exponentially with increasing energy, about 26% of the overall exoergicity of (5b) appearing in vibration. This was interpreted as signifying the intermediacy of an ONNO complex.

Carbon Dioxide. Reaction of $O(^1D_2)$ with CO_2 to produce $CO(^1\Sigma^+)$ and $O_2(^1\Delta)$ is exothermic by 67.1 kcal and both spin and symmetry allowed. No infrared absorption by CO is observed[49] following collisional deactivation of $O(^1D_2)$ by CO_2, however, and the yield of $O(^3P_J)$ is essentially identical with that observed following deactivation of a similar quantity of $O(^1D_2)$ by N_2.[21]

The dominance of physical quenching of $O(^1D_2)$ by CO_2 may be contrasted to the negligible significance of this process in the deactivation of $O(^1D_2)$ by the isoelectronic molecule N_2O.[31] This striking difference has been attributed[50] to the importance of relatively low-lying electronically excited states of N_2O that are absent in CO_2. Potential surfaces correlating with $O(^1D_2)$ + N_2O correlate *diabatically* with $N_2(^1\Sigma^+)$ and highly excited singlet states of O_2 (e.g., $O_2(^1\Delta_u)$) that arise from two $O(^1D_2)$. The presence of surfaces correlating with $O(^3P_J)$ and low-lying triplet states of N_2O such as $^3\Sigma^+$ and $^3\Delta$ induce avoided crossings along the reaction coordinate, thereby eliminating potential barriers asso-

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ciated with the abstraction of an oxygen atom along a singlet surface. No such low-lying states are available in CO_2.

The efficiency of the quenching by CO_2 reflects the likely formation of a long-lived CO_3 complex. This is confirmed by isotope exchange studies.[51,52] Vibrational excitation of CO_2 by E–V transfer has not been reported.

Water. Deactivation of $O(^1D_2)$ by H_2O results in the production of OH radicals only. Neither quenching[31] nor reaction to form $H_2(^1\Sigma^+)$ and $O_2(^1\Delta)$[53] occurs with a relative yield in excess of 2%.

A number of recent studies have been concerned with an examination of the energetics of the OH radicals produced in (6). Both high-resolution fluorescence[54] and absorption spectra[55] of OH were obtained following pulsed photolysis of O_3 and subsequent reaction of $O(^1D_2)$ with H_2O under single collision conditions. The absorption technique has the capability of probing vibrational levels above $v'' = 1$, a region denied to fluorescence measurements because of a strong predissociation in the $A^2\Sigma^+$ excited state. By use of isotopically substituted $H_2{}^{18}O$ it was possible to discriminate between the "old" and "new" OH bonds. In essence, approximately 60% of the reaction exothermicity (28.4 kcal) is released as translation, with the ^{18}OH being formed primarily (92%) in the ground vibrational level. The newly formed ^{16}OH bond formed as the result of hydrogen abstraction by $O(^1D_2)$ is substantially hotter vibrationally, with only 46% of the radicals being formed in $v'' = 0$. Rotational distributions in both ^{16}OH and ^{18}OH are similar. The results of these studies suggest that (6) proceeds by a direct abstraction and does not involve a long-lived intermediate resulting from insertion of $O(^1D_2)$ into an already existing OH bond.

Hydrocarbons. The reaction of $O(^1D_2)$ with methane to form OH has been hypothesized to proceed by two parallel paths.[56] The first and dominant mechanism involves insertion of electronically excited oxygen atoms into a C–H bond to produce vibrationally excited methanol that subsequently undergoes fragmentation

$$O(^1D_2) + CH_4 \rightarrow CH_3OH^{\ddagger} \quad (7b)$$

$$CH_3OH^{\ddagger} \rightarrow CH_3 + OH \quad (16)$$

Direct abstraction of hydrogen atoms as denoted by (7a) occurs to a lesser extent. Recent molecular beam studies[57] suggest that elimination of hydrogen atoms from $CH_3OH^{\ddagger}$

$$CH_3OH^{\ddagger} \rightarrow CH_3O \text{ (or } CH_2OH) + H$$

proceeds in competition with formation of OH. No evidence for the highly exothermic elimination of H_2 was obtained. Experiments carried out in this laboratory by monitoring Lyman-α resonance absorption following laser photolysis of $O_3/CH_4/He$ mixtures confirms that H atoms are indeed formed, but with a relative yield (with respect to the total deactivation of $O(^1D_2)$ by CH_4) of less than 10%.[58] Laser-induced fluorescence spectra of OH produced in the reaction of $O(^1D_2)$ with CH_4 clearly display a bimodal population distribution of rotational levels, thereby demonstrating the existence of two paths leading to formation of hydroxyl radicals.[59] Description of the reaction of $O(^1D_2)$ with alkanes larger than CH_4 is complicated by the presence of additional significant product channels, especially C–C bond scission in the excited alcohol produced by insertion of $O(^1D_2)$ into a C–H bond. The production of OH still remains important, with direct abstraction becoming the major route for the larger hydrocarbons. Because the rotational distribution observed for OH radicals produced via direct abstraction is similar to that seen in the reaction of $O(^3P_J)$ with hydrocarbons,[60] it has been hypothesized that the abstraction occurs following crossing to a triplet surface correlating with $OH(^2\pi)$ and $R(^2A)$.

Other Molecules. Detailed investigations of $O(^1D_2)$ reactions with such molecules as H_2,[61,62] HCl,[63] NH_3,[64,65] and halogenated alkanes[66] have also been reported. The chemistry of these reactions, which proceed via the formation of highly energized intermediates (e.g., $H_2O^{\ddagger}$ in the case of $O(^1D_2) + H_2$) and may result in the production of electronically excited products (as in the case of $O(^1D_2) + NH_3$), challenges the resourcefulness and creativity of experimentalists and theoreticians alike. Because the atmospheric fate of such hydrogenated molecules is primarily to react with OH rather than $O(^1D_2)$, the importance of the reactions of these species with electronically excited oxygen atoms is less than that of CH_4 and H_2O.

Concluding Remarks

The veritable "explosion" of experimental studies of ozone photochemistry and $O(^1D_2)$ reaction dynamics triggered by concern over the effects of man's activities on the chemical composition of the atmosphere has resulted in a substantial refinement of our understanding of atmospheric chemical cycles involving electronically excited oxygen atoms. Both deactivation rates and product branching ratios seem reasonably well-defined. The current state of knowledge concerning $O(^1D_2)$ reactivity is generally sufficient for atmospheric modeling, given the remaining major uncertainties involving transport phenomena. Some remaining aspects of $O(^1D_2)$ chemistry certainly are worthy of further examination. For example, were $O(^1D_2)$ to react with CO_2, even to a minor extent, this would have a major impact upon the atmospheric lifetime of this apparently inert molecule.

The details of ozone photodissociation require further elucidation, especially with regard to the yield of $O(^1D_2)$

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and $O(^3P_J)$ in the Hartley continuum. The apparent failure of direct studies[16] to agree within experimental error with earlier work[14] is disquieting. Further determination of $\Phi_{O(^1D_2)}(\lambda)$ over the stratospheric temperature range seems to be in order. The increasing availability of powerful tunable sources of photolysis energy in the ultraviolet region of the spectrum offers reasonable hope that such investigations may soon be carried out with unprecedented precision.

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