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MEMORANDUM

To: All Recipients of the DNA Reaction Rate Handbook  
(DNA 1948H)

From: The Editors

Subject: Revision Number 6

*This revision*

Enclosed herewith you will find a copy of Revision Number 6 to the Handbook. It comprises several re-corrected pages from Chapters 11 and 16, and updated versions of Chapters 17 and 19 -- *Electron*

You should immediately discard the previous copies of the portions affected, and place this new material in its proper order in your copy of the Handbook.

You should also enter on page iii in front of your Handbook the following information: Revision Number 6; Date of Issue - December 1975; Date of Receipt - whatever day you receive this; and sign your name in the last column.

We anticipate the issuance of Revision Number 7, updating Chapter 20 and revising Chapter 24, by midsummer, and Revision Number 8, providing new material for Chapter 2, shortly thereafter.

→ Attachment and Detachment Processes; and Chapter 19 -- Neutral Reactions.

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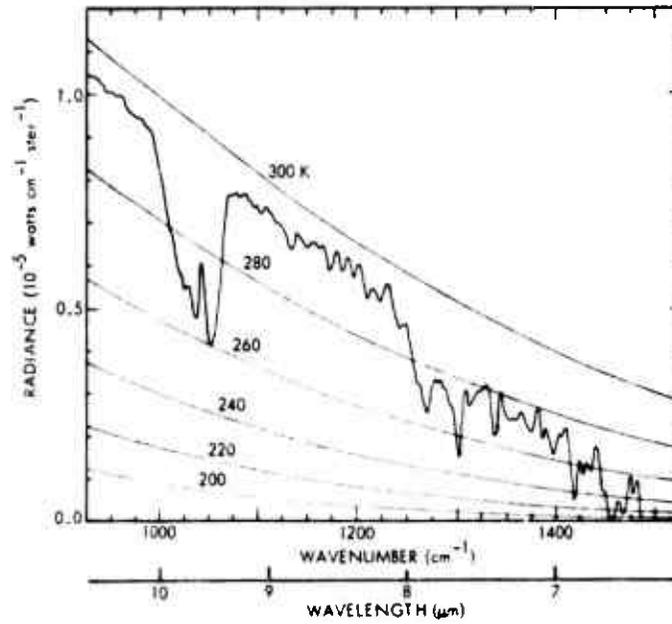


Figure 11-5. Earthshine in the  $1000\text{--}1450\text{ cm}^{-1}$  region (Reference 11-41).

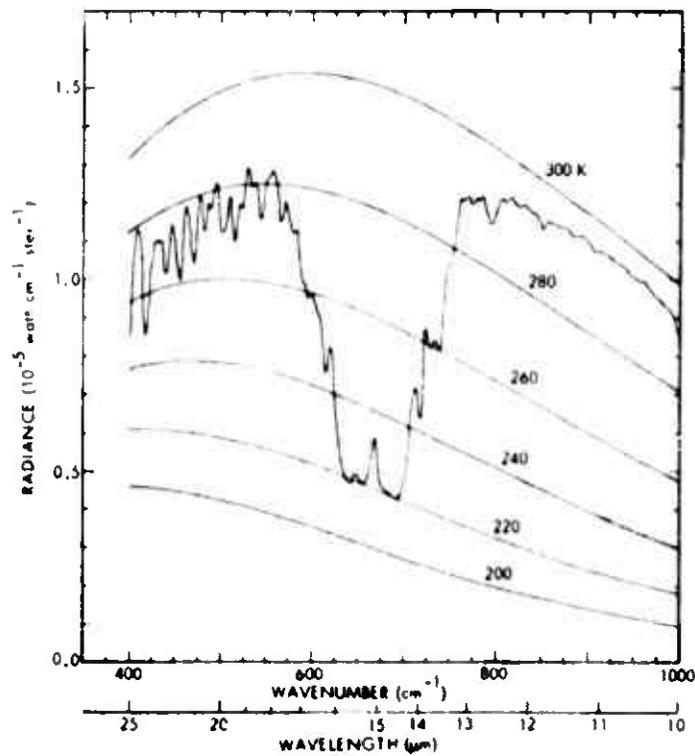


Figure 11-6. Earthshine in the  $400\text{--}1000\text{ cm}^{-1}$  region (Reference 11-41).

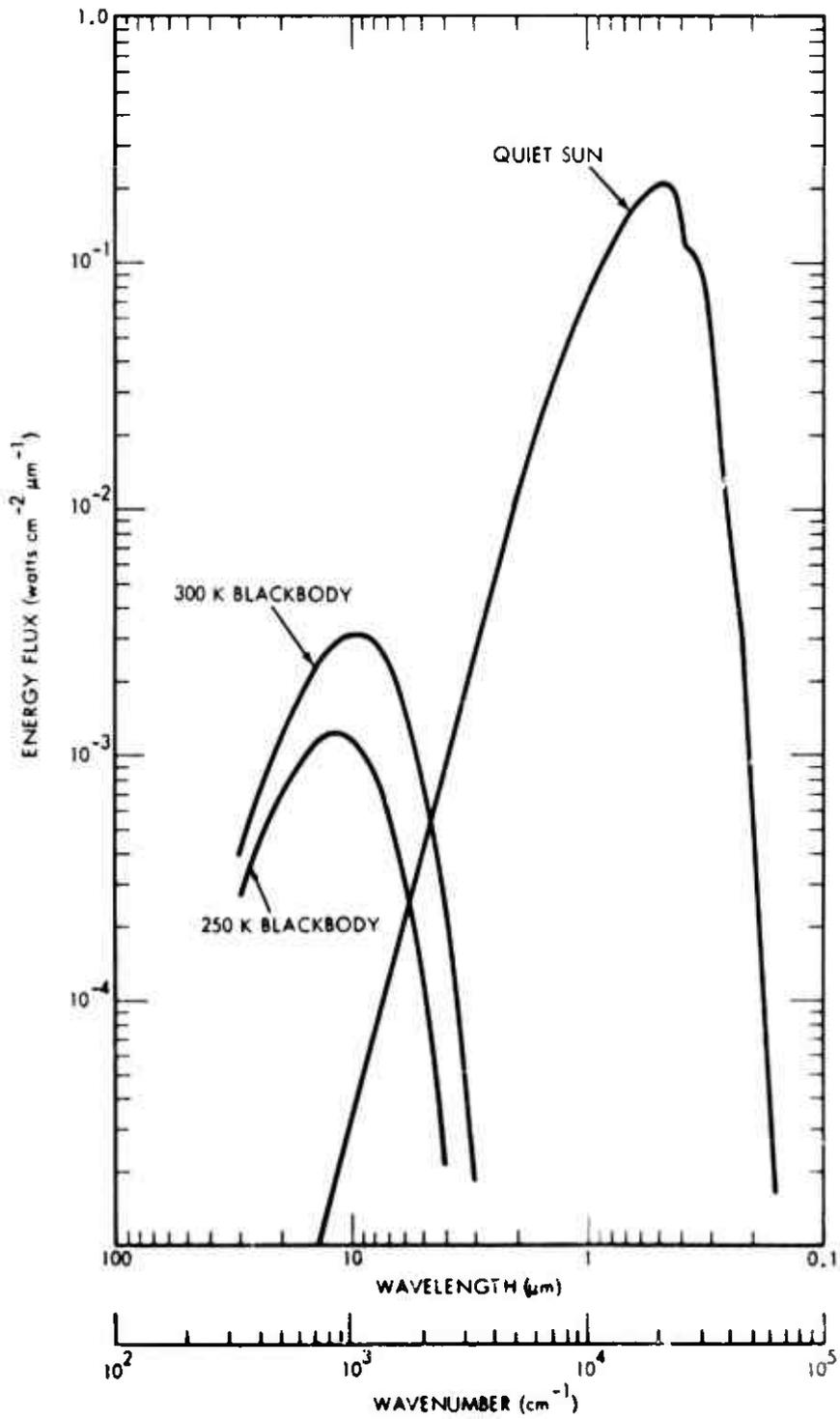


Figure 11-7. Irradiance at the top of the atmosphere, for quiet sun and two blackbody sources.

of the wave functions and potential-energy curves to determine the repulsive curves, concluding that the ( $^2\Sigma^+$ ) and ( $B^2\Pi$ ) states were important for electron capture by  $\text{NO}^+$  ( $v=0$ ) ions. While the two theories disagree by a factor of  $\sim 2.5$  (the approximate uncertainty in Michels' calculation of the initial capture step), they both indicate  $\sim T_e^{-0.5}$  temperature dependence over the whole energy range. Until the reasons for the discrepancies among the various determinations

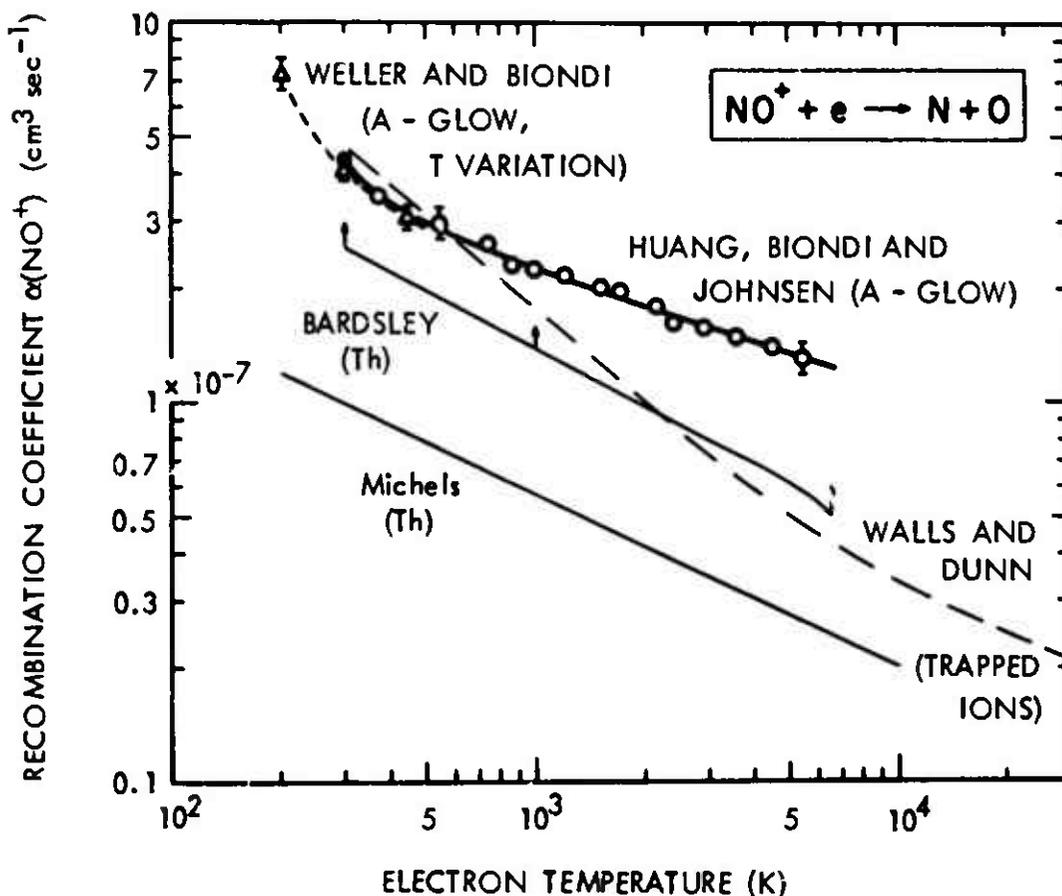
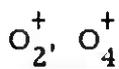


Figure 16-2. Two-body electron-ion recombination coefficient  $\alpha(\text{NO}^+)$  as a function of electron temperature. Experimental results are from Weller and Biondi (Reference 16-24), Walls and Dunn (Reference 16-26), and Huang, Biondi, and Johnsen (Reference 16-27). Theoretical curves are from Bardsley (Reference 16-28) and Michels (Reference 16-29).

can be clarified it is suggested that the value  $\alpha(\text{NO}^+) = (4.2 \pm 0.2) \times 10^{-7} (T_e/300)^{-(0.50 \pm 0.15)} \text{ cm}^3 \text{ sec}^{-1}$  be used over the range 300 - 5000 K.

Finally, as in the case of nitrogen it has been possible to obtain a value for the recombination of the dimer ion ( $\text{NO} \cdot \text{NO}^+$ ) by increasing the partial pressure of NO to  $\sim 0.2$  torr in the NO-Ne mixtures. From such studies Weller and Biondi (Reference 16-24) find  $\alpha(\text{NO} \cdot \text{NO}^+) = (1.7 \pm 0.4) \times 10^{-6} \text{ cm}^3/\text{sec}$  at  $T = 300 \text{ K}$ .



Simultaneous microwave and mass-spectroscopic measurements of electron and positive-ion decays in oxygen-neon mixtures have been used by Kasner and Biondi (Reference 16-30) to determine  $\alpha(\text{O}_2^+)$ . A "single-pulse-afterglow" method was used to avoid negative-ion accumulation effects and it was found that, in contrast to earlier repetitive pulse-afterglow studies (Reference 16-31), the  $\text{O}_2^+$  ion wall current accurately "tracked" the recombination-controlled electron-density decay. At 300 K, a value  $\alpha(\text{O}_2^+) = (2.2 \pm 0.5) \times 10^{-7} \text{ cm}^3/\text{sec}$  was found from  $1/\langle n_e \rangle$  versus  $t$  plots exhibiting linear regions,  $f \geq 10$  over the ranges  $3 \times 10^{-4} < p(\text{O}_2) < 10^{-2}$  torr and  $p(\text{Ne}) \approx 20$  torr. In these studies it is possible that the  $^3\text{P}_2$  neon metastables produce  $\text{O}_2^+$  ions in their ground electronic state and a high vibrational state ( $v \leq 20$ ) or even in the first excited electronic state ( $a^4\Pi_u$ ). In triple mixture (Ne:Ar:O<sub>2</sub>) studies, attempts were made to limit the  $\text{O}_2^+$  ions to the ground electronic and lower ( $v \leq 5$ ) vibrational states.

Mehr and Biondi (Reference 16-21) have used a microwave afterglow/mass-spectrometer apparatus employing microwave electron heating to determine  $\alpha(\text{O}_2^+)$  in oxygen-neon mixtures. Good  $\text{O}_2^+$  ion tracking of the electron-density decays was obtained and accurate values of  $\alpha(\text{O}_2^+)$  were determined from comparison of the experimental data with computer solutions of Equation (16-10). At  $T_e = 300 \text{ K}$  a value  $\alpha(\text{O}_2^+) = (1.95 \pm 0.2) \times 10^{-7} \text{ cm}^3/\text{sec}$  was obtained, in good agreement with Kasner and Biondi's results.

Previous microwave afterglow work without mass identification of the ions by Biondi and Brown (Reference 16-16) and by Mentzoni (Reference 16-32) led to values of  $\alpha \approx 3 \times 10^{-7}$  and  $2 \times 10^{-7} \text{ cm}^3/\text{sec}$ , respectively, at low pressures ( $\approx 2$  torr) of pure oxygen. However, at even lower oxygen pressures in oxygen-helium mixtures Kasner, Rogers, and Biondi (Reference 16-31) found substantial  $\text{O}_3^+$  ion concentrations, so that the afterglow ionic compositions in the studies without mass analysis are in doubt.



the rate constant of which was calculated to be  $k \approx 1 \times 10^{-26}$  cm<sup>6</sup>/sec at 300 K, and therefore should be of lesser importance than Thomson recombination.

Finally, the associative ion-ion recombination process, that is:



appears (Reference 16-68) to offer a much smaller coefficient,  $k \approx 10^{-27}$  cm<sup>6</sup>/sec at 300 K, than Thomson recombination; this mechanism is neglected in the present discussion, since its importance seems highly questionable.

#### 16.4 SUMMARY

Values for the appropriate recombination coefficients for all processes where there is either sufficient experimental and/or theoretical information, or where there is a critical need for an estimate, are contained in Table 16-1. In general, those values with larger quoted uncertainties reveal a greater degree of guesswork which has taken place in attempting to evaluate the kinetics of the process.

Table 16-1. Recombination coefficient tabulation according to the form  $k = (a \pm \Delta a) (T/T_r)^{b \pm \Delta b}$  for the case  $T_r = 300$  K. The notation  $[-x]$  signifies  $10^{-x}$ . The symbol  $\{T\}$  indicates the dependence for simultaneous variation of  $T_{\text{gas}}, T_i$ , and  $T_e$ , while the symbol  $\{T_e\}$  indicates the dependence for variation of  $T_e$  alone. Units are  $\text{cm}^3 \text{sec}^{-1}$  for all two-body, and  $\text{cm}^6 \text{sec}^{-1}$  for all three-body interactions.

Process	Reactants	$a \pm \Delta a$	$b \pm \Delta b$	Remarks
1. <u>Electron-Ion</u> a. <u>Disassociative</u>  [simple ions]	$\text{N}_2^+ + e$	$(2.7 \pm 0.3)[-7]$ $(1.8^{+0.4}_{-0.2})[-7]$	$-(0.2 \pm 0.2)\{T\}$ $-(0.39)\{T_e\}$	See Figure 16-1 for range of validity.
	$\text{NO}^+ + e$	$(4.1 \pm 0.3)[-7]$ $(4.2 \pm 0.2)[-7]$	$-(1.0 \pm 0.2)\{T\}$ $-(0.50 \pm 0.15)\{T_e\}$	200-300 K 300-5000 K See Figure 16-2.
	$\text{O}_2^+ + e$	$(2.1 \pm 0.2)[-7]$	$-(0.7 \pm 0.3)\{T\}$ $-(0.6 \pm 0.1)\{T_e\}$	See Figure 16-3.
[triatomic ions]	$\text{CO}_2^+ + e$	$(3.8 \pm 0.5)[-7]$	$-(0.5 \pm ?)\{T_e\}$	300 K. See Ref. 16-8.
	$\text{HCO}^+ + e$	$(3.3 \pm 0.5)[-7]$ $(2.0 \pm 0.3)[-7]$	$-(0.5 \pm ?)\{T_e\}$	205 K 300 K $T_e = T = T_n$ Afterglow

Table 16-1. (Cont'd.)

Process	Reactants	$a \pm \Delta a$	$b \pm \Delta b$	Remarks
a. Dissociative (Cont'd.) [dimer ions]	$N_4^+ + e$	$(2 \pm 1)[-6]$	$-(1 \pm ?)\{T\}$	See Figure 16-1.
	$(NO^+ \cdot NO) + e$	$(1.7 \pm 0.5)[-6]$	$-(1 \pm ?)\{T\}$	No temp. dependence has been determined.
	$O_4^+ + e$	$(2 \pm 0.5)[-6]$	$-(1 \pm ?)\{T\}$	Measurement at 205 K.
$[H_3O^+(H_2O)_n$ series ions] N.B.: These are designated by their respective mass numbers, i.e., as $(M)^+$ .	$(19)^+ + e$	$(1.3 \pm 0.3)[-6]$	$-(0.2^{+0.4}_{-0.1})\{T\}$	$(19)^+$ , $(37)^+$ , and $(55)^+$ measured at 540 K.
	$(37)^+ + e$	$(2.8 \pm 0.4)[-6]$		$(37)^+$ and $(55)^+$ also measured at 415 K.
	$(55)^+ + e$	$(5.1 \pm 0.7)[-6]$		$(55)^+$ and $(73)^+$ measured at 300 K. $(91)^+$ , $(109)^+$ , and $(127)^+$ measured at 205 K.
	$(73)^+ + e$	$(6.1 \pm 1.2)[-6]$		
	$(91)^+ + e$	$(7.4 \pm 1.5)[-6]$		
	$(109)^+ + e$	$(9.3 \pm 2)[-6]$		
	$(127)^+ + e$	$(10 \pm 2)[-6]$		

Table 16-1. (Cont'd)

Process	Reactants	$a \pm \Delta a$	$b \pm \Delta b$	Remarks
a. Dissociative (Cont'd) $[\text{NH}_4^+(\text{NH}_3)_n$ series ions]	$18^+ + e$	$(1.3 \pm 0.3) [-6]$	}	All at 300 K; $T_e = T_+ = T_n$ ; Afterglow
	$35^+ + e$	$(2.4 \pm 0.4) [-6]$		
	$52^+ + e$	$(2.8 \pm 0.4) [-6]$		
b. Radiative	$\text{H}^+$ thru $\text{K}^+ + e$	$(3.5 \pm 1) [-12]$	$-(0.7 \pm 0.1)$	See Figure 16-4.
c. Electron-stabilized	$\text{H}^+ + 2e$ and $\text{He}^+ + 2e$	$(1 \pm ?) [-19]$	$-(4.5 \pm ?)$	Valid for $T_e < 2000$ K.
d. Neutral-stabilized	"Air" ions + neutrals + e	$(1) [-26 \pm 1]$	$-(2.5 \pm ?)$	Rough estimate.
	$\text{He}_2^+ + e + \text{He}$	$(2 \pm 0.5) [-27]$	-	Measured at 300 K.
2. Ion-ion a. Mutual neutralization	$\text{I}_2^+ + \text{I}^-$ $\text{Br}_2^+ + \text{Br}^-$	$(1) [-7 \pm 0.5]$	$-(1.5 \pm 0.1)$	$300 < T < 340$ K
	$\text{H}^+ + \text{H}^-$	$(3.9 \pm 2.1) [-7]$	$-(0.45 \pm 0.05)$	See Refs. 16-58, 16-60.
	$\text{H}_2^+ + \text{D}^-$	$(4.7 \pm 0.7) [-7]$	$-(0.45 \pm 0.05)$	See Ref. 16-63.

## 17. ELECTRON ATTACHMENT AND DETACHMENT PROCESSES\*

A.V. Phelps, Joint Institute for Laboratory Astrophysics  
(Latest Revision 8 June 1973)

### 17.1 INTRODUCTION

The purpose of this chapter is to review the available data regarding the rates of electron attachment and detachment processes involving atmospheric gases. The various types of attachment-detachment processes are considered and the recommended values for the rate coefficients are listed. Next an attempt is made to estimate the stability of the various negative ions of ionospheric interest. Finally, the ionospheric significance of these processes is discussed briefly. The suggested rate coefficients are tabulated in Tables 17-1 through 17-6.

### 17.2 TYPES OF ATTACHMENT-DETACHMENT PROCESSES

Electron attachment and detachment processes of significance in the normal and disturbed atmosphere are: radiative attachment and its inverse, photodetachment; dissociative attachment and its inverse, associative detachment; and three-body attachment, with a ground-state molecule or an electron as the third body, and its inverse, collisional detachment.

#### 17.2.1 Photodetachment and Radiative Attachment:



Radiative detachment and attachment rates involving negative ions of atmospheric gases have been determined from measurements of the cross-sections for the photodetachment of electrons from negative ions. Measurements (References 17-1 through 17-6) of photodetachment cross-sections of possible interest (References 17-7

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\*Based on work done at the Westinghouse Research Laboratories, and supported in part by the U. S. Army Research Office—Durham.

through 17-9) include  $O^-$ ,  $H^-$ ,  $OH^-$ ,  $O_2^-$ ,  $H_2O_3^-$ ,  $NO^-$ ,  $O_3^-$ ,  $NO_3^-$ , and  $NO_2^-$ . Other ions of possible atmospheric interest (References 17-1, 17-7 through 17-9) which have not been studied are  $CO_3^-$ ,  $CO_4^-$ ,  $HO_2^-$ , and the hydrates of the ions listed. Mass-spectrometric studies (Reference 17-10) in the atmosphere have shown the presence of negative ions such as  $O^-$ ,  $O_2^-$ ,  $NO_3^-(H_2O)_n$ , and  $CO_4^-$ . The simpler ions are observed at higher altitudes and during periods of ionospheric disturbance.

The measured photodetachment cross-sections for  $O^-$  and  $O_2^-$  as a function of wavelength have been integrated (Reference 17-1) over the incident solar flux to give daytime photodetachment cross-sections. Also, measurements of photodetachment rates under white light illumination have been made (Reference 17-5) for  $O_2^-$  formed by the three-body attachment process and for  $O_3^-$ . Photodetachment cross-sections have been measured (References 17-1, 17-6) for  $NO_2^-$ ,  $NO_3^-$ , and  $NO^-$ . The angular dependence of the photodetachment cross-sections for  $O^-$  and  $H^-$  has been shown to agree with theory (Reference 17-11).

Theoretical calculations (Reference 17-12) of photodetachment rates for complex systems are not available because of uncertainties as to the range of energies over which threshold laws are valid and because of the difficulties of accurate calculations. Attempts (Reference 17-13) have been made to relate elastic scattering cross-sections and photodetachment cross-sections.

Radiative attachment is expected to be of significance only when an electronegative neutral species is present in appreciable concentrations, e.g., atomic oxygen. The rate coefficient (Reference 17-1) for radiative attachment to  $O$  is  $(1.3 \pm 0.1) \times 10^{-15}$   $cm^3/sec$  for electron energies below 1 eV. Because of differences between the apparent electron affinity derived from photodetachment experiments (References 17-1, 17-2) using theoretical "threshold laws" and from attachment-detachment equilibrium experiments (Reference 17-1), there is considerable uncertainty as to the radiative attachment coefficient for  $O_2$ . It is probably (References 17-1, 17-14) less than  $2 \times 10^{-18}$   $cm^3/sec$  for electrons at 230 K. Photodetachment measurements (Reference 17-4) have been made for  $OH^-$ , but because of the effects of rotational structure on the cross-section it has not been possible to calculate the radiative attachment rate coefficient for low-energy electrons to  $OH$ . Radiative attachment coefficients for  $O_3$  and  $NO$  are unknown. The other major components of the atmosphere,

i. e.,  $N_2$ ,  $CO_2$ , Ar, and  $H_2O$ , do not form stable negative ions by the attachment of low-energy electrons. Recommended photodetachment and radiative detachment rate coefficients are given in Tables 17-1 and 17-2.

Table 17-1. Radiative attachment.

Reaction	Rate Coefficient ( $cm^3/sec$ )	Reference
1. $e + O \rightarrow O^- + h\nu$	$(1.3 \pm 0.1) \times 10^{-15}$	17-1
2. $e + O_2 \rightarrow O_2^- + h\nu$	$2 \times 10^{-(19 \pm 1)}$	17-1, 17-14
3. $e + OH \rightarrow OH^- + h\nu$	$10^{-(15 \pm 1)}$	17-4
4. $e + O_3 \rightarrow O_3^- + h\nu$	unknown	
All others should be unimportant		

Table 17-2. Photodetachment.<sup>a</sup>

Reaction	Destruction Frequency ( $sec^{-1}$ )	Reference
1. $h\nu + O^- \rightarrow O + e$	1.4	17-2
2. $h\nu + O_2^- \rightarrow O_2 + e$	$0.3 \pm 0.1$	17-2, 17-5
3. $h\nu + O_3^- \rightarrow O_3 + e$	$0.2 \pm 0.1$	17-15
4. $h\nu + NO_2^- \rightarrow NO_2 + e$	$10^{-(2 \pm 1)^b}$	17-1, 17-16
5. $h\nu + OH^- \rightarrow OH + e$	$\sim 1^b$	17-4
6. $h\nu + CO_3^- \rightarrow CO + O_2 + e$	unknown	
7. $h\nu + NO_3^- \rightarrow ? + e$	unknown	

## Notes:

<sup>a</sup> Values given (Reference 17-1) are integrated cross-sections for solar radiation without corrections for atmospheric absorption, back-scattering, etc.

<sup>b</sup> The available photodetachment cross-section data do not appear to have been folded into the solar flux distribution. The values quoted are very rough estimates based on the cross-sections and photon energy dependences given in the references cited.

## 17.2.2 Dissociative Attachment and Associative

Detachment:  $e + XY \rightleftharpoons X^- + Y$ 

The process of dissociative attachment has been studied extensively in atmospheric gases for many years. Energy-dependent cross-sections are available (Reference 17-17) for dissociative attachment by electron impact for  $O_2$ ,  $NO$ ,  $H_2$ ,  $CO_2$ , and  $H_2O$  at room temperature. In each case the electron energy must exceed some threshold value in order for attachment to occur. Early attempts to predict the temperature dependence of the dissociative attachment reaction used the room-temperature determination of the threshold as the activation energy. However, later measurements for  $O_2$  (Reference 17-18) and for  $N_2O$  (Reference 17-19) have shown that the attachment cross-section at low electron energies increases rapidly with temperature. Theory is now capable of describing the dependence of dissociative attachment cross-sections on temperature in the case of  $O_2$  (Reference 17-20). In the lower ionosphere it appears that the only dissociative attachment process of probable significance is the attachment of low energy electrons to  $O_3$ . Recent measurements (Reference 17-21) yield rate coefficients varying from  $5 \times 10^{-12} \text{ cm}^3/\text{sec}$  at 200 K to  $9 \times 10^{-12} \text{ cm}^3/\text{sec}$  at 300 K. In this case the negative ion formed is expected to be  $O^-$  (Reference 17-22).

The process of associative detachment was predicted theoretically (Reference 17-23) many years ago as the logical inverse of dissociative attachment. However, experimental studies of this process have been reported (References 17-7, 17-24, 17-25) more recently. In many cases the observed rate coefficients are a large fraction of the ion-scattering cross-section due to the induced polarization interaction between the negative ion and the neutral atom or molecule (References 17-7, 17-23 through 17-26), i.e.,  $(2 - 10) \times 10^{-10} \text{ cm}^3/\text{sec}$ . Associative detachment reactions involving atomic oxygen (Reference 17-24) are of particular importance in the ionosphere (References 17-7 through 17-9). There is not much information available as to the temperature dependence of the rate coefficient for associative detachment. In many cases, the associative detachment rate coefficient is essentially independent of ion energy (Reference 17-25), e.g., for  $O^- + CO$  and  $O^- + H_2$  at ion energies below 0.15 eV. However, for  $O^- + NO$  the rate coefficient decreases (Reference 17-25) by approximately an order of magnitude as the average ion energy increases from 0.04 to 0.26 eV. In the case of the detachment of electrons in collisions of energetic  $O^-$  ions with  $O_2$ , it appears that associative detachment is less important than collisional detachment (Reference 17-27) and conversion to  $O_2^-$  (References 17-5, 17-25, 17-28). Associative

detachment in collisions of thermal  $O^-$  ions with  $N_2$  has not been observed (Reference 17-29) although energetic  $O^-$  ions appear (Reference 17-27) to undergo detachment collisions with  $N_2$ . The neutral molecule formed by associative detachment is usually in a highly excited state (Reference 17-26) so that the detailed-balance relations are not expected to be useful for relating the associative detachment and dissociative attachment coefficients. Recommended dissociative attachment and associative detachment rate coefficients are given in Tables 17-3 and 17-4.

Table 17-3. Dissociative attachment.\*

Reaction	Rate Coefficient ( $cm^3/sec$ )	Reference
1. $e + O_3 \rightarrow O^- + O_2$	$9 \times 10^{-12} (T/300)^{3/2}$ ( $200 < T < 300$ K)	17-21
2. $e + O_2 \rightarrow O^- + O$	$< 10^{-16}$ ( $T < 2000$ K)	17-18
3. $e + H_2O \rightarrow H^- + OH$	very small	17-17

\*No temperature-dependent rate coefficients are given for  $O_2$  and  $H_2O$  since the values will be critically dependent upon cross-section at energies below 1 eV and no experimental data are available for that region.

Table 17-4. Associative detachment.

Reaction	Rate Coefficient ( $cm^3/sec$ )	Reference
1. $O^- + O \rightarrow O_2 + e$	$2 \times 10^{-10}$	17-24, 17-30
2. $O^- + O_2(^1\Delta_g) \rightarrow O_3 + e$	$\sim 3 \times 10^{-10}$	17-30
3. $O^- + N \rightarrow NO + e$	$2.2 \times 10^{-10}$	17-7, 17-30
4. $O^- + H_2 \rightarrow H_2O + e$	$7.5 \times 10^{-10}$	17-24, 17-25
5. $O^- + NO \rightarrow NO_2 + e$	$3 \times 10^{-10} (T_{ion}/300)^{-1}$ ( $300 < T_{ion} < 2000$ K)	17-24, 17-25
6. $O^- + N_2 \rightarrow N_2O + e$	$< 1 \times 10^{-12} (T_{ion} \sim 300$ K) $< 4 \times 10^{-9} \exp(-26,000/T_{ion})$ ( $4000 < T_{ion} < 20,000$ K)	17-24 17-27

Table 17-4. (Cont'd.)

Reaction	Rate Coefficient (cm <sup>3</sup> /sec)	Reference
7. $O^- + O_2 \rightarrow O_3 + e$	$< 5 \times 10^{-15}$ ( $300 < T_{ion} < 10,000$ K) $< 2.3 \times 10^{-9} \exp(-26,000/T_{ion})$ ( $4000 < T_{ion} < 20,000$ K)	17-25 17-27
8. $O_2^- + O \rightarrow O_3 + e$	$3 \times 10^{-10}$	17-24, 17-30
9. $CO_3^- + O \rightarrow O_2 + CO_2 + e$ slow		17-7
10. $O_2^- + N \rightarrow NO_2 + e$	$5 \times 10^{-10}$	17-24
11. $O_3^- + O \rightarrow 2O_2 + e$	unknown	

### 17.2.3 Three-Body Attachment and Collisional Detachment with a Neutral Third Body: $e + X + M \rightleftharpoons X^- + M$

An apparent three-body attachment process has been found (References 17-14, 17-31 through 17-37) to be important in  $O_2$ ,  $NO$ ,  $N_2O$ , and  $NO_2$ , and in mixtures (References 17-14, 17-31, 17-36, 17-37) of these gases with other gases. The rate coefficients for three-body attachment processes in  $O_2$  and  $NO$  are found (References 17-31, 17-33, 17-34) to be a maximum at electron energies of about 0.1 eV. In general it has not been possible to distinguish between a three-body process involving an intermediate excited negative ion which is stabilized by collision (Bloch-Bradbury model) and an apparent three-body process involving the dissociative attachment of an electron in a collision with a temporary neutral complex composed of two molecules. A theoretical study (Reference 17-38) of the Bloch-Bradbury model for electron attachment in  $O_2$  predicts a three-body attachment coefficient approximately equal to the observed value. Because of uncertainties as to the proper model, as well as questions of excited states, the dependence of the apparent three-body attachment coefficient on electron energy cannot be assumed to be the same as the temperature dependence of the rate coefficient. The available experimental data are shown in Table 17-5. In view of the large rate coefficients for associative detachment in the presence of atomic nitrogen or oxygen discussed above there is no need to guess at the effectiveness of N or O atoms as third bodies in the attachment process. As pointed out in a review (Reference 17-32), measurements of the room-temperature attachment coefficient

Table 17-5. Three-body attachment.

Reaction	Rate Coefficient ( $\text{cm}^6/\text{sec}$ )	Reference
1. $e + \text{O}_2 + \text{O}_2 \rightarrow \text{O}_2^- + \text{O}_2$	$(1.4 \pm 0.2) \times 10^{-29}$ $\times (300/T) \exp(-600/T)$ ( $195 < T < 600 \text{ K}$ )	17-14, 17-32
2. $e + \text{O}_2 + \text{N}_2 \rightarrow \text{O}_2^- + \text{N}_2$	$(1 \pm 0.5) \times 10^{-31}$	17-14, 17-32
3. $e + \text{O}_2 + \text{CO}_2 \rightarrow \text{O}_2^- + \text{CO}_2$	$(3.3 \pm 0.7) \times 10^{-30}$ ( $300 < T < 525 \text{ K}$ )	17-14, 17-32
4. <sup>a</sup> $e + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_2^- + \text{H}_2\text{O}$	$(1.4 \pm 0.2) \times 10^{-29}$ ( $300 < T < 400 \text{ K}$ )	17-14
5. <sup>a</sup> $e + \text{NO} + \text{NO} \rightarrow \text{NO}^- + \text{NO}$	$8 \times 10^{-31}$	17-33
6. <sup>a</sup> $e + \text{NO}_2 + \text{N}_2 \rightarrow \text{NO}_2^- + \text{N}_2$	$4 \times 10^{-11}{}^b$	17-39, 17-40
7. $e + 2\text{CO}_2 \rightarrow \text{X}^- + ?$	$< 2 \times 10^{-36}$ ( $T_e = 300 \text{ K}$ )	17-14

<sup>a</sup> Products uncertain.

<sup>b</sup> In  $\text{cm}^3/\text{sec}$  units since observed to be a saturated three-body process.

for thermal electrons in  $\text{O}_2$  and in air at pressures below 100 torr which differ significantly from the presently accepted values of  $2 \times 10^{-30}$  and  $1 \times 10^{-31} \text{ cm}^6/\text{sec}$ , respectively, should be regarded as highly suspect. At sufficiently high pressures of  $\text{O}_2$  or dry air, the apparent attachment rate coefficient is lowered because attachment occurs before the electrons thermalize (Reference 17-37).

The inverse of the three-body attachment process is the collisional detachment process in which a negative ion collides with an atom or molecule and an electron is released. In the case of ground-state molecules this process has an activation energy in the center-of-mass coordinates equal to or greater than the electron affinity of the negative ion. This is observed (Reference 17-14) to be the case for  $\text{O}_2^-$  ions in  $\text{O}_2$  at temperatures between 375 and 580 K. There is now evidence (Reference 17-33) for collisional detachment in NO but there are questions (Reference 17-34) as to the identity of the ions present in some experiments. We have recommended attachment coefficients obtained in experiments which take into account that the

collisional detachment rate coefficients are much larger than for  $O_2$ . Collisional detachment has been observed (Reference 17-27) as the result of collisions of energetic  $O^-$  ions with  $O_2$ ,  $N_2$ , and  $H_2O$ . Collisional detachment caused by excited molecules has been observed (Reference 17-30) to occur with a large rate coefficient in the case of  $O_2(^1\Delta_g) + O_2^-$ . Recommended collisional detachment rate coefficients are given in Table 17-6.

Table 17-6. Collisional detachment.

Reaction	Rate Coefficient ( $cm^3/sec$ )	Reference
1. $O_2^- + O_2 \rightarrow O_2 + O_2 + e$	$(2.7 \pm 0.3) \times 10^{-10}$ $\times (T/300)^{1/2} \exp(-5590/T)$ ( $375 < T < 600$ K)	17-14
2. $O_2^- + N_2 \rightarrow N_2 + O_2 + e$	$(1.9 \pm 0.4) \times 10^{-12}$ $\times (T/300)^{3/2} \exp(-4990/T)$ ( $375 < T < 600$ K)	17-14
3. $O^- + O_2 \rightarrow O + O_2 + e$	$2.3 \times 10^{-9} \exp(-26,000/T_{ion})$ ( $T_i < 20000$ K)	17-27
4. $O^- + N_2 \rightarrow O + N_2 + e$	$2.3 \times 10^{-9} \exp(-26,000/T_{ion})$ ( $T_i < 20000$ K)	assumed (see 17-27)
5. $O_2^- + O_2(^1\Delta_g) \rightarrow 2O_2 + e$	$2 \times 10^{-10}$	17-30

#### 17.2.4 Three-Body Attachment and Detachment with an Electron as the Third Body: $e + e + X \rightleftharpoons e + X^-$

The only experimental data concerning the role of an electron as an agent for the attachment and detachment reactions are the measurements (Reference 17-41) of the cross-sections for the collisional detachment of electrons from  $H^-$  and  $O^-$  by electrons at electron energies between 9 and 500 eV. As a result one is forced to rely on theory for estimates of rate coefficients for low-energy electrons. Although more recent theory (Reference 17-42) yields considerably larger values for low-energy electrons than previous theories, it is unlikely that these processes will have a significant effect on the negative-ion density in the earth's atmosphere.

## 17.3 STABILITY OF NEGATIVE IONS

Table 17-7 contains a list of negative ions of interest in approximate order of increasing stability, i. e., electron affinity. The values are based on a variety of experiments and theory (References 17-15, 17-16, 17-39, 17-40, and 17-43 through 17-61). It may be noted that  $N_2^-$ ,  $H_2^-$ , and  $H_2O^-$  are not stable, i. e., if they are formed they have a very short lifetime (Reference 17-43). The  $CO_2^-$  ion has been produced in negative ion-molecule reactions (Reference 17-59), but consistency with electron-beam excitation experiments and molecular structure theory (Reference 17-60) seems to require that the  $CO_2^-$  ions be in a metastable state with a negative adiabatic electron affinity.

Many of the values cited in Table 17-7 are subject to significant uncertainties because of the preliminary nature of the data and because of incomplete analysis of the equilibrium-constant data. The analysis of equilibrium-constant data in terms of dissociation energies is made difficult by apparent differences in the internal structure of the complex negative ions. Thus, the data for  $CO_4^-$  have been interpreted (Reference 17-14) as showing that there is a large freedom of internal motion whereas the data for  $O_4^-$  appear to indicate a rather rigid structure (Reference 17-48). A further complication is the apparent existence of at least two forms of  $NO_3^-$ . Presumably at least one of these forms is in an excited metastable electronic state with a rather different molecular structure than that of the lower energy state. At present the only information available regarding these states is the differences in their reactivity (References 17-47, 17-57) with, for example, NO and  $CO_2$ . Some simplifications in the classification of negative-ion complexes have been pointed out (Reference 17-47); it appears that complexes formed from  $O_2^-$  in the order of increasing stability are:  $(O_2^- \cdot O_2)$ ,  $(O_2^- \cdot H_2O)$ ,  $(O_2^- \cdot CO_2)$ , and  $(O_2^- \cdot NO)$ . Similarly for  $O^-$ , the order of stability of known ions is (Reference 17-47):  $(O^- \cdot N_2)$ ,  $(O^- \cdot O_2)$ ,  $(O^- \cdot CO_2)$ ,  $(O^- \cdot NO)$ , and  $(O^- \cdot NO_2)$ . There are not sufficient data available to say whether similar series exist for other negative ions such as  $NO^-$  and  $OH^-$ . The relative concentrations of the various ions in the atmosphere will depend upon competing detachment reactions as well as on the concentrations of the minor neutral constituents. Furthermore these ions can form hydrates and so effectively become more stable. An important area of future investigation is the study of the reactivity of the larger and more stable negative-ion hydrates with species such as O,  $O_3$ , and  $NO_2$  (Reference 17-62).

Table 17-7. Stability of negative ions of possible ionospheric interest.<sup>a</sup>

Ion	Adiabatic Electron Affinity (eV)	Dissociation Energy <sup>c</sup> (eV)	Photodetachment Threshold (eV)
$\text{NO}^-$	0.024 (17-33, 17-44)	( $\text{O}^- \cdot \text{N}$ ) 5.2	<1.0 (17-6)
$\text{O}_2^-$	$0.43 \pm 0.01$ (17-14, 17-63)	( $\text{O}^- \cdot \text{O}$ ) 4.08	$\leq 0.5$ (17-2)
$\text{O}_4^-$	$1.0^b$	( $\text{O}_2^- \cdot \text{O}_2$ ) $0.54$ (17-48)	$\geq 1.0^b$
$\text{O}_2^-(\text{H}_2\text{O})$	$1.2^b$	( $\text{O}_2^- \cdot \text{H}_2\text{O}$ ) $0.8$ (17-46, 17-49)	$\geq 1.2^b$
$\text{CO}_4^-$	$1.2 \pm 0.1$ (17-14)	( $\text{O}_2^- \cdot \text{CO}_2$ ) $0.8 \pm 0.08$	$\geq 1.2^b$
$\text{H}_3\text{O}_2^-$	$\leq 1.2^b$	( $\text{OH}^- \cdot \text{H}_2\text{O}$ ) $\leq 1.2$	$2.95$ (17-6)
$\text{SF}_6^-$	$\sim 1.4$ (17-50, 17-51) $\text{EA}(\text{O}_2) < \text{EA}(\text{SF}_6) < \text{EA}(\text{O})$ (17-52)	( $\text{SF}_5^- \cdot \text{F}$ ) $\leq 1.4$ (17-61)	$1.47 \pm 0.1$ (17-1, 17-2)
$\text{O}^-$	$1.47 \pm 0.01$ (17-1, 17-2, 17-53)		$\geq 1.95^b$
$\text{O}_2^-(\text{H}_2\text{O})_2$	$1.95^b$	( $\text{O}_2^-(\text{H}_2\text{O}) \cdot \text{H}_2\text{O}$ ) $0.75$ (17-46)	$2.1$ (17-15)
$\text{O}_3^-$	$1.9$ (17-45, 17-58)	( $\text{O}^- \cdot \text{O}_2$ ) ( $\text{O}_2^- \cdot \text{O}$ ) $1.4$ $2.5$	
$\text{O}_2^-(\text{H}_2\text{O})_3$	$2.6^b$	( $\text{O}_2^-(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ ) $0.67$ (17-46)	$> 2.6^b$

Table 17-7. (Cont'd.)

Ion	Adiabatic Electron Affinity (eV)	Dissociation Energy <sup>c</sup> (eV)		Photodetachment Threshold (eV)
$\text{CO}_3^-$	$\leq 3.3$	$(\text{O}^- \cdot \text{CO}_2)$	$\leq 1.8 \pm 0.2$ (17-64)	
$\text{NO}_2^-$	$2.38 \pm 0.06$ (17-54)	$(\text{O}^- \cdot \text{NO})$	4.1	2.75 (17-1) $\geq 2.74$ (17-16)
$\text{O}_2^-(\text{H}_2\text{O})_4$	3.2 <sup>b</sup>	$(\text{O}_2^-(\text{H}_2\text{O})_3 \cdot \text{H}_2\text{O})$	0.6 (17-46)	$> 3.2$
$\text{O}_2^-(\text{H}_2\text{O})_5$	3.7 <sup>b</sup>	$(\text{O}_2^-(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O})$	0.5 (17-46)	$> 3.7$
$\text{NO}_3^-$ <sup>d</sup>	$3.9 \pm 0.2$ (17-65, 17-66)	$(\text{O}_2^- \cdot \text{NO})$	$> D(\text{O}_2^- \cdot \text{O}) = 2.5$ (17-7)	
		$(\text{O}^- \cdot \text{NO}_2)$	$3.5 \pm 0.2$	

<sup>a</sup> References given in parentheses. When no reference is given, the values cited are our calculations based on other entries for the same species.

<sup>b</sup> Calculated assuming that the neutral complex has a negligibly small dissociation energy for separation into the stable neutral fragment molecules, e.g.,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$ . For a discussion of the interaction of  $\text{O}_2$  with  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}$  see Reference 17-67. For  $\text{O}_2$  with  $\text{O}_2$  see Reference 17-68.

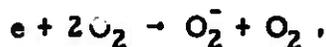
<sup>c</sup> This dissociation energy is for the bond indicated by the dot in the formula for the negative ion. The dot is not intended to indicate the structure of the complex. The dissociation energies for  $\text{NO}$  and  $\text{O}_2$  are from Reference 17-55 and that for the  $\text{O}_2 \cdot \text{O}$  bond from Reference 17-16.

<sup>d</sup> Recent evidence (Reference 17-47) shows that there is a metastable form of this ion with a sufficient lifetime so as to lead to different reaction sequences.

## 17.4 IONOSPHERIC SIGNIFICANCE

It is convenient to divide a discussion (References 17-1, 17-8, 17-9, 17-32) of the dominant attachment and detachment reactions in the earth's atmosphere into three categories: (1) the initial attachment of the free electrons to neutral species to form negative ions; (2) the ion-molecule reactions which convert the initial negative ions into more stable species; and (3) the detachment process.

The important attachment processes in undisturbed, dry air are:



and:



The relative importance of these processes varies with altitude and time because of the varying concentrations of O and O<sub>2</sub>. When the moisture content is high or when the gas temperature is high and the air composition is altered, other processes may be important, e.g.,  $e + O_2 + H_2O \rightarrow O_2^- + H_2O$  in moist air. At present it appears that the reaction:



can be important only under highly disturbed conditions.

The negative-ion-molecule reactions of importance in the atmosphere are discussed in Chapter 18A so that it need merely be noted that the initial O<sub>2</sub><sup>-</sup> and O<sup>-</sup> ions can react (References 17-7 through 17-9, 17-24, 17-30, 17-47, 17-57) with minor constituents of the normal atmosphere, i.e., O<sub>3</sub>, CO<sub>2</sub>, and NO, to form ions such as O<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>. The relative concentrations of the various ions will depend upon competing detachment reactions as well as on the ion conversion processes. Furthermore these ions can form hydrates and so effectively become more stable.

Associative detachment reactions have been shown (References 17-7 through 17-9) to play an important role in determining the concentrations of free electrons and negative ions. Ionospheric model studies (References 17-8, 17-9) have not been able to identify the detachment reactions controlling the changes in electron density which occur at sunrise and sunset. It seems certain that O<sup>-</sup> and O<sub>2</sub><sup>-</sup> are not the dominant negative ions. The identity of the dominant ions as determined by rocket-borne mass spectrometers

varies with altitude and with the degree of ionospheric disturbance. The negative ions observed (Reference 17-10) include  $O^-$ ,  $O_2^-$ ,  $NO_3^-$ , and  $NO_3^- (H_2O)_n$ .

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## 19. NEUTRAL REACTIONS

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## 19.1 INTRODUCTION

Much information on the chemical reactions of neutral species is required for an understanding of the normal and perturbed upper atmosphere. In general, such information, in the form of reaction rate constants as functions of temperature, represents a very small fraction of the vast field of chemical reaction kinetics, and might be expected to be found scattered throughout the literature on chemical rate processes. This does not turn out to be the case, because some of the reactants in most of the interesting steps are atomic species which are not normally present in chemical reactions except under extreme thermal or photochemical conditions. Thus, the quantitative studies of the reaction rates, as described in the following sections and summarized in Chapter 24, are mostly less than 15 years old, use special experimental techniques to prepare the reactants at controlled temperature and in specific quantum states, and owe their existence to the impetus of studies in aeronomy and to the renaissance in the field of atom reaction theory. The study of neutral reactions is both harder and easier than that of charged species which makes up much of this Handbook: harder because the rate constants span a much wider range in magnitude due to the frequent existence of energy barriers (energies of activation) whose a priori prediction is difficult; easier because most systems are thermally homogeneous, i. e., do not require the difficult experimental and theoretical extrapolation to thermal conditions inherent in beam or swarm experiments involving charged particles and applied electric fields.

In the following sections of this chapter some of the principal experimental methods will be described briefly and their strengths and weaknesses pointed out; five important reactions will then be discussed in some detail, followed by briefer expositions of some coupled reaction systems. In conclusion, some important gaps in our knowledge will be mentioned and suggestions made for future work.

## 19.2 EXPERIMENTAL METHODS

The data for the neutral reactions listed in Chapter 24 come from an astonishing variety of experimental techniques. These include classical gas reaction kinetics, shock-tube studies, photochemical decomposition, and low-pressure flow reactor methods with or without discharges to produce atomic species. This last method has been the most widely used and will be described in greater detail than the others.

Classical kinetic studies are particularly welcome in the few instances where they can be applied, e.g., thermal decomposition of ozone. Rate constants can be measured far more accurately in static, homogeneous systems than in shock tubes or discharge-flow systems because of better temperature control, absence of diffusion or convection effects, and more accurate analyses for changes in pressure or chemical composition. Their principal shortcoming for the purpose of the present survey is that they often deal with overall changes more complex than a single reaction, i.e., that the multi-step mechanism must be known, so that the increased experimental accuracy is lost in the apportioning of errors to the various elementary steps.

The shock-tube method has been by far the most productive technique for the study of dissociation and recombination reactions at high temperatures. Its accuracy is fairly low, for aerodynamic reasons such as boundary-layer effects and shock instabilities, because of deficiencies in the instrumentation techniques, e.g., low signal-to-noise ratios, and because of the chemical-interpretive consequences of these physical limitations, e.g., large uncertainties in kinetic temperature, vibrational relaxation effects, etc.

Photochemical studies under static conditions share with other static methods the advantages of easy temperature and composition control as well as good chemical analysis capability, but they suffer from several shortcomings such as the experimental difficulty of accurate actinometry, spatial inhomogeneity due to strong absorption, uncertainty in the nature of the electronically excited states, and hot-atom or radical effects in photolytic bond dissociation. There is an increasing and very welcome emphasis on the measurement of fundamental quantities such as radiative lifetimes, specific quenching cross-sections, fluorescence spectra, etc., rather than the less specific measurements of quantum yield as a function of

time, pressure, and composition. Flash-photolysis methods have been applied most successfully to iodine-atom recombination studies.

Steady-state flow methods, in which the desired reactant species are produced thermally or in a gas discharge, mixed with other reactants, and the progress of reaction measured as a function of a space coordinate, have found increasing use in recent years. Their principal advantages include: the wide range of energetic reactant species such as H, O, N, and OH which can be produced and measured quantitatively; the availability of the simple expedient by which rapid temporal variations are transformed into spatial variations in a cylindrical flow tube; and the great wealth of detection methods available, e.g., chemiluminescent light emission, mass spectrometry, optical absorption spectrometry, electron spin resonance spectrometry, hot-wire calorimetry. These techniques also have an appealing experimental simplicity. They have produced measurements of rate constants ranging from near-gas-kinetic collision frequency (and even higher when applied directly to ion-molecule reactions) to much lower values for reactions which have appreciable energy barriers.

The disadvantages or limitations of these methods fall into four categories:

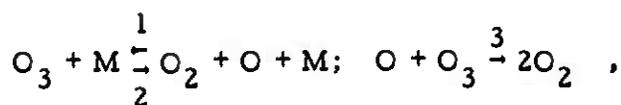
1. Characterization of the flow. Proper account must be taken of: viscous pressure drop along the tube; radial diffusion which should be fast enough to justify one-dimensional analysis; axial diffusion which should be slow enough to entail only a small correction to the measured spatial decay; and onset of turbulence at large flow velocities and high pressures. Some of these and other effects are discussed in detail elsewhere (References 19-1 through 19-3). In the case of very fast reactions, rapid mixing of reactants becomes a major problem.
2. Detector interference. Although closely related to (1), this requires special consideration, particularly in the case of catalytic probe detectors where the convective flow may be disturbed well upstream of the probe if diffusion is fast, or in the case of scavenger (titration) methods where another reactant is introduced which greatly reduces the atom concentration by rapid reaction.

3. Surface recombination. This is often a principal limitation. Gas reactions of reactive species can only be studied if the rate at which these species are removed at the wall is a small fraction of their total rate of disappearance. Thus, the surface recombination coefficient (the ratio of atom-removing to total number of wall collisions) must be smaller than  $10^{-3}$  (or preferably smaller than  $10^{-4}$ ) and walls must, therefore, be kept sufficiently clean or suitably poisoned. At the large throughputs of gases in fast-flow experiments it is often not possible to keep surfaces clean. In most studies, surface coatings of strong acids ( $H_3PO_4$ ,  $H_2SO_4$ ), teflon, or organic silicon compounds have been used on glass or silica flow tubes.
4. Metastable states. Insofar as flow discharges are used to produce the desired atomic or other reactant species, the presence and reactions of undesirable metastables may interfere grossly with the processes under study. This interference is particularly severe in the case of  $N_2$  or  $O_2$  discharges, and has led to serious errors in measurements of rate constants. There are, of course, no general remedies against it except the use of more nearly thermal sources (e.g., ozone decomposition as a source of O-atoms, thermal dissociation of  $H_2$  or  $O_2$  to yield the corresponding atoms), or the removal of metastables in discharge-flow systems. When the latter cannot be achieved, the harmlessness of these metastables to the particular process under investigation must be clearly established.

### 19.3 DETAILED DISCUSSION OF SOME IMPORTANT REACTIONS\*

#### 19.3.1 $O + O_3 \rightarrow 2O_2$ ( $\Delta E^0 = -93.7 \text{ kcal} = -4.06 \text{ eV}$ )

Although this reaction has been studied by all the methods described in the preceding section, a substantial uncertainty in its energy of activation has been resolved comparatively recently. The thermal work summarized by Benson and Axworthy (Reference 19-4) and the shock-tube study of Jones and Davidson (Reference 19-5) suffer from the unavoidable limitation that in the mechanism:



experiments in dilute ozone under steady-state conditions only determine  $(k_1/k_2) \times k_3$ . The large temperature coefficient of this expression is due mostly to the equilibrium constant of the first step ( $\Delta E^0 = 24.2 \text{ kcal} = 1.05 \text{ eV}$ ) and, therefore, needs to be measured with unattainable accuracy in order to determine the desired activation energy  $E_3$  (known to be in the range of 3 to 6 kcal) to within  $\pm 0.2 \text{ kcal}$ . In shock-tube experiments where a steady state is not reached because reaction 1 is very fast and reaction 2 is negligible, the situation is equally bad because the large activation energy of reaction 1 overshadows that of reaction 3. The reported values of  $k_3$  are  $5.6 \times 10^{-11} \exp(-5.7/RT)$ ,  $c = 2900$  (Reference 19-4, from data in the range 340-390 K) and  $(4.0 \pm 0.8) \times 10^{-11} \exp[-(5.6 \pm 0.5)/RT]$ ,  $c = 2800$

\*Reaction energies are here given in both kcal and eV units. It is understood that the proper units are kcal/g mole and eV/molecule and that 1 eV/molecule equals 23.069 kcal/g mole. The symbol  $\Delta E^0$  stands for the change in energy at  $T = 0 \text{ K}$  and therefore also for the change in enthalpy,  $\Delta H^0$ , at  $T = 0 \text{ K}$ , per g mole of reaction proceeding as written. Rate constants  $k$  are in units of  $\text{cm}^3 \text{ sec}^{-1}$  for two-body, and  $\text{cm}^6 \text{ sec}^{-1}$  for three-body processes. These are presented in two forms, viz;  $k = A(T/T_r)^B \exp(-E/RT)$ , corresponding to the form of expression of most of the published data, where the reference temperature ( $T_r$ ) is usually 300 K but may be designated otherwise,  $E$  is the activation energy in kcal/g mole/K, and  $R = 1.987 \times 10^{-3} \text{ kcal/g mole}$ ; and  $k = a(T/300)^b \exp(-c/T)$ , corresponding to the practice used and explained elsewhere in the Handbook and in Table 19-1 of this chapter, i. e.,  $c = E/R$ ,  $b = B$ , and  $a = A$  unless  $T_r \neq 300 \text{ K}$ .

$\pm 300$  (Reference 19-5,  $T = 700-900$  K). Results of measurements in which O-atoms (from a glow discharge) and  $O_3$  (ozone) were mixed in a flow-tube experiment gave  $8.2 \times 10^{-12} \exp [-(3.3 \pm 1.0)/RT]$ ,  $c = 1700 \pm 500$ , as recalculated by Campbell and Nudelman (Reference 19-6) from data by Leighton et al (Reference 19-7), but this result as well as others based on the measured steady-state ozone concentration in afterflows of oxygen discharges are suspect due to the known presence of sizable concentrations of metastable  $O_2(a^1\Delta_g)$ , and to a lesser extent,  $b^1\Sigma_g^+$ , which react rapidly with  $O_3$ .

The photochemical study by Castellano and Schumacher (Reference 19-8), in which  $O_3$  was photolyzed by red light (thereby producing  $O_2 + O$  in their electronic ground states), obviated the above difficulties by measuring the ratio  $k_2/k_3$ , the temperature coefficient of which is determined mainly by  $E_3$ . Unfortunately, these experiments were carried out at only three temperatures in the range 278-298 K. Combining these ratios with a value of  $k_2 = 6.5 \times 10^{-34} (T/300)^{-2.6}$ , which is discussed further below (Par. 19.3.4), and putting  $k_3 = A_3 \exp [-E_3/RT]$ , one obtains  $(1.4 \pm 0.3) \times 10^{-12} \exp [-(3.0 \pm 0.4)/RT]$ ,  $c = 1500 \pm 200$ . This gives rate constants in excellent agreement with the expression of Reference 19-4 near 400 K, but is a factor of 6 lower than the value developed in Reference 19-5 near 800 K. The situation is complicated further by the fact that shock-tube work (References 19-9 and 19-10) on ozone in the temperature range 1600-3300 K suggests a larger value of  $k_3/k_1$  than that given by Jones and Davidson (Reference 19-5) whose  $k_3$  is 20-30 times larger than the present one at those temperatures.

Two experimental studies of the reaction were cited in a review by Schiff (Reference 19-11): Kondratiev and Intezarova (Reference 19-12) reported  $k = (4.8 \pm 1.5) \times 10^{-12} \exp (-3.7/RT)$ ,  $c = 1900$ , and Lundell, Ketcheson, and Schiff (Reference 19-13) found  $k = 3.2 \times 10^{-11} \exp (-4.5/RT)$ ,  $c = 2300$ . Two additional investigations have clarified this problem further: Krezenski (Reference 19-14) measured the competitive reactions of O with OCS and  $O_3$  from 197 to 299 K and obtained  $1.1 \times 10^{-12} \exp (-4.33/RT)$ ,  $c = 2180$ , for the rate constant of the  $O + O_3$  reaction, and McCrumb and Kaufman (Reference 19-15) found  $k = 1.1 \times 10^{-11} \exp (-4.31/RT)$ ,  $c = 2170$ . Johnston's critical review (Reference 19-16) analyzed data obtained up to 1967 and therefore did not include the four later studies. He recommended  $2.0 \times 10^{-11} \exp (-4.79/RT)$ ,  $c = 2400$ . A more recent measurement by the flash photolysis-resonance fluorescence technique (Reference 19-17) over the temperature range 220-353 K has

given  $2.0 \times 10^{-11} \exp(-4.52/RT)$ ,  $c = 2350$ . Therefore, a compromise recommendation of  $1.5 \times 10^{-11} \exp(-4.45/RT)$ ,  $c = 2240$ , which represents a reasonable summary of the more reliable experimental results, is proposed here and is considered unlikely to require further revision.

### 19.3.2 $N + O_2 \rightarrow NO + O$ ( $\Delta E^0 = -32.07 \text{ kcal} = -1.39 \text{ eV}$ )

This reaction has been studied by flow methods in the forward direction, at temperatures in the range 400-750 K, and by static methods in the reverse direction, at temperatures in the range 1500-1700 K. There is substantial agreement that the forward reaction has a small activation energy whose magnitude lies in the range 5.9-7.5 kcal. The work of Clyne and Thrush (Reference 19-18), for example, gave a forward rate constant of  $(1.4 \pm 0.2) \times 10^{-11} \exp[-(7.1 \pm 0.4)/RT]$ ,  $c = 3600 \pm 200$ , in good agreement with one calculated from the reverse step and the equilibrium constant as reported by Kaufman and Decker (Reference 19-19). Consequently this was cited as the value of preference in the first edition of this Handbook, although it was acknowledged that a larger value would help explain the relatively large densities of NO measured in the upper atmosphere.

A more recent measurement by Wilson (Reference 19-20) over the large temperature range 300-910 K has yielded  $2.4 \times 10^{-11} \exp(-7.9/RT)$ ,  $c = 4000$ , which differs only slightly from the earlier recommendation, and is now recommended.

### 19.3.3 $N + NO \rightarrow N_2 + O$ ( $\Delta E^0 = -74.99 \text{ kcal} = -3.25 \text{ eV}$ )

This very fast reaction was first studied by Kistlakowsky and Volpi (Reference 19-21) by mass spectrometry in a "stirred reactor", low-pressure flow system and by Kaufman and Kelso (Reference 19-22) who explained the sequence of visible afterglows when increasing amounts of NO are added to "active nitrogen," in terms of radiation originating from electronically excited products of  $N + N$ ,  $N + O$ , and  $O + NO$  recombinations. The  $N + NO$  reaction represents the key to the understanding of these phenomena by the rapid, quantitative formation of O from N, and makes possible the "titration" of N by NO with a clearly observable "endpoint" in low-pressure flow systems. Its rate constant was indirectly determined by Clyne and Thrush (Reference 19-18) to be  $4 \times 10^{-11}$ , independent of temperature over the range 475-755 K, and directly by Phillips and Schiff (Reference 19-23), who reported  $(2.2 \pm 0.6) \times 10^{-11}$  at 300 K in a

low-pressure flow system with mass-spectrometric detection. As there should be some steric requirements for a reactive collision of N and NO, the above value of one-tenth the gas-kinetic collision frequency indicates a very small (<0.5 kcal) or zero energy barrier. In the absence of any experimental temperature dependence this value of  $(2.2 \pm 0.6) \times 10^{-11}$  will be adopted here.

The reaction has been shown to yield  $N_2$  with extensive vibrational excitation (References 19-24 and 19-25), the average energy of  $N_2^{\ddagger}$  being  $21 \pm 5$  kcal, corresponding to 3 or 4 vibrational quanta, and  $N_2^{\ddagger}$  was found to decompose  $O_3$  [ $k = (5.4 \pm 1.1) \times 10^{-13}$  near 300 K]. The latter behavior appears to be in contrast to that of  $O_2^{\ddagger}$  formed in the  $O + O_3$  reaction, with the possible explanation that O deactivates  $O_2^{\ddagger}$  much more efficiently (Reference 19-10) than N does  $N_2^{\ddagger}$ .

#### 19.3.4 $O + O_2 + M \rightarrow O_3 + M$ ( $\Delta E^{\circ} = -24.25$ kcal = $-1.05$ eV)

Some of the above discussion (Cf. Par. 19.3.1) is applicable here, since the recombination step is the reverse of the decomposition of ozone as studied by static (Reference 19-4) or shock-tube (References 19-5, 19-9 and 19-10) methods. From the measured decomposition rate constant and the equilibrium constant, Benson and Axworthy reported  $k = 8.2 \times 10^{-35} \exp(+0.89/RT)$ ,  $c = -450$ , near 360 K for  $M = O_2$ . Jones and Davidson reported  $(2.6 \pm 0.3) \times 10^{-35} \exp\{+(1.7 \pm 0.3)/RT\}$ ,  $c = -860 \pm 150$  or  $4.1 \times 10^{-34} (T/300)^{-1.66}$  to represent the combined shock-tube and lower temperature data for  $M = N_2$ , which should be multiplied by  $1.5 \pm 0.05$  for  $M = O_2$ . There have been further, direct measurements by Kaufman and Kelso (Reference 19-26) at 300 K for various M, and Ciyne, McKenney, and Thrush (Reference 19-27) for  $M = Ar$  in the range 188-373 K. The former authors found  $k = 6.5 \times 10^{-34}$  for  $M = O_2$  and  $5.5 \times 10^{-34}$  for  $M = N_2$ ; the latter reported  $2.5 \times 10^{-35} \exp\{+(1.8 \pm 0.4)/RT\}$ ,  $c = -910 \pm 200$ , or  $5.6 \times 10^{-34} (T/300)^{-3.4 \pm 0.8}$  from their own data, and  $9.1 \times 10^{-36} \exp\{+2.3/RT\}$ ,  $c = -120$  or  $5.0 \times 10^{-34} (T/300)^{-2.6}$  from a combination of all data, for  $M = Ar$ . By pulse radiolysis of Ar- $O_2$  mixtures with great excess of Ar, Sauer and Dorfman (Reference 19-28) were able to measure the ozone recombination rate at pressures up to 100 atmospheres, and reported  $(2.3 \pm 0.2) \times 10^{-34}$  at 296 K for  $M = Ar$ , in good agreement with other results. The relative efficiencies of  $N_2$  and Ar were found to be  $1.54 \pm 0.17$  in the shock-tube work (Reference 19-5) near 800 K,  $1.56 \pm 0.20$  in photolysis (Reference 19-8), and  $1.4 \pm 0.2$  in direct-flow-tube experiments (Reference 19-26), and one would calculate  $(7.5 \pm 2.0) \times 10^{-34} (T/300)^{-2.6}$

for  $M = N_2$ , somewhat higher than the direct results of  $5.5 \times 10^{-34}$  and  $3.5 \times 10^{-34}$  of References 19-26 and 19-28, respectively (the latter value representing the reported datum multiplied by the 1.5 efficiency ratio for  $N_2:Ar$ ).

Further experimental measurements have included studies at 300 K using pulse radiolysis (References 19-29 and 19-30) as well as flash and flow methods (References 19-31 through 19-33) which are in substantial agreement with earlier work. In addition, two investigations covered specific temperature ranges, viz.: Mulcahy and Williams (Reference 19-34), in the range 213-386 K, reported  $4.7 \times 10^{-35} \exp(+1.7/RT)$ ,  $c = -860$ , for  $M = Ar$ , with He,  $CO_2$ , and  $O_2$  having relative efficiencies of 0.8, 3.1, and 1.1, respectively; Huie, Herron, and Davis (Reference 19-35), in the range 200-346 K, reported  $6.6 \times 10^{-35} \exp(+1.01/RT)$ ,  $c = -510$ , for  $M = Ar$ , with He and  $N_2$  being, respectively, 0.9 and 1.7 times as efficient as Ar. The latter value is adopted here as the most reliable.

#### 19.3.5 $O + O + M \rightarrow O_2 + M$ ( $\Delta E^0 = -117.98 \text{ kcal} = -5.11 \text{ eV}$ )

Although the gap between the results of low-temperature extrapolations of shock-tube data and those of flow-tube experiments has been narrowed, particularly for  $M = Ar$ , several discrepancies remain.

Among the latter studies, there is excellent agreement between Morgan and Schiff's (Reference 19-36) rate constant of  $2.8 \times 10^{-33}$  at 294 K for  $M = N_2$  and Campbell and Thrush's (Reference 19-37)  $3.2 \times 10^{-33}$  for the same conditions. (The recombination rate constant is here defined by  $d[O_2]/dt = k[O]^2[M]$ .) These authors did not agree, however, on the relative efficiency of  $N_2$  and Ar, the former claiming a ratio  $>3.3$  and finding no measurable increase in rate for an addition of 40 percent Ar, the latter reporting a ratio of 1.9. This is of particular importance for comparison with shock-tube work, much of which was done for  $M = Ar$ . Much shock-tube work was also done for  $M = O_2$ , a case which is difficult to do in flow tubes because of the interfering ozone recombination. No shock-tube work was done for  $M = N_2$ . Earlier flow-tube results may have been in error due to the presence of metastables or hydrogenous impurities. Campbell and Thrush (Reference 19-37) also measured the temperature dependence in the range 190-350 K.

Results of shock-tube studies have shown very large ratios of relative efficiencies for different M such as 1:18:50 for  $Ar:O_2:O$ .

Extrapolated values at 300 K (Reference 19-38) of  $1.3 \times 10^{-31}$  for  $M = O_2$  using a  $T^{-2.5}$  dependence and of  $2.5 \times 10^{-30}$  for  $M = O$  using a  $T^{-3}$  dependence seem impossibly high. Yet most temperature dependence studies of recombination reactions near 300 K have given a  $T^{-n}$  dependence with  $n = 2.0-3.5$ , in qualitative agreement with the  $n$ 's found for the most efficient third-body species at high temperatures. To bring these data into agreement there would have to be a temperature range within the 500-2000 K interval where  $n$  decreases greatly. Careful studies are needed, which would overlap the lower part of this temperature interval. For the present, Campbell and Thrush's (Reference 19-37)  $3.0 \times 10^{-33} (T/300)^{-2.9 \pm 0.4}$  or  $2.8 \times 10^{-34} \exp(+1.4/RT)$ ,  $c = -700$ , will be adopted for  $M = N_2$  for the range 190-400 K, and  $3.9 \times 10^{-34} (T/3000)^{-2.5 \pm 0.5}$  (Reference 19-38) for  $M = O_2$  (and  $N_2$ ) for the range 2500-5000 K.

#### 19.4 BRIEF DISCUSSION OF OTHER REACTIONS

##### 19.4.1 The O + NO System

In the presence of NO, O-atoms undergo three reactions: the overall three-body recombination  $O + NO + M \rightarrow NO_2 + M$ ; the concurrent chemiluminescent recombination  $O + NO \rightarrow NO_2 + h\nu$ ; and the reaction with the product ( $NO_2$ ) of the first two reactions,  $O + NO_2 \rightarrow NO + O_2$ . The chemical equations are not meant to imply that the processes occur in single kinetic steps as there is good experimental evidence that they do not. Nevertheless, the equations properly represent the kinetic orders of the first and third reactions over the pressure range 0-10 torr and that of the second at least in the range 0.1-10 torr. The behavior of the chemiluminescent reaction below 0.1 torr is still in some doubt, although recent work favors a fall-off in the second-order rate constant below about 0.05 torr and a possible return to second-order behavior below  $10^{-3}$  torr.

For  $O + NO + M \rightarrow NO_2 + M$  ( $\Delta E^\circ = -71.76 \text{ kcal} = -3.11 \text{ eV}$ ) there is very good agreement on the rate constant among several studies. For  $M = N_2$  at 300 K, Klein and Herron (Reference 19-39) found  $(1.03 \pm 0.04) \times 10^{-31}$ , Kaufman and Kelso (Reference 19-40) found  $(0.93 \pm 0.13) \times 10^{-31}$ , and Ford and Endow (Reference 19-41) found  $0.83 \times 10^{-31}$ . For its temperature dependence, Reference 19-39 reported a negative activation energy of  $1.93 \pm 0.1 \text{ kcal}$  which corresponds to a  $T^{-2.4 \pm 0.1}$  dependence. Clyne and Thrush (Reference 19-42) reported an  $\exp[(+1.8 \pm 0.4)/RT]$ ,  $c = -910 \pm 200$ , dependence for  $M = O_2$  corresponding to  $T^{-3.3 \pm 0.8}$ . Estimates of  $(1.0 \pm 0.1) \times 10^{-31} (T/300)^{-2.5 \pm 0.3}$  for  $M = N_2$ , and  $(7 \pm 2) \times 10^{-32}$

$(T/300)^{-2.5 \pm 0.3}$  for  $M = O_2$  are made, but further work on the temperature dependence is in progress.

The third reaction,  $O + NO_2 \rightarrow NO + O_2$  ( $\Delta E^0 = -46.22 \text{ kcal} = -2.00 \text{ eV}$ ) is very fast (though considerably slower than the  $N + NO$  reaction in the previous section) and is often used to "titrate" O-atoms in flow systems. Its much greater speed than the three-body  $O + NO + M$  reaction in the 1-torr pressure range tends to keep the NO concentration constant and thereby makes the chemiluminescent intensity emitted by the second reaction depend on the O-atom concentration in a single experiment (Reference 19-2). Its rate constant at 298 K was reported as  $(2.5 \pm 0.7) \times 10^{-12}$  by Phillips and Schiff (Reference 19-25), and as  $(5.5 \pm 0.6) \times 10^{-12}$  by Klein and Herron (Reference 19-39). The latter authors also measured its temperature dependence in the range 278-374 K, finding an activation energy of  $1.1 \pm 0.2 \text{ kcal}$ . The reaction leads to appreciable vibrational excitation of the product  $O_2$  molecule, but its quantitative extent is still in doubt. The temperature dependence of this rate constant has been determined by several other groups: Smith (Reference 19-43) reported  $1.8 \times 10^{-11} \exp [(-0.70 \pm 0.45)/RT]$ ,  $c = 350 \pm 230$ ; Westenberg and DeHaas (Reference 19-44) found  $1.6 \times 10^{-11} \exp (-0.6/RT)$ ,  $c = 300$ ; Davis, Herron, and Huis (Reference 19-45) found  $9.1 \times 10^{-12}$ , independent of temperature in the range 230-339 K; and Bernand, Clyne, and Watson (Reference 19-46) reported  $(9.5 \pm 1.1) \times 10^{-12} (T/300)^{-0.53}$ . The value of Davis et al (Reference 19-45) is recommended here.

The spectrum, rate constant, and temperature dependence of the chemiluminescent recombination of O and NO are well known and all available information has been summarized and reviewed (Reference 19-47). The emission extends from 397.5 nm, corresponding to the full energy of the reaction, to well past 3  $\mu\text{m}$  and has maximum intensity near 600 nm. It is continuous, but has small intensity fluctuations which correspond to the strongest features of the complex absorption spectrum of  $NO_2$ . There is little doubt that the same electronically excited state(s) is (are) involved in the  $O + NO$  emission and in  $NO_2$  absorption and fluorescence, as is further indicated by similar, slight spectral shifts with pressure in fluorescence (Reference 19-48) and chemiluminescence (References 19-49 through 19-51). The second-order radiative rate constant, integrated over all wavelengths, was reported to be  $6.4 \times 10^{-17}$  ( $M = O_2$ ,  $T = 296 \text{ K}$ ) by Fontijn, Meyer, and Schiff (Reference 19-52), who underestimated its near-infrared component, and to be  $6.8 \times 10^{-17}$  ( $M = O_2$ ,  $T =$

367 K) by Vanpee, Hill, and Kineyko (Reference 19-53). Its temperature dependence was variously found to be  $T^{(-2.8 \pm 0.8)}$  by Clyne and Thrush (Reference 19-42),  $T^{(-1.55 \pm 0.30)}$  over the range 500 - 1100 K by Hartunian, Thompson, and Hewitt (Reference 19-54), and  $T^{-2.5} \exp(-0.3/RT)$ ,  $c = 150$ , over the range 140-380 K where  $M = O_2$  or  $N_2$  by Parkes and Kaufman (Reference 19-55). At total pressures in excess of about 0.3 torr, and including the infrared contribution, an integrated rate constant of  $(8 \pm 2) \times 10^{-17} (300/T)^{2.0}$  is recommended. It is important to note that the rapid vibrational relaxation in excited  $NO_2^*$ , now well established, brings about a decrease in the radiative rate constant with decreasing pressure as well as a leveling off to an irreducible second-order component of  $k$  at low pressures ( $\leq 10^{-3}$  torr), which is due to radiation from unstabilized  $NO_2^*$  (References 19-47, 19-50, 19-51, and 19-56). This low-pressure  $k$  is about  $(7 \pm 2) \times 10^{-18} (300/T)^{2.0}$ .

#### 19.4.2 The H + O<sub>2</sub> System

Although H is not a major constituent of the normal or slightly perturbed upper atmosphere, the following reactions are included here because they represent an efficient path for the recombination of O-atoms, due mainly to the much larger recombination rate constant of  $H + O_2 + M$  than of  $O + O_2 + M$ . Thus, the first step,  $H + O_2 + M \rightarrow HO_2 + M$  ( $\Delta E^0 = -46 \pm 2$  kcal =  $-2.0 \pm 0.1$  eV), is followed by the fast bimolecular steps,  $HO_2 + O \rightarrow OH + O_2$  ( $\Delta E^0 = -55.4 \pm 2$  kcal =  $-2.4 \pm 0.1$  eV), and  $OH + O \rightarrow O_2 + H$  ( $\Delta E^0 = -16.6 \pm 0.5$  kcal =  $-0.72 \pm 0.02$  eV) which result in the regeneration of H and the overall recombination of two O-atoms.

The first direct study of the  $H + O_2$  recombination by Clyne and Thrush (Reference 19-57) gave  $k = (2.2 \pm 0.2) \times 10^{-32}$  for  $M = Ar$  or  $He$ , and  $(5 \pm 2) \times 10^{-31}$  for  $M = H_2O$  at 295 K. These authors also reported a  $T^{(-1.8 \pm 0.7)}$  dependence. Several other investigations which used pulse radiolysis, flash photolysis, or discharge-flow methods have been in substantial agreement with these early measurements, with the exception of the work of Ahumada, Michael, and Osborne (Reference 19-57) who reported  $0.75$  and  $0.60 \times 10^{-32}$  for  $M = He$  and  $Ar$ , respectively. The range of relative  $N_2:Ar$  efficiencies for several investigations was 2.1-3.1. The most accurate and probably the most reliable results were those of Kurylo (Reference 19-58) who reported  $6.7 \times 10^{-33} \exp(0.467/RT)$ ,  $c = -235$ , for  $M = Ar$ , and those of Wong and Davis (Reference 19-59) who reported  $6.8 \times 10^{-33} \exp(0.675/RT)$ ,  $c = -340$ , for  $M = Ar$ . Using their  $N_2:Ar$  efficiency ratios of 3.4 and 2.9, respectively, a value of  $2.1 \times 10^{-32} \exp(0.595/RT)$ ,  $c = -300$ , is recommended here for  $M = N_2$ .

Indirect evidence is cited in Reference 19-60 that the  $O + HO_2$  reaction is fast and second-order, and a rate constant of  $>10^{-11}$  can be estimated.

The last of the three steps,  $OH + O \rightarrow H + O_2$ , is also discussed in Reference 19-60. It is a very fast, second-order reaction with a rate constant of  $(5 \pm 2) \times 10^{-11}$  near 300 K. It cannot have an appreciable activation energy ( $E < 0.5$  kcal), but may have a  $T^{0.5}$  dependence.

#### 19.4.3 Other Neutral Reactions (List in Chapter 24)

Among the atom recombination reactions there is still a surprising lack of agreement on the rate constant ( $d[N_2]/dt = k[N]^2[M]$ ) of  $N + N + M \rightarrow N_2 + M$ , for which values in the range  $(7-17) \times 10^{-33}$  were cited in a review by Barth (Reference 19-61). Two additional values are  $(11.5 \pm 1.0) \times 10^{-33}$  (Reference 19-62) and  $3.6 \times 10^{-33}$  (Reference 19-37) for  $M = N_2$ ,  $T = 300$  K. The latter authors also reported a  $T^{-2.0 \pm 0.4}$  dependence.

A summary of all available high-temperature shock-tube work by Baurer et al (Reference 19-63) suggested a value of  $4.6 \times 10^{-33} (T/3000)^{-1.7}$  for  $M = N_2$ . This again points up the discrepancy with low-temperature work as it would provide a rate constant at 300 K which is one to two orders of magnitude too large.

In the temperature range 90-600 K, Clyne and Stedman (Reference 19-64) reported  $7 \times 10^{-34} \exp(+1.0/RT)$ ,  $c = -500$ , and Campbell and Thrush (Reference 19-65) found  $8.3 \times 10^{-34} \exp(+1.0/RT)$ ,  $c = -500$ , for  $N + N + N_2 \rightarrow 2N_2$ . An average of the two,  $7.6 \times 10^{-34} \exp(+1.0/RT)$ ,  $c = -500$ , is recommended.

For  $N + O + M \rightarrow NO + M$ , older work (Reference 19-61) gave  $(5-16) \times 10^{-33}$  at  $T = 300$  K for  $M = N_2$ , whereas Reference 19-37 reported  $11 \times 10^{-33} (T/300)^{-0.5 \pm 0.2}$  or  $6.9 \times 10^{-33} \exp(+0.3/RT)$ ,  $c = -150$ .

The reactions  $O + NO \rightarrow O_2 + N$  and  $O + N_2 \rightarrow NO + N$  are the reverse of reactions discussed above. They are therefore highly endothermic and unlikely to be important except at high temperatures. For this reason, the forward reaction rates previously mentioned have been combined with simple expressions for the equilibrium constants,  $K = A \exp(E/RT)$ , which represent least-squares fits to the JANAF Thermochemical Values for the range  $T = 1000-5000$  K. The

resulting expressions are  $(5.3 \pm 1.1) \times 10^{-12} \exp [-(40.1 \pm 0.4)/RT]$ ,  $c = 20,200 \pm 200$ , for  $O + NO \rightarrow O_2 + N$ , and  $(1.0 \pm 0.3) \times 10^{-10} \exp [-(75.3 \pm 0.5)/RT]$ ,  $c = 37,800 \pm 300$  for  $O + N_2 \rightarrow NO + N$ .

The two reactions of O with  $N_2O$  which produce  $2NO$  or  $N_2 + O_2$  are known to have large activation energies and are unlikely to be important except at high temperatures. Some of the experimental evidence was reviewed in Reference 19-2. The expression for the first reaction by Fenimore and Jones (Reference 19-66) of  $(1.5 \pm 0.5) \times 10^{-10} \exp [-(28 \pm 3)/RT]$ ,  $c = 14,000 \pm 1500$ ,  $(d[NO]/dt = 2k[O][N_2O])$ , seems to be correct even though its pre-exponential factor is unusually large. The formation of  $N_2 + O_2$  appears to be about a factor of 3 slower, but its rate constant is more uncertain. A value of  $(5 \pm 2) \times 10^{-11} \exp [-(29 \pm 3)/RT]$ ,  $c = 15,000 \pm 1500$ , is suggested.

The reaction of N with  $NO_2$  can apparently give four sets of products: (1)  $N_2O + O$ ; (2)  $2NO$ ; (3)  $N_2 + O_2$ ; and (4)  $N_2 + 2O$ . Phillips and Schiff (Reference 19-67) found the relative rates of (1) to (4) to be  $(0.43 \pm 0.04):(0.33 \pm 0.07):(0.10 \pm 0.12):(0.13 \pm 0.11)$ , and they reported a total rate constant of  $(1.8 \pm 0.2) \times 10^{-11}$  at 300 K.

The reaction  $NO + O_3 \rightarrow NO_2 + O_2$  ( $\Delta E^0 = -47.5 \text{ kcal} = -2.1 \text{ eV}$ ) was investigated by Clyne, Thrush, and Wayne (Reference 19-68), who reported a rate constant of  $9.5 \times 10^{-13} \exp [-(2.45 \pm 0.15)/RT]$ ,  $c = 1230 \pm 80$ , in good agreement with earlier results.

Finally, the reaction  $NO_2 + O_3 \rightarrow NO + 2O_2$  (or  $NO_3 + O_2$ ) may be important at low altitude under highly perturbed conditions. Johnston and Yost's (Reference 19-69) value of  $9.8 \times 10^{-12} \exp (-7.0/RT)$ ,  $c = 3500$ , is recommended.

## 19.5 CONCLUSIONS

Rate constants for some of the reactions discussed above are listed in Table 19-1. Several conclusions may be reached from the preceding sections:

1. The general field is a very active one, most of the relevant work dating back a relatively few years, on the average.
2. For most of the principal neutral reactions of aerodynamic interest, rate constants are fairly well known, especially near 300 K.

3. Greatly increased experimental effort appears to be needed, however, in two distinct areas:
  - a. Many of the important steps, especially simple recombination processes, must be studied over wider temperature ranges, i. e., about 100-1000 K, where possible, in order to establish clearly the functional form of the temperature dependence, resolve the existing discrepancies with shock-tube work, and measure accurately activation energies where they exist.
  - b. In many of the reactions, the role of internal excitation in the reactants or products must be established, i. e., steps should be taken to proceed from studies of overall rates to those of detailed molecular dynamics. Excellent progress has been made in this area, and one may hope that the near future will bring further solutions to such problems as the formation, quenching, and reactions of  $O(^1D$  and  $^1S)$ ,  $O_2(b^1\Sigma_g^+$  and  $a^1\Delta_g)$ , vibrationally excited  $O_2$ ,  $N_2$ , or  $NO_2$ , and the like. While some of these species and their reactions are discussed separately in Chapter 20, their intimate relationships with the overall field of neutral reactions should not be overlooked.

The general field of elementary reactions which are of interest to DNA has remained a very active one. A welcome by-product of this activity has been the considerable effort which has gone into the preparation of thorough reviews, some of them on a major continuing basis. These include the NSRDS-NBS series, the British series by Baulch and co-workers at Leeds University, a review by Schofield (Reference 19-70), the proceedings of certain International Association of Geomagnetism and Aeronomy Symposia (References 19-71 and 19-72), and many specific reviews in series such as Annual Reviews of Physical Chemistry, Progress in Reaction Kinetics, Advances in Chemical Physics, and others.

Table 19-1. Neutral reaction rate constants.\*

$$k = (a \pm \Delta a) (T/T_p)^{b \pm \Delta b} \exp [-(c \pm \Delta c)/T]$$

Reaction	$a \pm \Delta a$	$b \pm \Delta b$	$c \pm \Delta c$	Remarks	Cf. Par. No.
<u>Rearrangement</u>					
$O + O_3 \rightarrow 2O_2$	$(1.5 \pm 0.3)[-11]$		$(2.24 \pm 0.2)[3]$		19.3.1
$O + NO_2 \rightarrow NO + O_2$	9.1[-12]				19.4.1
$O + NO \rightarrow O_2 + N$	$(5.3 \pm 1.1)[-12]$		$(2.02 \pm 0.02)[4]$		19.4.3
$O + N_2 \rightarrow NO + N$	$(1.0 \pm 0.3)[-10]$		$(3.79 \pm 0.03)[4]$		19.4.3
$O + N_2O \rightarrow 2NO$	$(1.5 \pm 0.5)[-10]$		$(1.4 \pm 0.2)[4]$		19.4.3
$O + N_2O \rightarrow N_2 + O_2$	$(5 \pm 2)[-11]$		$(1.4 \pm 0.2)[4]$		19.4.3
$O + OH \rightarrow O_2 + H$	$(5 \pm 2)[-11]$				19.4.2
$O + HO_2 \rightarrow OH + O_2$	1[-11]				19.4.2
$N + O_2 \rightarrow NO + O$	$(2.4 \pm 0.3)[-11]$		$(4.0 \pm 0.2)[3]$		19.3.2
$N + NO \rightarrow N_2 + O$	$(2.2 \pm 0.6)[-11]$				19.3.3
$N + NO_2 \rightarrow \text{Products}$	$(1.8 \pm 0.2)[-11]$				19.4.3

Table 19-1. (Cont'd.)

Reaction	$a \pm \Delta a$	$b \pm \Delta b$	$c \pm \Delta c$	Remarks	Cf. Par. No.
<u>Rearrangement (Cont'd.)</u>					
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	9.5[-13]		(1.3 ± 0.1)[3]		19.4.3
$\text{NO}_2 + \text{O}_3 \rightarrow \begin{cases} \text{NO}_3 + \text{O}_2 \\ \text{NO} + 2\text{O}_2 \end{cases}$	(9.8 ± 1.5)[-12]		(3.5 ± 0.2)[3]		19.4.3
<u>Three-Body Recombination</u>					
$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	1.1[-34]		-(5.1 ± 2.0)[2]	$\text{M} = \text{N}_2$	19.3.4
$\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	(1.0 ± 0.1)[-31]	-(2.5 ± 0.3)		$\text{M} = \text{N}_2$	19.4.1
$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$\begin{cases} 3.0[-33] \\ 2.8[-34] \\ 3.9[-34] \end{cases}$	-(2.9 ± 0.4)	-(7 ± 2)[2]	$\begin{cases} \text{M} = \text{N}_2, T = 200-500 \text{ K} \\ T_r = 3000 \text{ K}, \\ \text{M} = \text{N}_2 \end{cases}$	19.3.5
$\text{N} + \text{N} + \text{M} \rightarrow \text{N}_2 + \text{M}$	$\begin{cases} (7.6 \pm 2.0)[-34] \\ 4.6[-33] \end{cases}$	-(2.5 ± 0.5)	-(5.0 ± 2.0)[2]	$\begin{cases} \text{M} = \text{N}_2 \\ T_r = 3000 \text{ K}, \\ \text{M} = \text{N}_2 \end{cases}$	19.4.3

Table 19-1. (Cont'd.)

Reaction	$a \pm \Delta a$	$b \pm \Delta b$	$c \pm \Delta c$	Remarks	Cf. Par. No.
<u>Three-Body Recombination (Cont'd.)</u>					
$N + O + M \rightarrow NO + M$	$\{(6.9 \pm 2.0)[-33]$ $\{(1.1 \pm 0.3)[-32]$	$-(0.5 \pm 0.2)$	$-(1.5 \pm 1.0)[2]$	$T = 200-400\text{ K}$ $M = N_2$	19.4.3
$H + O_2 + M \rightarrow HO_2 + M$	$(2.1 \pm 0.4)[-32]$		$-3.0[2]$	$M = N_2$	19.4.2
<u>Radiative Recombination</u>					
$O + NO \rightarrow NO_2 + h\nu$	$\{(8 \pm 2)[-17]$ $\{(7 \pm 2)[-18]$	$-(2.0 \pm 0.5)$ $-(2.0 \pm 0.5)$		$p \geq 0.3 \text{ torr}$ $p \leq 10^{-3} \text{ torr}$	19.4.1

\*In this table,  $T_r = 300\text{ K}$  except where otherwise noted. The notation  $[-p]$  signifies  $10^{-p}$ . When the space under one or more of the parameters is left blank this does not imply that the parameter is zero but that it is either unknown or that the data do not warrant the use of a three-parameter expression. The units are  $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  for all reactions of the type  $A + B \rightarrow$ , and  $\text{cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  for all reactions of the type  $A + B + C \rightarrow$ .

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