Thermal-Energy Negative Ion–Molecule Reactions

ELDON E. FERGUSON

Aeronomy Laboratory, Environmental Science Services Administration Research Laboratories, Boulder, Colorado 80302

The study of negative ion–molecule reactions is a subject of current interest with applications in the fields of radiation chemistry, combustion, gas discharge, ionospheric chemistry, and astrophysics. The recent development of an experimental technique, the flowing afterglow system, has made possible the quantitative determination of rate constants for a wide variety of such reactions.

Ordinary flowing systems have been utilized in kinetic studies for some time, but ions, when formed, were not normally detected very far downstream because of slow flow rates and small tube diameters. The existence of ions far downstream in a large-diameter, fast-pumped Pyrex flow tube, such as used in spectroscopic studies, is made evident to the naked eye by the light given off in certain recombination reactions. This observation led naturally to the development of the flowing afterglow system by the incorporation of mass spectrometric detection at the end of the tube and by provision for the addition of neutral reactants into the flowing stream.

A schematic diagram of the flowing afterglow system, as originally developed by Schmeltekopf, Fehsenfeld, and the author, is presented in Figure 1. Details of the system have been discussed at length elsewhere.[1] Very briefly, suitable gases are added at the front end of the tube, usually with helium or another buffer gas. The gas is then subjected to electron bombardment. The name of the technique, incidentally, arises from the characteristic emission or afterglow of the helium after it is subjected to electron bombardment. (Argon has also been used as a carrier gas and it has afterglow properties similar to those of helium.) The neutral reactant is added downstream, at a point where there is no longer production of reactant ions. The rate of loss of reactant, detected mass spectrometrically, leads directly to a reaction rate constant, accurate in chemically favorable cases to ±10%. Figure 2 shows a typical example of data, the slope of the negative ion loss curve being proportional to the reaction rate constant.

Part of the versatility of the flowing afterglow system derives from the variety of negative ions which can be produced. The conventional low-pressure mass spectrometer is restricted in this regard to negative ions that can be produced by electron impact on stable molecules. In flowing afterglow systems, however, negative ions can be produced either by direct electron impact, by electron attachment, or by secondary reactions which occur with the primary or additionally added gases.

As an example, H^- can be produced by direct electron impact on H_2, NH_3, or CH_4, *e.g.*, eq 1. When oxygen

$$e + H_2 \longrightarrow H^- + H^+ + e \qquad (1)$$
$$\longrightarrow H^- + H$$
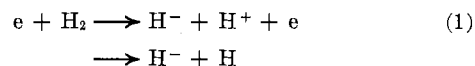
is added to a helium afterglow, O_2^- is produced by attachment (eq 2), where attachment occurs in the

$$e + O_2 \xrightarrow{M} O_2^- \qquad (2)$$

gas phase and possibly also on the filament. Addition of N_2O with the helium buffer leads to a usable NO^- concentration as a result of reaction 3, followed by

$$e + N_2O \longrightarrow O^- + N_2 \qquad (3)$$
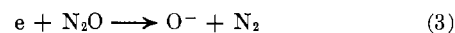
reaction 4. Negative ions so far studied include O_2^-,

$$O^- + N_2O \longrightarrow NO^- + NO \qquad (4)$$
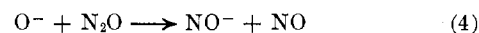
NO^-, CO_3^-, CO_4^-, O_3^-, O_4^-, $O_2^- \cdot H_2O$, AlO^-, and SF_6^-.

The flowing afterglow system has also proved to be versatile in respect to the kinds of neutral reactants which can be employed. Because the neutral reactant is added downstream, it is not subject to excitation or dissociation. This greatly simplifies the interpretation of results by eliminating concurrent reactions which would occur were all reactants subject to the same ionizing conditions. Also this implies that the neutral reactant is in a Boltzmann distribution of electronic, vibrational, and rotational states corresponding to the temperature of the tube walls. Unstable species, not generally amenable to mass spectrometric investigation, may also be studied in a flowing afterglow system. Atoms such as N, O, and H, and even radicals such as OH, have been so studied.

The flowing afterglow system has been modified so that the gas temperature can be varied from 80 to 600°K. The pressure can be varied from 0.1 to about 5 Torr and three-body reactions, such as (5), can

$$O_2^- + O_2 + M \longrightarrow O_4^- + M \qquad (5)$$
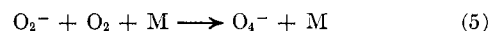
be investigated. Control of these parameters will permit really detailed studies and give new insights into the nature of ion–molecule reactions. This Account is largely confined to negative ion–molecule reactions whose measurement to date has been almost entirely restricted to the flowing afterglow technique.

Associative-Detachment Reactions

One kind of negative ion reaction which has no counterpart in positive ion reactions is associative detachment (reaction 6). In this process an electron

(1) E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Advan. At. Mol. Phys.*, **5**, 1 (1969).
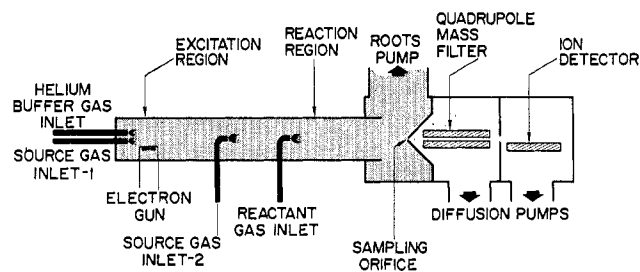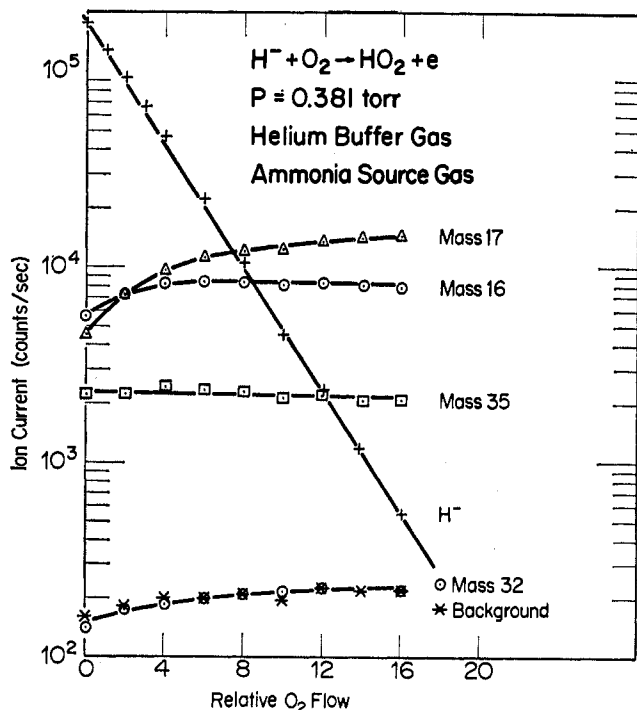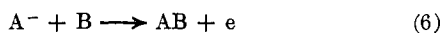
Figure 1. Schematic diagram of ESSA flowing afterglow system.

Figure 2. Raw data for $H^- + O_2 \rightarrow HO_2 + e$ reaction.

$$A^- + B \longrightarrow AB + e \qquad (6)$$

is detached from a stable atomic or molecular negative ion by a neutral atom or molecule with the formation of a larger molecule. Bond formation provides the exothermicity of the reaction. This process requires that a stable bond be formed between A and B, and this usually requires that A and/or B be chemically unsaturated radicals.

The process of associative detachment had been proposed for many years because of its potential importance in gas discharges,[2] aeronomy,[3] and astrophysics;[4] however the first laboratory observations[5] were carried out as recently as 1966. All of the several dozen reactions studied to date are listed in Table I. The measurements were all carried out in the ESSA flowing afterglow system, except for the reactions of O^- with H_2, CO, and NO, which have also been measured by Moruzzi, Ekin, and Phelps[6] in a drift tube.

(2) H. S. W. Massey, "Negative Ions," 2nd ed, Cambridge University Press, Cambridge, England, 1950, p 119.
(3) A. Dalgarno, Ann. Geophys., 17, 16 (1961).
(4) A. Dalgarno, quoted in a communication to B. E. J. Pagel, Mon. Notic. Roy. Astron. Soc., 119, 609 (1959).
(5) F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys., 45, 1844 (1966).
(6) J. L. Moruzzi, J. W. Ekin, and A. V. Phelps, ibid., 48, 3070 (1968).

Table I

Associative-Detachment Reactions Which Have Been Measured

Reaction	ΔE, eV	k, cm³/molecule sec	Ref
$H^- + H \rightarrow H_2 + e$	3.8	1.3 (−9)	a, d
$O^- + O \rightarrow O_2 + e$	3.6	1.4 (−10)	b, d
$O^- + N \rightarrow NO + e$	5.1	2.0 (−10)	b, d
$O^- + H_2 \rightarrow H_2O + e$	3.6	6.0 (−10)	b–d
$O^- + NO \rightarrow NO_2 + e$	1.4	1.6 (−10)	b–d
$O^- + CO \rightarrow CO_2 + e$	4.0	4.4 (−10)	b–d
$Cl^- + H \rightarrow HCl + e$	0.7	9.0 (−10)	b, d
$O_2^- + O \rightarrow O_3 + e$	0.6	3.0 (−10)	b
$O_2^- + N \rightarrow NO_2 + e$	4.1	5.0 (−10)	b
$OH^- + O \rightarrow HO_2 + e$	0.9	2.0 (−10)	b, d
$H^- + O_2 \rightarrow HO_2 + e$	1.25	1.2 (−9)	e
$OH^- + H \rightarrow H_2O + e$	3.2	1.0 (−9)	d
$CN^- + H \rightarrow HCN + e$	1.6	8.0 (−10)	d
$O^- + N_2 \rightarrow N_2O + e$	0.2	<1 (−14)	b, c
$OH^- + N \rightarrow HNO + e$	2.4	<1 (−11)	b
$O^- + SO_2 \rightarrow SO_3 + e$	2.1	7 (−10)	f
$S^- + H_2 \rightarrow H_2S + e$	0.9	<1 (−15)	g
$S^- + O_2 \rightarrow SO_2 + e$	3.8	3 (−11)	g
$O^- + C_2H_4 \rightarrow C_2H_4O + e$	1.2	7.7 (−10)	h
$O^- + O_2(^1\Delta_g) \rightarrow O_3 + e$	0.5	~3 (−10)	i
$O^- + CO_2 \rightarrow CO_3 + e$	Endothermic	<1 (−13)	f
$S^- + CO \rightarrow COS + e$	1.6	3.1 (−10)	f
$C^- + CO \rightarrow C_2O + e$	1.1	4.1 (−10)	j
$C^- + CO_2 \rightarrow 2CO + e$	4.3	4.7 (−11)	j
$C^- + N_2O \rightarrow CO + N_2 + e$	8.2	9.0 (−10)	j
$C^- + N_2O \rightarrow CN + NO + e$	1.6		
$C^- + H_2 \rightarrow CH_2 + e$	2.0	<1 (−13)	j

^{a} A. L. Schmeltekopf, F. C. Fehsenfeld, and E. E. Ferguson, Astrophys. J., 148, L155 (1967). ^{b} F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys., 45, 1844 (1966). ^{c} J. L. Moruzzi, J. W. Ekin, and A. V. Phelps, ibid., 48, 3070 (1968). ^{d} E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, Advan. Chem. Ser., No. 80, 83 (1969). ^{e} D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys., 53, 987 (1970). ^{f} F. C. Fehsenfeld, unpublished results. ^{g} F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys., 51, 3512 (1969). ^{h} D. K. Bohme and L. B. Young, J. Amer. Chem. Soc., 92, 3301 (1970). ^{i} F. C. Fehsenfeld, D. L. Albritton, J. A. Burt, and H. I. Schiff, Can. J. Chem., 47, 1793 (1969). ^{j} F. C. Fehsenfeld and E. E. Ferguson, J. Chem. Phys., 53, 2614 (1970).
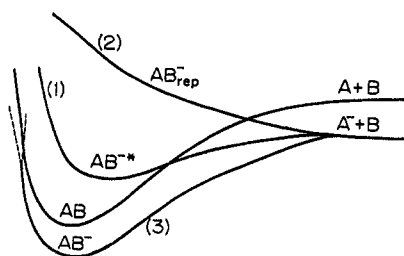

Figure 3. Schematic representation of possible negative ion molecular potential curves.

The mechanism by which associative detachment occurs is readily visualized with the aid of Figure 3. When the species A^- and B approach, three essentially different types of interaction can occur, designated by the potential curves 1, 2, and 3 in Figure 3.

If the interaction is repulsive as shown in curve 2, then at low energies only reflection or elastic scattering

can occur. If the interaction potential curve is an attractive one (curve 1) which cuts the AB potential curve at some geometry, then associative detachment can occur. After the curve crossing, that is, when the AB^{-*} curve lies above the AB curve, then autodetachment $AB^{-*} \rightarrow AB + e$ is exothermic. The autodetachment (or autoionization) time is usually short compared to the collision time so that a high probability for an associative-detachment reaction exists *when* a curve such as curve 1 exists. The case where a stable AB^- curve exists (curve 3) is less common, since most molecules do not have stable negative ions. The consequences of collisons on such reaction paths are less clear. Unless the curve cuts the AB curve somewhere below the $A^- + B$ dissociation limit, associative detachment is not likely.[7]

The autodetaching intermediate negative ion states in many cases are identical with the so-called negative ion "resonances" which lead to dissociation following electron attachment (*i.e.*, $e + AB \rightarrow AB^{-*} \rightarrow A^- + B$), vibrational excitation (*i.e.*, $e + AB \rightarrow AB^{-*} \rightarrow AB(v) + e$), and structure in electron scattering by the molecule. These resonances are the subject of very active theoretical and experimental investigation in current molecular physics. The associative-detachment studies provide complementary information in many cases.

If only one potential curve (molecular state) arises from A^- and B collisions, then associative-detachment measurements give direct information concerning this potential curve. As an example, the rapid occurrence of reaction 7 establishes that the $HCl^-(^2\Sigma)$ ground-

$$Cl^-(^1S) + H(^2S) \longrightarrow HCl + e \qquad (7)$$

state curve is of the form of curve 1, *i.e.*, attractive into the autodetaching region of HCl. One would therefore not expect HCl^- to be a stable negative ion, and it has never been observed. The observation of a large rate constant for reaction 8 has the same

$$OH^-(^1\Sigma) + H(^2S) \longrightarrow H_2O + e \qquad (8)$$

implication for the H_2O^- ground-state potential curve (and H_2O^- has not been observed). The low (or negative) electron affinity of species like HCl, H_2O, H_2, He, etc., follows from simple structural chemical considerations as well. The saturated valence electron configuration inhibits stable electron attachment, just as it inhibits stable H atom attachment or bond formation generally. On the other hand species forming bonds with H, such as H, OH, and Cl, might be expected to have positive electron affinities.

The occurrence of attractive, autodetaching, negative ion potential curves is evidently very common when associative detachment is exothermic (a very selective situation, of course), as evidenced by the large number of fast reactions listed in Table I. When both A and B are atomic, no reaction is yet known in which exothermic associative detachment is not fast!

The most usual situation arising is for a number of potential curves to exist, some attractive, some repulsive, and sometimes one or more stable curves so that the measured associative-detachment constant is a measure of the fraction of autodetaching curves. The associative-detachment reaction (9) is perhaps

$$H^-(^1S) + H(^2S) \longrightarrow H_2 + e \qquad (9)$$

the most rigorously understood theoretically of all ion-neutral chemical reactions. The two resulting H_2^- potential curves have been calculated.[8] A $^2\Sigma_g^+$ curve is repulsive, and a $^2\Sigma_u^+$ curve is attractive into the autodetaching region, where its lifetime against autodetachment is $\sim 10^{-15}$ sec. It therefore follows that the associative-detachment rate constant should be about one-half the H^-–H collision rate constant which is determined largely by the long-range charge-induced dipole force, leading to the familiar Langevin expression $k = 2\pi e \sqrt{\alpha/\mu}$ (α = polarizability, μ = reduced mass). This prediction has been checked experimentally,[9] although not with the precision the theory merits because of as yet unsolved problems of H atom concentration measurement. Reaction 9 is of considerable astrophysical interest as it controls the loss of H^- in the solar photosphere. The H^- ion in turn determines the solar opacity in certain regions of the spectrum.

When either A or B (or both) is molecular rather than atomic, the possibility of inhibiting chemical factors arises which leads to some exothermic associative-detachment reactions having unobservably small rate constants. Four such examples are known (Table I). Consider reaction 10. In spite of the fact

$$O^- + H_2 \longrightarrow H_2O + e$$
$$k_{10} = 6 \times 10^{-10} \text{ cm}^3/\text{sec} \qquad (10)$$
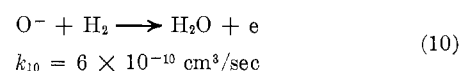
that the reactant O^- must insert into the H_2 bond the rate constant is large and independent of ion energy,[6] *i.e.*, there is no activation energy. On the other hand the similar reaction (11) is extremely slow, if it occurs

$$S^- + H_2 \longrightarrow H_2S + e$$
$$k_{11} < 10^{-15} \text{ cm}^3/\text{sec} \qquad (11)$$
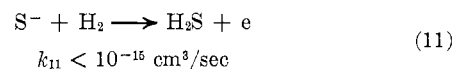
at all. Perhaps it is reasonable to view reaction 10 as

$$O^- + H_2 \longrightarrow OH^- \cdots H \longrightarrow H_2O + e$$
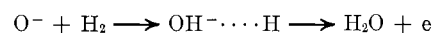
in which the initial phase of the reaction is H abstraction from H_2 to form OH^-, which is exothermic by 0.16 eV. Gas-phase abstraction of H from saturated hydrocarbons by O^- is typically a fast reaction.[10] This would solve the problem of breaking the H_2 bond, and the subsequent $OH^- + H$ associative detachment is independently known to be efficient (Table I). On the other hand reaction 11 could not occur this way since the initial step $S^- + H_2 \rightarrow SH^- + H$ is endothermic by 0.4 eV. Similarly, for the slow reaction

(7) J. C. Y. Chen, *Phys. Rev.*, **156**, 12 (1967).

(8) J. N. Bardsley, A. Herzenberg, and F. Mandl, *Proc. Phys. Soc.*, **89**, 305 (1966).

(9) A. L. Schmeltekopf, F. C. Fehsenfeld, and E. E. Ferguson, *Astrophys. J.*, **148**, L155 (1967).
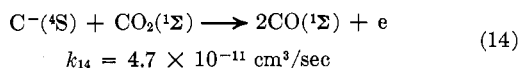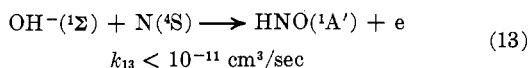
(10) D. K. Bohme and F. C. Fehsenfeld, *Can. J. Chem.*, **47**, 2717 (1969).

12, an initial hydrogen atom abstraction, $C^- + H_2 \rightarrow$

$$C^- + H_2 \longrightarrow CH_2 + e$$
$$k_{12} < 10^{-13} \text{ cm}^3/\text{sec} \tag{12}$$
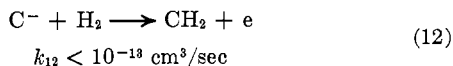
$CH^- + H$, is endothermic by 0.6 eV. Alternatively, it has been suggested[11] that the lower exothermicities of (11) and (12), as compared, to (10), could reasonably give rise to activation energies. A detailed study of the energy dependence of reactions 11 and 12 might be revealing in this connection.

Two of the reactions in Table I violate the spin conservation rule. They are reactions 13 and 14. The

$$OH^-(^1\Sigma) + N(^4S) \longrightarrow HNO(^1A') + e$$
$$k_{13} < 10^{-11} \text{ cm}^3/\text{sec} \tag{13}$$

$$C^-(^4S) + CO_2(^1\Sigma) \longrightarrow 2CO(^1\Sigma) + e$$
$$k_{14} = 4.7 \times 10^{-11} \text{ cm}^3/\text{sec} \tag{14}$$

electron, of course, has doublet spin. It is of interest that (13) is not observed and (14) is the second slowest reaction yet observed which does occur. This strongly suggests the validity of a spin conservation rule in associative-detachment reactions. This is in contrast to normal ion–molecule reactions in which overall spin conservation appears not to be important. (For example, one of the fastest ion–molecule reactions observed is $O^+(^4S) + CO_2(^1\Sigma) \rightarrow O_2^+(^2\Pi) + CO(^1\Sigma)$ which occurs on every collision.)[12] On the basis of spin conservation, one can argue that the ground state of C_2O has been correctly assigned as a triplet state,[13] because reaction 15 is very fast. If the ground

$$C^-(^4S) + CO(^1\Sigma) \longrightarrow C_2O(^3\Sigma) + e$$
$$k_{15} = 4.1 \times 10^{-10} \text{ cm}^3/\text{sec} \tag{15}$$
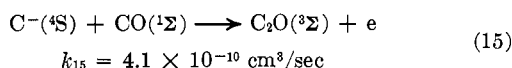
state of C_2O were a singlet, a lower rate constant would be expected.

The spin conservation rule might arise differently in the case of reactions 13 and 14. In the case of (13) (or in the general case where the reactants A^- and B associate to form AB^{-*}), the radiationless transition HNO^{-*} (quartet) $\rightarrow$ HNO (singlet) + e (doublet) is spin forbidden and consequently improbable. In the case of (14), where the final product is presumably 2CO and not C_2O_2, the initial step would be visualized as $C^-(^4S) + CO_2(^1\Sigma) \rightarrow CO^-(^2\Pi) + CO(^1\Sigma)$, followed by $CO^-(^2\Pi) \rightarrow CO(^1\Sigma) + e$ (doublet). In this case the O atom abstraction, not the autodetachment process, is the spin-hindered step, and this may be somewhat less rigorously spin forbidden.

The only associative-detachment reaction so far reported for an organic molecule is reaction 16. In

$$O^- + C_2H_4 \longrightarrow C_2H_4O + e \tag{16}$$
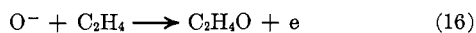
reactions with allene, propene, and several other olefins, O^- either abstracts a hydrogen atom to yield OH^- or abstracts a proton to yield a carbanion.[14]

Ion–Molecule Reactions

Negative ion reactions in which heavy particles are exchanged are not essentially different from analogous reactions for positive ions, and a similar range of reaction rate constants is encountered. The fast reaction 17 is of some interest in the negative ion chem-

$$O_3^- + CO_2 \longrightarrow CO_3^- + O_2$$
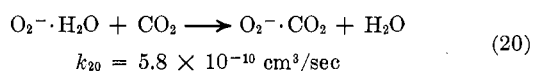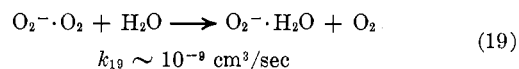$$k_{17} = 4 \times 10^{-10} \text{ cm}^3/\text{sec} \tag{17}$$
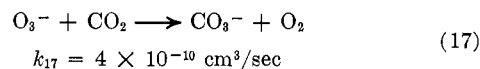
istry of the earth's atmosphere. Because of the large terrestrial CO_2 concentration, this reaction precludes O_3^- from being a significant atmospheric negative ion.[15]

Reaction 18 established that the electron affinity

$$NO_2^- + NO_2 \longrightarrow NO_3^- + NO$$
$$k_{18} \cong 4 \times 10^{-12} \text{ cm}^3/\text{sec} \tag{18}$$
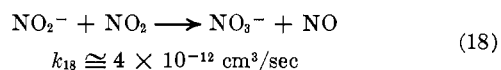
(EA) of NO_3 exceeds that of NO_2 by at least 0.9 eV. The electron affinity of neither NO_2 nor NO_3 has yet been firmly established.

An interesting kind of ion–neutral reaction process recently studied[16] involves "switching" reactions of weakly bound cluster ions, for example, reactions 19

$$O_2^-\cdot O_2 + H_2O \longrightarrow O_2^-\cdot H_2O + O_2$$
$$k_{19} \sim 10^{-9} \text{ cm}^3/\text{sec} \tag{19}$$

$$O_2^-\cdot H_2O + CO_2 \longrightarrow O_2^-\cdot CO_2 + H_2O$$
$$k_{20} = 5.8 \times 10^{-10} \text{ cm}^3/\text{sec} \tag{20}$$

and 20. The occurrence of (19) establishes that the bond energy $D(O_2^-\cdot H_2O) > D(O_2^-\cdot O_2) = 0.59$ eV.[17] The occurrence of (20) establishes that $D(O_2^-\cdot H_2O) < D(O_2^-\cdot CO_2) = 0.8 \pm 0.08$ eV,[18] and we therefore conclude that $D(O_2^-\cdot H_2O) = 0.7 \pm 0.2$ eV. Since the electrostatic forces would be more important in H_2O than CO_2 bonding, it is apparent that the $O_2^-\cdot CO_2$ bond involves some specifically chemical forces.

Charge-Transfer Reactions

Negative ion charge-transfer reactions are not essentially different from their positive ion counterparts. There are many situations, such as the earth's lower ionosphere, combustion, gas discharges, etc., where both positive and negative ion charge transfers are important in the ion chemistry. The observation of a negative ion charge-transfer reaction establishes the direction of exothermicity of the reaction and consequently the relative electron affinities of the reactant species. The same is true of positive ion charge transfer, but ionization potentials are usually known by other means, whereas in the negative ion case charge-transfer data supply a fair fraction of the available information on molecular electron affinities.

One example of this application occurred with reaction 21.[5] At the time this measurement was made

(11) F. C. Fehsenfeld and E. E. Ferguson, *J. Chem. Phys.*, **51**, 3512 (1969).

(12) F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, *ibid.*, **44**, 3022 (1966).

(13) K. H. Becker and K. D. Bayes, *ibid.*, **48**, 653 (1968).

(14) D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 3301 (1970).

(15) F. C. Fehsenfeld, A. L. Schmeltekopf, H. I. Schiff, and E. E. Ferguson, *Planet. Space Sci.*, **15**, 373 (1967).

(16) N. G. Adams, D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *J. Chem. Phys.*, **52**, 3133 (1970).
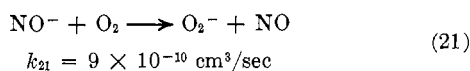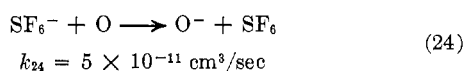
(17) D. C. Conway and L. E. Nesbitt, *ibid.*, **48**, 509 (1968).

(18) J. L. Pack and A. V. Phelps, *ibid.*, **45**, 4316 (1966).

$$NO^- + O_2 \longrightarrow O_2^- + NO$$
$$k_{21} = 9 \times 10^{-10} \text{ cm}^3/\text{sec} \tag{21}$$

the most widely accepted value for $EA(O_2)$ was 0.43 eV and the *only* published value of $EA(NO)$ was 0.9 eV. It was clear from (21) that $EA(O_2) > EA(NO)$. A recent (as yet unpublished) value for $EA(NO)$ of 0.048 eV[19] would be consistent with the charge-transfer data.
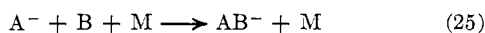
A reaction of great importance in the ionosphere is (22). Observations of reactions[20] 23 and 24 bracket

$$O_2^- + O_3 \longrightarrow O_3^- + O_2$$
$$k_{22} = 4 \times 10^{-10} \text{ cm}^3/\text{sec} \tag{22}$$

$$O_2^- + SF_6 \longrightarrow SF_6^- + O_2$$
$$k_{23} = 7 \times 10^{-11} \text{ cm}^3/\text{sec} \tag{23}$$

$$SF_6^- + O \longrightarrow O^- + SF_6$$
$$k_{24} = 5 \times 10^{-11} \text{ cm}^3/\text{sec} \tag{24}$$
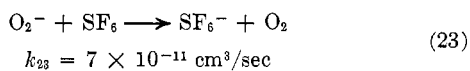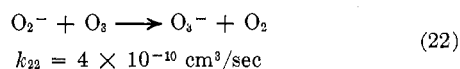
the $EA(SF_6)$ between that of O_2 and O, *i.e.*, $0.43 < EA(SF_6) < 1.465$ eV.

Three-Body Ion Association Reactions

Association reactions of type 25 are receiving a great

$$A^- + B + M \longrightarrow AB^- + M \tag{25}$$

deal of current interest. This is stimulated in part by the recent awareness of the vital role both positive and negative ion association reactions have in aeronomy; it is now apparent that they dominate the lower ionosphere ion chemistry. In part the current interest is simply a reflection of the recent advances in experimental technology which now allow such studies. This includes high-pressure mass spectrometry, drift-tube techniques, and static afterglow studies in various laboratories, as well as the flowing afterglow studies.

In addition to this applied interest, the study of three-body reactions is a potentially powerful way to investigate chemical reaction dynamics. This can be demonstrated by taking the simplest possible approach to (25), the two-step energy transfer processes 26 and 27. In this oversimplified picture, the overall

$$A^- + B \underset{k_r}{\overset{k_f}{\rightleftarrows}} AB^{-*} \tag{26}$$

$$AB^{-*} + M \overset{k_s}{\longrightarrow} AB^- \tag{27}$$

three-body rate constant for (25) becomes (28) at

$$k^{(3)} = \frac{k_f}{k_r} k_s \tag{28}$$

low pressure ($k_r \gg k_s[M]$). At high pressure ($k_r \ll k_s[M]$) the association becomes an apparent binary process, where eq 29 obtains. k_r^{-1} is of course the

$$k^{(2)} = k_f \tag{29}$$

lifetime of AB^{-*} for unimolecular decomposition. Thus it is apparent that measurements of $k^{(3)}$ relate to the efficiency of formation of AB^{-*} complexes, their lifetimes, and the efficiency of stabilization of third bodies. Unimolecular decomposition theory can be applied to

$$k_r^{-1} \approx \tau_0 \left(\frac{D}{nkT}\right)^{s-1} \tag{30}$$

AB^{-*} with some validity, *e.g.*, (30), where D is the AB^- bond energy, τ_0 is a collision lifetime, s is the number of effective degrees of internal freedom, and n is a small factor. Measurements of $k^{(3)}$ over a range of temperature, pressure, and different third bodies allow some constraints to be placed on molecular properties and permit collision models to be tested.

As an example consider reactions 31–33, where the

$$O_2^- + N_2 + He \longrightarrow O_2^-\cdot N_2 + He$$
$$k_{31} \sim 4 \times 10^{-32} \text{ cm}^6/\text{sec} \tag{31}$$

$$O_2^- + O_2 + He \longrightarrow O_2^-\cdot O_2 + He$$
$$k_{32} = 3.4 \times 10^{-31} \text{ cm}^6/\text{sec} \tag{32}$$

$$O_2^- + CO_2 + He \longrightarrow O_2^-\cdot CO_2 + He$$
$$k_{33} = 4.7 \times 10^{-29} \text{ cm}^6/\text{sec} \tag{33}$$

rate constants were measured at $200°K$.[16] The rate constant increases sharply from (31) to (33), paralleling the increase in D, which is 0.26, 0.59, and 0.8 eV for $O_2^-\cdot N_2$, $O_2^-\cdot O_2$, and $O_2^-\cdot CO_2$, respectively. This is consistent with (28) and (30) which predict $k^{(3)} \approx (D)^{s-1}$. The inverse temperature dependence (*i.e.*, $k^{(3)} \sim T^{1-s}$) predicted is qualitatively observed as well.[21]

Reaction 34 has a large rate constant at $200°K$,

$$O^- + CO_2 + He \longrightarrow CO_3^- + He$$
$$k = 2.6 \times 10^{-28} \text{ cm}^6/\text{sec} \tag{34}$$
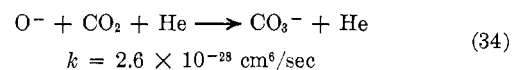
consistent with its known large binding energy.[21] The exothermicity of reaction 17 establishes that $D(O^-\text{–}CO_2) \gtrsim 1.7$ eV. Taking collision rate constants as upper limits for k_f and k_r one can establish a lower limit of $\sim 3 \times 10^{-10}$ sec for the lifetime of CO_3^{-*} formed in the binary O^- and CO_2 collision (or an upper limit of $\sim 3 \times 10^{11}$ sec^{-1} for k_r). If either k_f or k_s is substantially less than Langevin collision rate constants, the lifetime is correspondingly longer.

Negative Ion Chemistry in the Lower Ionosphere

Much of the laboratory research on negative ion-molecule reactions has been stimulated by an interest in understanding the negative ion chemistry of the D region of the earth's ionosphere. Very recently, Narcisi has carried out the first successful direct measurements of the negative ion composition of the ionosphere.[22] From several rocket-borne negative ion mass spectrometer flights, Narcisi finds the negative ions to be concentrated largely below 90 km and to consist predominantly of the cluster ions $NO_3^-\text{–}(H_2O)_n$ with $n = 0$–5 in the undisturbed atmosphere. This is a very

(19) M. W. Siegel, Thesis, Department of Physics, Colorado University, 1970; also M. W. Siegel, R. Celotta, J. Levine, and J. Hall, *Bull. Amer. Phys. Soc.*, **15**, 326 (1970). This reference, however, has a typographical error such that the electron affinity is reported as ten times larger than was measured.
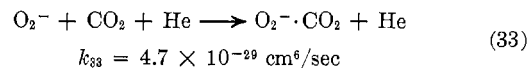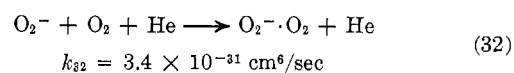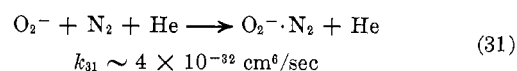(20) F. C. Fehsenfeld, *J. Chem. Phys.*, in press.

(21) D. K. Bohme, D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *ibid.*, **51**, 863 (1969).
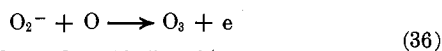(22) R. S. Narcisi, *Bull. Amer. Phys. Soc.*, **15**, 518 (1970).

gratifying confirmation of predictions we have made based on our laboratory studies of negative ion reactions in the flowing afterglow system.[23][24] (This situation contrasts sharply with that of D-region positive ion chemistry in which the ionospheric measurements, again due to Narcisi,[25] were made a number of years before the origin of the major positive ion, $H_5O_2^+$, was explained by laboratory studies.[26])

The problem can be divided into two stages: first, the production of NO_3^- as an important negative ion; secondly, its hydration. The quantitative details of hydration are still not worked out, but it is abundantly clear that any long-lived positive or negative ion in the D region will become hydrated, and we concentrate on the ion chemistry leading to NO_3^- being the major negative ion produced. In the absence of hydration we would expect NO_3^- to be the dominant or "terminal" negative ion of the D region. That is, there are no known reactions to convert NO_3^- to another negative ion, and it would presumably be lost by eventual recombination with a positive ion. The complex system of reactions, all leading eventually to NO_3^-, is shown in graphic form in Figure 4.
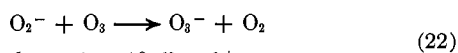
The initial negative ion production step is the three-body attachment of electrons to O_2, i.e., (35). The

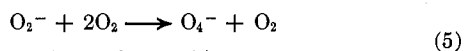$$e + 2O_2 \longrightarrow O_2^- + O_2 \qquad (35)$$
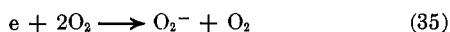
O_2^- so produced has three possible reaction channels, all sufficiently rapid so that O_2^- itself will not attain a significant concentration. They are

$$O_2^- + O \longrightarrow O_3 + e$$
$$k_{36} = 3 \times 10^{-10} \text{ cm}^3/\text{sec} \qquad (36)$$

$$O_2^- + O_3 \longrightarrow O_3^- + O_2$$
$$k_{22} = 4 \times 10^{-10} \text{ cm}^3/\text{sec} \qquad (22)$$

$$O_2^- + 2O_2 \longrightarrow O_4^- + O_2$$
$$k_5 \cong 10^{-30} \text{ cm}^6/\text{sec} \qquad (5)$$

The O/O_3 ratio is obviously critical in the competition between (36) and (22). This ratio increases drastically with altitude above $\sim$70 km where it may be near unity. This explains (and led to the prediction) of few negative ions above $\sim$80 km. The concentration of neither O nor O_3 is well known in the D region, neither having been directly measured, and this lack of knowledge of the neutral composition is a limiting factor in allowing an analysis of the D-region negative ion chemistry. The ion composition measurements to date are also only qualitative, so that the D-region negative ion chemistry is still only a qualitative science, both theoretically and experimentally.

Reaction 5, in contrast to reactions 36 and 22, is expected to have a large temperature dependence (combining eq 28 and 30), and the rate constant will therefore vary with altitude because the temperature

(23) F. C. Fehsenfeld and E. E. Ferguson, *Planet. Space Sci.*, **16**, 701 (1968).
(24) F. C. Fehsenfeld, E. E. Ferguson, and D. K. Bohme, *ibid.*, **17**, 1759 (1969).
(25) R. S. Narcisi and D. A. Bailey, *J. Geophys. Res.*, **70**, 3687 (1965).
(26) E. E. Ferguson and F. C. Fehsenfeld, *ibid.*, **74**, 5743 (1969).
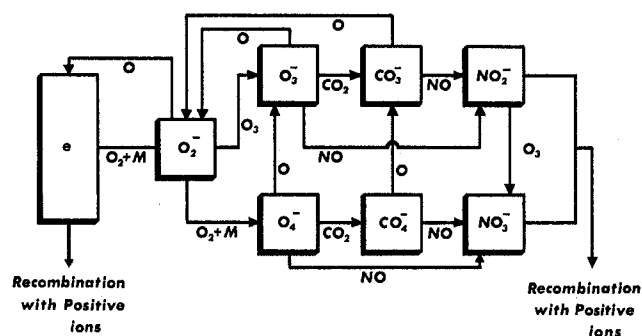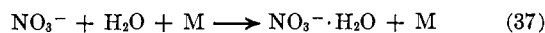
Figure 4. Schematic representation of D-region negative ion chemistry of earth's ionosphere.
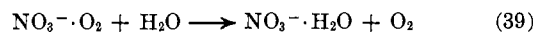
does and will be larger than measured room temperature values because the D region is colder than 300°K. The temperature varies with altitude, latitude, and time and can be as low as 140°K at the temperature minimum (mesopause) near 80 km. The value of k_5 given is therefore only an estimate. Reaction 5 will increase in importance relative to both reactions 36 and 22 with decreasing altitude, because of the rapidly (exponential) increasing pressure of the atmosphere. Reaction 5 should become competitive with the other two somewhere below 70 km and rapidly dominate the O_2^- loss as the altitude is further decreased.

Both O_3^- and O_4^- undergo further reactions which lead to NO_3^-, as shown in Figure 4, and also reactions which lead ultimately to electron detachment. The occurrence of associative detachment, reaction 36, is of extreme practical importance, as it leads to much higher electron/negative ion ratios in the D region than would otherwise exist, and this affects the radio propagation characteristics of the ionosphere. Electrons in the D region (where their collision frequency with neutrals is high) attenuate radiofrequency electromagnetic waves, whereas negative ions do not. The strong variation in day–night radio propagation is a familiar manifestation of this effect, the D-region electron density dropping drastically to near zero at night. This is associated both with the decrease in direct electron production by solar ionization and the decrease in electron production by associative detachment, reaction 36. The latter is a consequence of the decreased nighttime O atom concentration, the O atoms converting to O_3 in the absence of solar photodissociation.

Following NO_3^- formation, the NO_3^- can be hydrated directly (reaction 37) or possibly in the two-

$$NO_3^- + H_2O + M \longrightarrow NO_3^- \cdot H_2O + M \qquad (37)$$

step processes 38 and 39. The sequence (38 and (39)

$$NO_3^- + O_2 + M \longrightarrow NO_3^- \cdot O_2 + M \qquad (38)$$
$$NO_3^- \cdot O_2 + H_2O \longrightarrow NO_3^- \cdot H_2O + O_2 \qquad (39)$$

is likely to be substantially faster than reaction 37 because of the very large O_2/H_2O ratio ($\sim$10^5) in the D region which is likely to more than offset the small (but unknown) k_{38}/k_{37} ratio (perhaps $\sim 10^{-3}$). A

sequence like (38) and (39) but involving CO_2 rather than O_2 is also a possibility.

This application of recent laboratory negative ion reaction measurements to the D-region ion chemistry involves the full utilization of present laboratory capability. Reactions of several "nonsimple" ions, O_2^-, O_4^-, CO_3^-, CO_4^-, and NO_2, are required and these ions need to be allowed to react with the "difficult" neutrals O and O_3. It is only in the past few years (since 1967) that such laboratory measurements have been achieved.

Gas-Phase Organic Chemistry

An important application of the flowing afterglow technique to negative ion studies which is not discussed in this review is the application to gas-phase organic reactions. Two postdoctoral fellows working in our laboratory, D. K. Bohme and L. B. Young, have amply demonstrated the value of this approach (ref 14 and other papers submitted for publication). Quantitative reaction rate constants can be readily obtained for such ions as O^-, OH^-, $C_3H_3^-$, $C_4H_7^-$, CH_3O^-, $(CH_3)_2$-CHO^-, $C_6H_5^-$, $C_6H_5C(CH_3)_2^-$, etc., with organic (and other) neutrals having appreciable vapor pressures. A

wealth of detail concerning kinetic mechanisms and energetics can then be obtained. This work is not being continued at ESSA, our only purpose in the work done so far being to demonstrate the potential of the technique to a field other than our own. Dr. Bohme will be continuing this work in the chemistry department at York University in Toronto.

Summary

Some results of quantitative studies of negative ion reactions with neutrals by the recently developed flowing afterglow technique have been discussed. The versatility of the method allows a wide variety of reactants to be investigated. The laboratory study of associative-detachment reactions has been opened up by this technique. The results obtained to date have contributed some information on negative ion energetics and mechanisms and have played a key role in advancing our understanding of D-region ionospheric chemistry. As the measurements are digested and extended it is to be anticipated that our theoretical understanding will be increased and other areas of application such as gas discharges, combustion, and radiation chemistry will become involved.
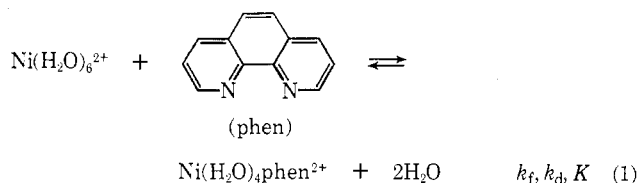
Mechanisms of Ligand Replacement in Octahedral Nickel(II) Complexes

RALPH G. WILKINS

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York

The replacement of one ligand coordinated to a metal center by another free ligand in solution is a fundamental process which permeates all aspects of coordination chemistry. The substitution of a coordinated solvent molecule, usually water, by another complexing molecule is the basis of the *formation* of metal complexes, while the reverse process is variously referred to as *hydrolysis, aquation,* or *dissociation.* These are illustrated in eq 1, with k_f representing the second-order formation rate constant and k_d, the first-order dissociative rate constant. The *direct* replacement of one ligand by another, without intervention of solvent molecules, appears not to be important with octahedral complexes, with which we are concerned in

this Account. The replacement of coordinated by free solvent molecules (*solvent exchange*) is therefore a key process in our understanding of these replacement reactions.

Most of the early kinetic studies of substitution were concerned with the inert Co(III) complexes which Werner had so well characterized and which usually underwent reaction at conveniently measured rates. Taube's review in 1952[1] drew attention to the wider world of *labile* octahedral complexes of transition metals and to reactions which were complete within mixing time. Although the survey was based almost exclusively on qualitative observations taken from the literature, nevertheless, important conclusions relating to reactivity and electronic configuration of the complex ion could be made.[2] The collection of quantitative

$$Ni(H_2O)_6^{2+} + \text{(phen)} \rightleftharpoons$$

$$Ni(H_2O)_4phen^{2+} + 2H_2O \qquad k_f, k_d, K \quad (1)$$

(1) H. Taube, *Chem. Rev.,* **50,** 69 (1952).
(2) The relevance of electronic configuration to the reaction rate was appreciated by others at about the same time, albeit with a quite restricted series of transition metals.[3,4]
(3) A. W. Adamson, J. P. Welker, and W. B. Wright, *J. Amer. Chem. Soc.,* **73,** 4786 (1951); A. W. Adamson, *ibid.,* **73,** 5710 (1951).
(4) J. Bjerrum and K. G. Poulsen, *Nature,* **169,** 463 (1952).