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U.S. DEPARTMENT OF COMMERCE
Environmental Science Services Administration
Research Laboratories

ESSA Technical Report ERL 135-AL 3

Compilation of Reaction Rate Constants Measured in the ESSA Flowing Afterglow System to August, 1969

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For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
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U.S. Environmental Science Services Administration.
ESSA technical report ERL 135-AL 3.

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COMPILATION OF REACTION RATE CONSTANTS MEASURED IN THE ESSA FLOWING AFTERGLOW SYSTEM TO AUGUST, 1969

F. C. Fehsenfeld, A. L. Schmeltekopf, D. B. Dunkin, and E. E. Ferguson

The reaction rate constants measured to August, 1969 in the ESSA flowing afterglow system have been compiled and tabulated in this report. The references to original publications are included along with references to several published reviews on specialized aspects of ion-molecule reactions. Because of the large number of measured rate constants (several hundred) this report should be useful as a reference source and "finding list".

INTRODUCTION

During the past half dozen years the flowing afterglow technique for ion-neutral reaction rate constant measurements has been developed and utilized in the Atmospheric Collision Processes Section of the Aeronomy Laboratory of ESSA. In the course of these studies a large number of rate constants have been determined. We have recently found it necessary for our own purposes to collect these reaction rate constants in one place. This technical report is a comprehensive tabulation of the experimental data obtained to August, 1969. The references to the published papers are given and this report may be useful to others as well as ourselves in serving as a "finding list". The compilation is divided into three sections: Positive Ion-Molecule Reactions, Negative Ion-Molecule Reactions, and Neutral Reactions. Each section is subdivided into categories depicting individual reaction types. Each category lists experimentally determined reaction channels, branching ratios, and rate constants. The temperature at which the measurement was taken and the references in which detailed information concerning the measurement is given, have also been included. The individual reactions are listed principally in order of increasing mass of the primary ion. Branching ratios are given explicitly when so determined. Rate constants refer to the loss of the primary ion or neutral particle. The most recently published value of the rate constant is listed. (-9) denotes 10^{-9}. The reaction temperature is that listed last and is the kinetic gas temperature unless otherwise indicated. The references are divided into review papers and individual publications. The compilation was largely carried out by D. K. Bohme who was a member of the group as a Postdoctoral Research Associate from October 1967 to October 1969. The other members of the Atmospheric Collision Processes Laboratory are: D. L. Albritton, D. B. Dunkin, F. C. Fehsenfeld, E. E. Ferguson, W. J. Harrop, W. R. Saxton, A. L. Schmeltekopf, and Mrs. Alice Keysor, Secretary.

A. I. POSITIVE ION-MOLECULE REACTIONS:

General Bimolecular Ion-Molecule Reactions

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$C^+ + O_2 \rightarrow CO^+ + O$	300	1.1(-9)	10
$C^+ + CO_2 \rightarrow CO^+ + CO$		1.9(-9)	10
$N^+ + H_2 \rightarrow NH^+ + H$		5.6(-10)	13
$N^+ + CO \rightarrow CO^+ + N$		5 (-10)	9
$N^+ + NO \rightarrow NO^+ + N$		8(+1, -4) (-10)	8
$N^+ + O_2 \rightarrow O_2^+ + N$ $\rightarrow NO^+ + O$		6 (-10)[a]	2, 8, 19
$N^+ + CO_2 \rightarrow CO_2^+ + N$		1.3(-9)	9
$NH^+ + H_2 \rightarrow NH_2^+ + H$		~ 1 (-9)	13
$NH^+ + N_2 \rightarrow N_2H^+ + N$		~ 1 (-9)	13
$NH_2^+ + H_2 \rightarrow NH_3^+ + N$		~ 1 (-9)	13
$O^+ + H_2 \rightarrow OH^+ + H$		2.0(-9)	13
$O^+ + N_2 \rightarrow NO^+ + N$		1.2(-12)[b]	2, 17, 18, 19, 23
$O^+ + NO \rightarrow NO^+ + O$		≤ 2.4(-11)	8
$O^+ + O_2 \rightarrow O_2^+ + O$		2 (-11)[c]	3, 19, 23
$O^+ + CO_2 \rightarrow O_2^+ + CO$		1.1(-9)[d]	7, 19

[a] Rate constant for loss of N^+ does not vary between 300 and 600°K within experimental uncertainty. Splits into comparable channels.

[b] Decrease in rate constant ($\sim T^{-1/2}$) between kinetic temperatures 80 and 600°K. Increase in rate constant by a factor of 40 with increased vibrational temperature of N_2.

[c] Slight decrease in rate constant between 80 and 600°K.

[d] Slight decrease in rate constant between 300 and 600°K (almost within experimental uncertainty and data scatter). Violates Wigner spin-conservation rule.

Positive Ion-Molecule Reactions (continued)

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$OH^+ + H_2 \rightarrow H_2O^+ + H$	300	~ 1.5(-9)	13
$OH^+ + O_2 \rightarrow O_2^+ + OH$		~ 2 (-10)	13
$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$		1.6(-9)	27
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$		~ 1.4(-9)	13
$H_2O^+ + O_2 \rightarrow O_2^+ + H_2O$		~ 2 (-10)	13
$CO^+ + H_2 \rightarrow COH^+ + H$		2.0(-9)	13
$CO^+ + O_2 \rightarrow O_2^+ + CO$		2.0(-10)	10
$CO^+ + CO_2 \rightarrow CO_2^+ + CO$		1.1(-9)	10
$N_2^+ + H_2 \rightarrow N_2H^+ + H$		1.7(-9)	13
$N_2^+ + N \rightarrow N_2 + N^+$		< 1.0(-11)	4
$N_2^+ + O \rightarrow NO^+ + N$		2.5(± 1)(-10)	4
$N_2^+ + O \rightarrow N_2 + O^+$		< 1.0(-11)	4
$N_2^+ + CO \rightarrow CO^+ + N_2$		7 (-11)[e]	9
$N_2^+ + NO \rightarrow NO^+ + N_2$		5(+1, -3) (-10)	8
$N_2^+ + O_2 \rightarrow O_2^+ + N_2$		4.7(-11)[f]	2, 8, 19
$N_2^+ + CO_2 \rightarrow CO_2^+ + N_2$		9 (-10)	9
$O_2^+ + H_2 \rightarrow$ products		< 1 (-11)	13
$O_2^+ + N \rightarrow NO^+ + O$		1.8(+ 0.2, -0.9) (-10)	8
$O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$		2.6(-9)	27
$O_2^+ + N_2 \rightarrow NO^+ + NO$		< 1 (-15)[g]	5

[e] Rate constant similar for isotopic N_2: $^{15}N^{15}N$, $^{15}N^{14}N$.

[f] Slight decrease in rate constant between 80 and 520°K.

[g] Not observed at 300 and 600°K.

Positive Ion-Molecule Reactions (continued)

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$O_2^+ + NO \rightarrow NO^+ + O_2$	300	8(+2, -5) (-10)	8
$O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H$		7.8(-12)	32
$O_2^+ + C_2H_4 \rightarrow C_2H_4^+ + O_2$		1.9(-9)	32
$O_2^+ + C_2H_6 \rightarrow$ products		1.6(-9)[h]	32
$O_2^+ + C_3H_8 \rightarrow$ products		1.8(-9)	32
$O_2^+ + C_4H_{10} \rightarrow$ products		2.4(-9)	32
$CO_2^+ + H_2 \rightarrow CO_2H^+ + H$		1.4(-9)	13
$N_2O^+ + H_2 \rightarrow N_2OH^+ + H$		4 (-10)	13
$NO_2^+ + NO \rightarrow NO^+ + NO_2$		2.9(-10)	34

[h] $C_2H_5^+$ was observed to be the dominant production (91.5 percent).

A. II. POSITIVE ION-MOLECULE REACTIONS:

Bimolecular Ion-Molecule Reactions of Rare Gas Atomic, Molecular, and Hydride Ions

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$He^+ + Ne \rightarrow He + Ne^+$	300	< 1 (-13)	6
$He^+ + Ar \rightarrow He + Ar^+$		< 1 (-13)	6
$He^+ + H_2 \rightarrow$ products		< 1 (-13)	6
$He^+ + N_2 \xrightarrow{0.7} N^+ + N + He$ $\xrightarrow{0.3} N_2^+ + He$		1.2(-9)[a]	1, 6, 18, 19
$He^+ + O_2 \rightarrow O^+ + O + He$		1.5(+0.2, -0.7)(-9)	1, 6
$He^+ + CO \rightarrow C^+ + O + He$		1.7(+0.2, -0.8)(-9)	6
$He^+ + NO \rightarrow N^+ + O + He$		1.5(+0.2, -0.8)(-9)	6
$He^+ + CO_2 \xrightarrow{0.80} CO^+ + O + He$ $\xrightarrow{0.15} O^+ + CO + He$ $\xrightarrow{0.05} CO_2^+ + He$		1.1 ± 0.2(-9)	6
$HeH^+ + H_2 \rightarrow$ products	200	≥ 3.5(-11)	35
$HeH_2^+ + H_2 \rightarrow$ products		≥ 2.4(-11)	35
$He_2^+ + Ne \rightarrow Ne^+ + 2He$		6.0(-10)	33
$He_2^+ + Ar \rightarrow Ar^+ + 2He$		2.0(-10)	33
$He_2^+ + Kr \rightarrow Kr^+ + 2He$		1.85(-11)	33
$He_2^+ + H_2 \rightarrow$ products		5.3(-10)	35
$He_2^+ + N_2 \rightarrow N_2^+ + 2He$		1.3(-9)	33

[a] Loss of He^+ is independent of T_{kin}(300 - 600°K). Mechanism is a resonant charge-transfer into v = 3, 4 of $N_2^+(C^2\Sigma_u^+)$, followed by spin-forbidden predissociation in v = 4 yielding N^+ and radiation yielding $N_2^+(X^2\Pi_g^+)$. Branching ratio increases by a factor of about 2 with T_{vib}(300 - 6000°K) of N_2. No change in specific rate for loss of He^+ with T_{vib}(300 - 6000°K) of N_2 within experimental error.

Bimolecular Ion-Molecule Reactions of Rare Gas Atomic, Molecular, and Hydride Ions (continued)

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$He_2^+ + CO \rightarrow CO^+ + 2He$	200	1.4(-9)	33
$He_2^+ + O_2 \rightarrow O_2^+ + 2He$ $\rightarrow O^+ + O + 2He$		1.05(-9)	33
$He_2^+ + NO \rightarrow NO^+ + 2He$		1.3(-9)	33
$He_2^+ + CO_2 \rightarrow CO_2^+ + 2He$ $\rightarrow O^+ + CO + 2He$ $\rightarrow CO^+ + O + 2He$		1.8(-9)	33
$He_2H^+ + H_2 \rightarrow$ products		3.0(-10)	35
$NeH^+ + H_2 \rightarrow$ products		2.0(-11)	35
$NeH_2^+ + H_2 \rightarrow$ products		$\leq$ 4.0(-13)	35
$Ne_2^+ + Ar \rightarrow Ar^+ + 2Ne$		$\leq$ 5 (-14)	33
$Ne_2^+ + Kr \rightarrow Kr^+ + 2Ne$		$\leq$ 5 (-13)	33
$Ne_2^+ + H_2 \rightarrow$ products		1.1(-10)	35
$Ne_2^+ + O_2 \rightarrow O_2^+ + 2Ne$ $\rightarrow O^+ + O + 2Ne$		7.1(-10)	33
$Ne_2^+ + N_2 \rightarrow N_2^+ + 2Ne$		9.1(-10)	33
$Ne_2^+ + CO \rightarrow CO^+ + 2Ne$		5.1(-10)	33
$Ne_2^+ + NO \rightarrow NO^+ + 2Ne$		7.0(-10)	33
$Ne_2^+ + CO_2 \rightarrow CO_2^+ + 2Ne$ $\rightarrow O^+ + CO + 2Ne$ $\rightarrow CO^+ + O + 2Ne$		1.1(-9)	33
$Ne_2H^+ + H_2 \rightarrow$ products		9.6(-11)	35
$Ar^+ + H_2 \rightarrow ArH^+ + H$	280	$\sim$ 7 (-10)[b]	11, 13, 37
$Ar^+ + D_2 \rightarrow ArD^+ + D$		5.9(-10)[b]	37

[b] Increase in rate constant between 80 and 500°K; $k = a + bT^x$, $0.5 \leq x \leq 1.0$.

Bimolecular Ion-Molecule Reactions of Rare Gas Atomic, Molecular, and Hydride Ions (continued)

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$Ar^+ + N_2 \rightarrow N_2^+ + Ar$	280	4 to 10 (-12)[c]	37
$Ar^+ + NO \rightarrow NO^+ + Ar$	200	~ 3 (-10)	39
$Ar^+ + O_2 \rightarrow O_2^+ + Ar$	280	4.6(-11)[d]	8, 11, 37
$Ar^+ + CO \rightarrow CO^+ + Ar$	300	9.0(-11)	11
$Ar^+ + CO_2 \rightarrow CO_2^+ + Ar$		5.8(-10)	11
$ArH^+ + H_2 \rightarrow H_3^+ + Ar$		~ 5 (-10)[e]	13, 37
$ArD^+ + D_2 \rightarrow D_3^+ + Ar$		~ 4 (-10)[e]	37
$ArH_2^+ + H_2 \rightarrow$ products	200	≤ 1.0(-14)	35
$Ar_2^+ + Kr \rightarrow Kr^+ + 2Ar$		7.5(-10)	33
$Ar_2^+ + CO \rightarrow ArCO^+ + Ar$ $\rightarrow CO^+ + 2Ar$		8.5(-10)	33
$Ar_2^+ + O_2 \rightarrow O_2^+ + 2Ar$		1.2(-10)	33
$Ar_2^+ + NO \rightarrow NO^+ + 2Ar$		2.4(-10)	33
$Ar_2^+ + CO_2 \rightarrow CO_2^+ + 2Ar$		1.1(-9)	33
$Ar_2^+ + H_2 \rightarrow$ products		4.9(-10)	35
$Ar_2H^+ + H_2 \rightarrow$ products		3.0(-11)	35

[c] Dependent on Ar number density.

[d] Decrease in rate constant between 80 and 500°K: $k = 7.8 \times 10^{-10} T^{-0.5}$.

[e] Rate constant does not vary between 80 and 500°K within experimental uncertainty.

A. III. POSITIVE ION-MOLECULE REACTIONS:

Bimolecular Meteor Ion-Molecule Reactions

Reaction	Temp. (°K)	Rate Constant[a] (cm^3/molecule sec)	Reference
$Na^+ + O_3 \rightarrow NaO^+ + O_2$	300	< 1.0(-11)	21
$Mg^+ + O_3 \rightarrow MgO^+ + O_2$		2.3(-10)	21
$Si^+ + O_2 \rightarrow SiO^+ + O$		< 1 (-11)	26
$K^+ + O_3 \rightarrow KO^+ + O_2$		< 1.0(-11)	21
$Ca^+ + O_3 \rightarrow CaO^+ + O_2$		1.6(-10)	21
$Fe^+ + O_3 \rightarrow FeO^+ + O_2$		1.5(-10)	21
$MgO^+ + O \rightarrow Mg^+ + O_2$		~ 1.0(-10)	21
$SiO^+ + N \xrightarrow{0.5} Si^+ + NO$ $\xrightarrow{0.5} NO^+ + Si$		~ 3 (-10)	26
$SiO^+ + O \rightarrow Si^+ + O_2$		~ 2.0(-10)	26

[a] Rate constants are probably reliable to within a factor of 2. Reactions with the alkaline earth ions Ca^+, Mg^+, Fe^+ are obviously exothermic, so that the bond energies $D_o(M^+\text{-}O) > D_o(O_2\text{-}O) = 1$ eV. The possibility exists that the reactions with the alkali metal ions Na^+ and K^+ are endothermic, i.e., that the bond energies $D_o(Na^+\text{-}O)$ and $K_o(K^+\text{-}O) < D_o(O_2\text{-}O) = 1$ eV. In the course of these studies the following metal ion oxides were observed: MgO_n^+(n = 1 to 5), $Mg_2O_n^+$(n = 2, 3), $Mg_3O_3^+$, CaO_n^+(n = 1 to 3), $Ca_2O_n^+$(n = 2, 3), $Ca_2O_4^+$, FeO_n^+(n = 1 to 5), $Fe_2O_4^+$. The dimer Fe_2^+ ion was also observed.

A. IV. POSITIVE ION-MOLECULE REACTIONS:

Switching Reactions

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$HeNe^+ + Ne \rightarrow Ne_2^+ + He$	200	1.4(-10)	33
$ArKr^+ + Kr \rightarrow Kr_2^+ + Ar$		3.2(-10)	33
$ArCO^+ + CO \rightarrow CO^+ \cdot CO + Ar$		4.6(-10)	33
$ArO_2^+ + O_2 \rightarrow O_4^+ + Ar$	80	2.5(-11)	37
$O_2^+ \cdot N_2 + O_2 \rightarrow O_2^+ \cdot O_2 + N_2$	80	$\geq$ 5.0(-11)	38
$O_2^+ \cdot O_2 + N_2O \rightarrow O_2^+ \cdot N_2O + O_2$	200	2.5(-10)[a]	38
$O_2^+ \cdot O_2 + SO_2 \rightarrow O_2^+ \cdot SO_2 + O_2$	200	8.2(-10)	38
	300	4.2(-10)[b]	38
$O_2^+ \cdot N_2O + H_2O \rightarrow O_2^+ \cdot H_2O + N_2O$		> 1.0(-10)	38
$O_2^+ \cdot N_2O + SO_2 \rightarrow O_2^+ \cdot SO_2 + N_2O$	200	5.6(-10)	38
$O_2^+ \cdot SO_2 + H_2O \rightarrow O_2^+ \cdot H_2O + SO_2$	300	> 1.0(-10)	38

[a] The equilibrium constant K = 1.3(3), ΔF^o = 0.13 eV.

[b] The equilibrium constant K = 3.2(4), ΔF^o = 0.27 eV.

A. V. POSITIVE ION-MOLECULE REACTIONS:

Termolecular Ion-Neutral Association Reactions

Reaction	Temp. (°K)	Rate Constant (cm^6/molecule^2 sec)	Reference
$H_3^+ + Ar + Ar \rightarrow H_3^+ \cdot Ar + Ar$	300	$\approx 1.0(-31)$	13
$N^+ + N_2 + He \rightarrow N^+ \cdot N_2 + He$	80	7.2(-29)	24
$O^+ + N_2 + He \rightarrow (O^+ \cdot N_2)^* + He$		5.4(-29)	24
$NH_4^+ + NH_3 + O_2 \rightarrow NH_4^+ \cdot NH_3 + O_2$	300	1.8(-27)	27
$Na^+ + O_2 + Ar \rightarrow Na^+ \cdot O_2 + Ar$		$< 2.0(-31)$	21
$Mg^+ + O_2 + Ar \rightarrow Mg^+ \cdot O_2 + Ar$		$\sim 2.5(-30)$	21
$N_2^+ + N_2 + He \rightarrow N_2^+ \cdot N_2 + He$	80	1.2(-28)	22, 24
	280	1.9(-29)	24
$NO^+ + H_2O + He \rightarrow NO^+ \cdot H_2O + He$	300	5.5(-29)	36
$NO^+ + H_2O + N_2 \rightarrow NO^+ \cdot H_2O + N_2$		2.2(-28)	36
$NO^+ + H_2O + Ar \rightarrow NO^+ \cdot H_2O + Ar$		1.9(-28)	36
$O_2^+ + H_2 + He \rightarrow O_2^+ \cdot H_2 + He$	80	7.4(-31)	38
$O_2^+ + H_2O + He \rightarrow O_2^+ \cdot H_2O + He$	300	8.5(-29)	36
$O_2^+ + H_2O + N_2 \rightarrow O_2^+ \cdot H_2O + N_2$		4.5(-28)	36
$O_2^+ + H_2O + Ar \rightarrow O_2^+ \cdot H_2O + Ar$		3.5(-28)	36
$O_2^+ + N_2 + He \rightarrow O_2^+ \cdot N_2 + He$	80	1.9(-29)	38
$O_2^+ + O_2 + He \rightarrow O_2^+ \cdot O_2 + He$		3.1(-29)	22, 24
	200	2.4(-30)	24
$O_2^+ + CO_2 + He \rightarrow O_2^+ \cdot CO_2 + He$	200	2.3(-29)	38
$O_2^+ + N_2O + He \rightarrow O_2^+ \cdot N_2O + He$		5.2(-29)	38
$O_2^+ + SO_2 + He \rightarrow O_2^+ \cdot SO_2 + He$		~ 6 (-28)	38
$K^+ + O_2 + Ar \rightarrow K^+ \cdot O_2 + Ar$	300	$< 2.0(-31)$	21
$Ca^+ + O_2 + Ar \rightarrow Ca^+ \cdot O_2 + Ar$		$\sim 6.6(-30)$	21

Termolecular Ion-Neutral Association Reactions (continued)

Reaction	Temp. (°K)	Rate Constant ($cm^6/molecule^2$ sec)	Reference
$Ar^+ + Ar + He \rightarrow Ar^+ \cdot Ar + He$	80	1.6(-30)	24
	290	~ 1.3(-31)	24
$Fe^+ + O_2 + Ar \rightarrow Fe^+ \cdot O_2 + Ar$		~ 1.0(-30)	21
$O_2^+ \cdot N_2 + N_2 + He \rightarrow O_2^+ \cdot 2N_2 + He$	80	~ 1.0(-29)	38
$O_2^+ \cdot O_2 + N_2 + He \rightarrow O_2^+ \cdot O_2 \cdot N_2 + He$		~ 1.0(-29)	38
$O_2^+ \cdot O_2 + O_2 + He \rightarrow O_2^+ \cdot 2O_2 + He$		~ 5.0(-30)	38
$Ar_2^+ + Ar + He \rightarrow Ar_3^+ + He$	80	~ 5.5(-31)	29
$Xe^+ + H_2O + He \rightarrow Xe^+ \cdot H_2O + He$	300	1.5(-29)	36

B. I. NEGATIVE ION-MOLECULE REACTIONS:

Charge-Transfer Reactions

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$H^- + NO_2 \rightarrow NO_2^- + H$	300	2.9(-9)	C
$NH_2^- + NO_2 \rightarrow NO_2^- + NH_2$		1.0(-9)	C
$O^- + NO_2 \rightarrow NO_2^- + O$		1.2(-9)	C
$O^- + O_3 \rightarrow O_3^- + O$		5.3(-10)	15, C
$OH^- + NO_2 \rightarrow NO_2^- + OH$		1.0(-9)	C
$F^- + NO_2 \rightarrow NO_2^- + F$		< 2.5(-11)	C
$NO^- + O_2 \rightarrow O_2^- + NO$		9 (-10)	12
$O_2^- + NO_2 \rightarrow NO_2^- + O_2$		8 (-10)	20, C
$O_2^- + O_3 \rightarrow O_3^- + O_2$		4.0(-10)	15, C
$O_2^- + SO_2 \rightarrow SO_2^- + O_2$		5.4(-10)	D
$Cl^- + NO_2 \rightarrow NO_2^- + Cl$		< 6 (-12)	20, C

B. II. NEGATIVE ION-MOLECULE REACTIONS:

Bimolecular Ion-Molecule Reactions

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$O^- + NH_3 \rightarrow OH^- + NH_2$	300	1.2(-9)	27
$N_2O^- + O_2 \rightarrow O_3^- + N_2$	80	fast	B
$NO_2^- + N \rightarrow$ products	300	< 1 (-11)	39
$NO_2^- + O \rightarrow$ products		< 1 (-11)	39
$NO_2^- + NO_2 \rightarrow NO_3^- + NO$		~ 4 (-12)	30
$NO_2^- + O_3 \rightarrow NO_3^- + O_2$		1.8(-11)	20
$O_3^- + CO \rightarrow$ products		≤ 1.0(-12)	B, 39
$O_3^- + N_2 \rightarrow$ products		< 1 (-15)	B
$O_3^- + NO \rightarrow NO_3^- + O$		1.0(-11)	15
$O_3^- + SiO \rightarrow SiO_3^- + O$		fast	B
$O_3^- + CO_2 \rightarrow CO_3^- + O_2$		4.0(-10)[a]	15, 38
$O_3^- + NO_2 \rightarrow$ products		1.9(-10)	B
$O_3^- + SO_2 \rightarrow SO_4^- + O$ $\rightarrow SO_3^- + O_2$		5.1(-10)	B
$CO_3^- + O \rightarrow O_2^- + CO_2$		8.0(-11)	15
$CO_3^- + NO \rightarrow NO_2^- + CO_2$		9.0(-12)[b]	15, 38
$CO_3^- + N_2 \rightarrow$ products		< 1.0(-12)	39
$CO_3^- + NO_2 \rightarrow NO_3^- + CO_2$		8.0(-11)	B
$NO_3^- + O \rightarrow$ products		< 1 (-11)	30
$NO_3^- + N \rightarrow$ products		< 1 (-11)	30

[a] The equilibrium constant $K \geq 1.4(5)$, $\Delta F^o \geq 0.31$ eV.

[b] The equilibrium constant $K = 11$, $\Delta F^o = 0.06$ eV.

Bimolecular Ion-Molecule Reactions (continued)

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$NO_3^- + CO \rightarrow$ products	300	< 1 (-12)	39
$NO_3^- + NO \rightarrow NO_2^- + NO_2$		< 1 (-12)	30
$O_4^- + O \rightarrow O_3^- + O_2$ $\rightarrow O^- + 2O_2$		4 (-10)	30
$CO_4^- + O \rightarrow CO_3^- + O_2$ $\rightarrow O_3^- + CO_2$		1.5(-10)	30

B. III. NEGATIVE ION-MOLECULE REACTIONS:

Associative Detachment Reactions

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$H^- + H \rightarrow H_2 + e$	300	1.3(-9)	14
$H^- + O_2 \rightarrow HO_2 + e$		1.8(-9)	39
$O^- + H_2 \rightarrow H_2O + e$		$\simeq$ 1.5(-9)	12, B, C, 31
$O^- + N \rightarrow NO + e$		2.0(-10)	12, 15, B
$O^- + O \rightarrow O_2 + e$		1.4(-10)	12, 15, B, C
$O^- + N_2 \rightarrow N_2O + e$		< 1.0(-14)	12, 31
$O^- + CO \rightarrow CO_2 + e$		4.4(-10)	12, B, C
$O^- + NO \rightarrow NO_2 + e$		1.6(-10)	12, B, C
$O^- + O_2 \rightarrow O_3 + e$		< 1 (-12)	12
$O^- + O_2(^1\Delta_g) \rightarrow O_3(^1A_1) + e$		~ 3.0(-10)	25
$O^- + CO_2 \rightarrow CO_3 + e$		< 1 (-13)	24
$O^- + SO_2 \rightarrow SO_3 + e$		6.9(-10)[a]	39
$OH^- + H \rightarrow H_2O + e$		1.0(-9)	B
$OH^- + N \rightarrow HNO + e$		< 1 (-11)	12, 31
$OH^- + O \rightarrow HO_2 + e$		2.0(-10)	12, B
$CN^- + H \rightarrow HCN + e$		8 (-10)	B, C
$O_2^- + N \rightarrow NO_2 + e$		3.0(-10)	12, 15, B
$O_2^- + O \rightarrow O_3 + e$		3.0(-10)	12, 15, B
$O_2^- + O_2(^1\Delta_g) \rightarrow 2O_2(^3\Sigma_g) + e$		~ 2 (-10)	25
$S^- + H_2 \rightarrow H_2S + e$		< 1.0(-15)	31
$S^- + CO \rightarrow COS + e$		3.1(-10)	39

[a] There is the possibility of some charge-transfer.

Associative Detachment Reactions (continued)

Reaction	Temp. (°K)	Rate Constant (cm^3/molecule sec)	Reference
$S^- + O_2 \rightarrow SO_2 + e$	300	5.5(-11)	31
$Cl^- + H \rightarrow HCl + e$		9 (-10)	12, B, C
$Cl^- + N \rightarrow ClN + e$		< 1 (-11)	12
$Cl^- + O \rightarrow ClO + e$		< 1 (-11)	12

B. IV. NEGATIVE ION-MOLECULE REACTIONS:

Switching Reactions

Reaction	Temp. (^{o}K)	Rate Constant (cm^3/molecule sec)	Reference
$O_2^-.H_2O + NO \rightarrow O_2^-.NO + H_2O$	300	3.1(-10)	38
$O_2^-.H_2O + CO_2 \rightarrow O_2^-.CO_2 + H_2O$		5.8(-10)	38
$O_2^-.O_2 + CO \rightarrow O_2^-.CO + O_2$		< 2.0(-11)	38
$O_2^-.O_2 + N_2 \rightarrow O_2^-.N_2 + O_2$		< 1.0(-11)	38
$O_2^-.O_2 + NO \rightarrow O_2^-.NO + O_2$		2.5(-10)	30, 38
$O_2^-.O_2 + H_2O \rightarrow O_2^-.H_2O + O_2$		> 1.0(-10)	38
$O_2^-.O_2 + CO_2 \rightarrow O_2^-.CO_2 + O_2$		4.3(-10)	30, 38
$O_2^-.O_2 + N_2O \rightarrow O_2^-.N_2O + O_2$		< 1.0(-12)	38
$O_2^-.CO_2 + NO \rightarrow O_2^-.NO + CO_2$		4.8(-11)	30, 38

B. V. NEGATIVE ION-MOLECULE REACTIONS:

Termolecular Ion-Neutral Association Reactions

Reaction	Temp. (^{o}K)	Rate Constant ($cm^6/molecule^2$ sec)	Reference
$O^- + N_2 + He \rightarrow O^-.N_2 + He$	80	$\sim 1.0(-30)$	D
	200	$\sim 4.0(-32)$	38
$O^- + CO_2 + He \rightarrow O^-.CO_2 + He$	280	$1.5(-28)$	24
	200	$2.6(-28)$	38
$O_2^- + N_2 + He \rightarrow O_2^-.N_2 + He$	200	$\sim 4.0(-32)$	38
$O_2^- + O_2 + He \rightarrow O_2^-.O_2 + He$	200	$3.4(-31)$	38
$O_2^- + CO_2 + He \rightarrow O_2^-.CO_2 + He$	200	$4.7(-29)$	38
$O_3^- + N_2 + N_2 \rightarrow$ products	300	$< 1.5(-31)$	D

B. VI. NEGATIVE ION-MOLECULE REACTIONS:

Bimolecular Ion-Organic Molecule Reactions

Reaction	Branching Ratio	Rate Constant at 300°K (cm^3/molecule sec)	Reference
$O^- + CH_4 \rightarrow OH^- + CH_3$		1.0(-10)	28
$O^- + C_2H_6 \rightarrow OH^- + C_2H_5$		7.0(-10)	28
$O^- + C_3H_8 \rightarrow OH^- + C_3H_7$		9.3(-10)	28
$O^- + n\text{-}C_4H_{10} \rightarrow OH^- + C_4H_9$		1.2(-9)	28
$O^- + C_2H_4 \rightarrow C_2H_4O + e$		7.7(-10)	40
$O^- + C_3H_4 \rightarrow C_3H_3^- + OH$	0.90 ± 0.05	1.0(-9)	40
$\rightarrow OH^- + C_3H_3$	0.10 ± 0.05		
$O^- + C_3H_6 \rightarrow OH^- + C_3H_5$	0.95 ± 0.05	1.0(-9)	40
$\rightarrow C_3H_5^- + OH$	0.05 ± 0.05		
$O^- + \underline{iso}\text{-}C_4H_8 \rightarrow OH^- + C_4H_7$	0.95 ± 0.05	1.4(-9)	40
$\rightarrow C_4H_7^- + OH$	0.05 ± 0.05		
$O^- + 1\text{-}C_4H_8 \rightarrow C_4H_7^- + OH$	0.6 ± 0.1	1.4(-9)	40
$\rightarrow OH^- + C_4H_7$	0.4 ± 0.1		
$O^- + \underline{cis}\text{-}2\text{-}C_4H_8 \rightarrow C_4H_7^- + OH$	0.6 ± 0.1	1.2(-9)	40
$\rightarrow OH^- + C_4H_7$	0.4 ± 0.1		
$O^- + \underline{trans}\text{-}2\text{-}C_4H_8 \rightarrow C_4H_7^- + OH$	0.6 ± 0.1	1.6(-9)	40
$\rightarrow OH^- + C_4H_7$	0.4 ± 0.1		
$OH^- + RH \rightarrow R^- + H_2O$		≤ 1 (-12)[a]	28
$OH^- + C_2H_4 \rightarrow C_2H_3^- + H_2O$		≤ 1 (-12)	40

[a] RH = CH_4, C_2H_6, C_3H_8, C_4H_{10}

Bimolecular Ion-Organic Molecule Reactions (continued)

Reaction	Branching Ratio	Rate Constant at 300°K (cm^3/molecule sec)	Reference
$OH^- + C_3H_4 \rightarrow C_3H_3^- + H_2O$		7.5(-10)	40
$OH^- + C_3H_6 \rightarrow C_3H_5^- + H_2O$		2.6(-10)	40
$OH^- + \underline{iso}\text{ - }C_4H_8 \rightarrow C_4H_7^- + H_2O$		6.3(-10)	40
$OH^- + 1\text{ - }C_4H_8 \rightarrow C_4H_7^- + H_2O$		8.8(-10)	40
$OH^- + \underline{cis}\text{ - }2\text{ - }C_4H_8 \rightarrow C_4H_7^- + H_2O$		7.2(-10)	40
$OH^- + \underline{trans}\text{ - }2\text{ - }C_4H_8 \rightarrow C_4H_7^- + H_2O$		8.7(-10)	40
$C_3H_3^- + O_2 \rightarrow C_2HO^- + H_2CO$		1.0(-12)	40
$C_3H_5^- + O_2 \rightarrow O_2^- + C_3H_5$	0.98 ± 0.01	2.9(-10)	40
$\rightarrow C_2H_3O^- + CH_2O$	0.02 ± 0.01		
$C_4H_7^- + O_2 \rightarrow O_2^- + C_4H_7$	0.69 ± 0.05	3.2(-10)[b]	40
$\rightarrow C_3H_3^- + CH_4O_2$	0.14 ± 0.03		
$\rightarrow O_2H^- + C_4H_6$	0.08 ± 0.04		
$\rightarrow C_2HO^- + C_2H_6O$	0.05 ± 0.02		
$\rightarrow C_2H_3O^- + C_2H_4O$	0.04 ± 0.01		
$C_4H_7^- + O_2 \rightarrow O_2H^- + C_4H_6$	0.62 ± 0.05	5.3(-10)[c]	40
$\rightarrow O_2^- + C_4H_7$	0.34 ± 0.03		
$\rightarrow C_2H_3O^- + C_2H_4O$	0.02 ± 0.01		
$\rightarrow C_2HO^- + C_2H_6O$	0.01 ± 0.01		
$\rightarrow C_3H_3^- + CH_4O_2$	0.01 ± 0.01		

[b] $C_4H_7^-$ derived from $\underline{iso}\text{ - }C_4H_8$.

[c] $C_4H_7^-$ derived from $1\text{ - }C_4H_8$, $\underline{cis}\text{ - }2\text{ - }C_4H_8$, and $\underline{trans}\text{ - }2\text{ - }C_4H_8$.

C. I. NEUTRAL REACTIONS:

Metastable Helium Reactions (Reference 41)

Reactant	Rate Constant (cm^3/molecule sec) at 300°K.	
	$He(^1S)$	$He(^3S)$
Ne	6.46(-11)	3.85(-12)
Ar	2.20(-10)	7.04(-11)
Kr	3.62(-10)	9.94(-11)
Xe	4.62(-10)	1.24(-10)
H_2	4.88(-11)	3.18(-11)
D_2	4.15(-11)	2.60(-11)
NH_3	1.33(-9)	8.40(-10)
N_2	1.67(-10)	6.96(-11)
CO	3.17(-10)	9.85(-11)
NO	4.33(-10)	2.42(-10)
O_2	5.80(-10)	2.10(-10)
N_2O	9.18(-10)	4.33(-10)
CO_2	1.10(-9)	5.75(-10)
CH_4	3.75(-10)	1.37(-10)
C_2H_6	5.67(-10)	2.50(-10)
C_3H_8	7.00(-10)	3.17(-10)
C_4H_{10}	9.00(-10)	4.17(-10)
SF_6	6.66(-10)	2.62(-10)

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