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The Oxygen Dimers, Clusters, and Cluster Ions in the Gas Phase

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The formation, thermodynamic properties, and chemical reactions of neutral and charged oxygen clusters of the type O_{2n} ($n \geqslant 2$), (O_4^- and $O_4^+ - O_{18}^+$) as well as oxygen clusters with other molecules (N_2, N_2O, SO_2, H_2O, CO_2, NO, and CO) are examined.
The bibliography includes 49 references.

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I. INTRODUCTION

In a mass-spectrometric study of oxygen which had passed through an ozoniser Grundland[1] observed in 1953 weak currents due to ions with masses of 48 and 64 and attributed them to the presence in the ozonised oxygen of ozone (O_3) and "oxozone" (O_4) molecules. He was apparently the first to attempt the detection in oxygen at normal temperatures and pressures of polymeric oxygen molecules as well as oxygen ions with large masses.

Although Grundland's data were subsequently disproved in a number of studies[2-4], the presence of dimeric molecules O_2-O_2 in oxygen under normal conditions and the formation of clusters on adiabatic expansion of the gas has been recently demonstrated mass-spectrometrically and spectroscopically.

Improvements in technique of mass-spectrometric and certain other physical research methods for reactions in gases made it possible to investigate the thermodynamics and kinetics of the formation of positive and negative oxygen cluster ions $O_{2n}^{\pm}$ and also heteromolecular oxygen cluster ions $O_{2n}^{\pm}X_kY_lZ_m$ incorporating neutral molecules X, Y, and Z such as H_2O, CO_2, and NO.

It has been shown mass-spectrometrically[5,6] that these ions are very reactive. One of the causes of this is their capacity to form a relatively long-lived ion-molecule (molecules) complex, i.e. a cluster ion. The reaction time proved to be sufficient for bond rearrangement[7]. For example, the complex $O_2^-.H_2O$, formed as an intermediate in the reduction of oxygen by low-energy electrons, plays an important role in the chemistry of the ionosphere. Other oxygen cluster ions are also characteristic of the chemistry of the low-temperature plasma and of the radiation chemistry of gases.

The bond in the $AB^{\pm}$ cluster ion is mainly due to the polarisation of the molecule A under the influence of the ion $B^{\pm}$; the bond energy is given to a first approximation by the equation $V_n = -\alpha e^2/2r^4$, where α is the polarisability of the molecule A, r the distance between the centres of A and $B^{\pm}$, and e the electronic charge.

Comparison with experimental values of bond energies and other parameters of oxygen cluster ions, which have now been calculated by quantum-mechanical and statistical physical methods, yields valuable data for the theory of the chemical bond. The knowledge of the chemistry of oxygen cluster ions may be useful in the development of ways of synthesising new potential sources of oxygen which are valuable in practice.

II. THE O_4 MOLECULE, OXYGEN CLUSTERS

The existence of O_4 molecules is due to weak intermolecular interactions. The bond strength in such molecules is hundreds of times smaller than in the usual chemical compounds, for example the O_2-O_2 bond energy has been estimated as 460 cal $mole^{-1}$.[8]

The interaction of oxygen molecules in the gas phase leads to three types of binary species: collision pairs, metastable dimers, and bound dimers[9]. The collision pair is a pair of molecules in the gas phase subjected to appreciable mutual attraction (the molecules are usually separated by a distance of 5-10 Å during the collision) and having a kinetic energy greater than the height of the potential barrier on the intermolecular potential. The lifetime of the molecules of this type has been estimated as 10^{-13} s under the usual conditions.

When a so-called "triple" collision occurs and the third species acquires part of the kinetic energy of the other two colliding molecules, the metastable dimer—the O_2-O_2 molecule with energy greater than its dissociation energy but smaller than the maximum on the potential curve—may be formed. The lifetime of the metastable dimer has been estimated as $10^{-11}-10^{-16}$ s. The triple collision can result also in the formation of the bound dimer—a stable molecule with energy below the dissociation energy of the O_2-O_2 bond.

Metastable dimers can decompose spontaneously as a result of the tunnel effect. Since the rotational energy of the dimer in the gas phase at normal temperatures is comparable to the depth of the well on the potential energy curve for the dimer, the concentrations of the bound and metastable dimers are approximately equal.

The O_2 molecule does not have a dipole moment and therefore does not absorb in the infrared. On contact with another molecule, its quadrupole moment generates a dipole moment in its neighbour, which modulates the vibrational and rotational frequencies of the molecule, so that absorption in the infrared becomes possible. In other words, the pair of colliding oxygen molecules

absorbs due to transitions which are forbidden in the absence of the collision. The bands of such absorption should be broad and diffuse owing to the short lifetime of the colliding pair. On the other hand, the bound dimer should give rise to narrow absorption bands in consequence of its relatively long lifetime.

There are numerous spectroscopic data showing that at room temperature oxygen contains only collision pairs[10,11,12]. The infrared spectra of solutions of oxygen in liquid nitrogen show a broad shoulder on the vibrational absorption band induced by collisions, which vanishes on dilution; this phenomenon can be attributed to the presence of the dimer[13].

However, the infrared absorption spectrum of solid oxygen does not support the conclusion that individual $(O_2)_2$ molecules exist[14]. An X-ray diffraction study of solid oxygen also ruled out the presence of dimeric species[15]. In 1971 Long and Ewing[16] obtained the infrared absorption spectrum of gaseous oxygen (Fig. 1) at 87 K and a pressure of 559 torr for an optical path length of 152 m. A diffuse doublet with the centre at 1591.2 cm^{-1} was observed. The doublet had components with a width $\Delta\nu_{1/2} \simeq 7$ cm^{-1} and with centres at 1586.1 and 1596.6 cm^{-1}. These data confirm the presence of bound dimers in gaseous oxygen, which naturally exist also at other temperatures.

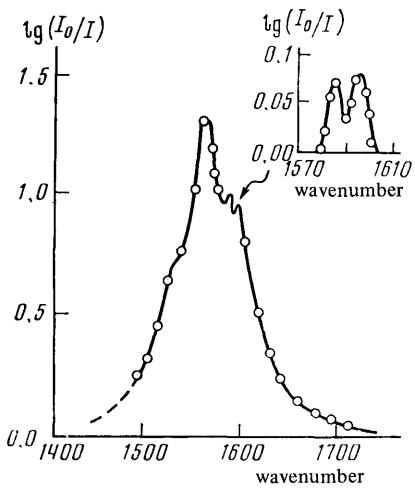


Figure 1. The infrared spectrum of gaseous oxygen induced by collisions.

The energy of formation of $(O_2)_2$ observed in the above study is 830 cal $mole^{-1}$, in good agreement with the value calculated by Stogrin and Hirschfelder[17]. The lifetime of the absorbing species is linked to the width of the corresponding line by the relation $\tau = (2\pi c\Delta\nu_{1/2})^{-1}$. The lifetime of the oxygen dimer, estimated from the doublet width $\Delta\nu \simeq 7$ cm^{-1}, is 10^{-12} s. This shows that the absorbing O_4 species must be regarded as the bound dimer. The actual lifetime of the dimer is somewhat greater than the above value, since the doublet contains a number of unresolved lines.

In 1966 Leckenby and Robbins[18] demonstrated mass-spectrometrically for the first time the presence of dimers in gaseous oxygen at the usual temperature and pressure. The oxygen dimers were detected with the aid of a mass-spectrometer of special design, in which oxygen was admitted into an ion source of the open type through an aperture in a 1 μm foil, the ion accelerating and ion focussing plates having been replaced by grids to increase the pumping rate. The concentration of the $(O_2)_2$ dimers in oxygen at a pressure of 100 torr and 300 K amounted to about 5×10^{-7}.

Previously Leckenby et al.[19] detected mass-spectrometrically dimers, trimers, and heavier clusters in a number of gases, including oxygen, during supersonic adiabatic flow of the gas from a reservoir (of gas pressures up to 40 atm) into a high vacuum maintained by a powerful pump. They found that the variation in the concentration of clusters with the reservoir temperature and pressure is approximately the same for each of the gases investigated; the differences are determined by the critical temperature T_c and pressure p_c and the ratio of the specific heats $C_p/C_V = \gamma$ for the given gas. It was noted that, for gases with similar critical constants T_c and p_c but with different values of γ, the maximum concentration of the polymer is observed at different pressures in the reservoir. Thus in argon ($T_c = -122°C$, $p_c = 48$ atm, $\gamma = 1.66$) the maximum concentration of clusters is reached at a reservoir pressure of 20 atm (at about $\sim 20°C$), while in oxygen ($T_c = -119°C$, $p_c = 50$ atm, $\gamma = 1.40$) it is reached at a pressure in excess of 50 atm. It was also established that gases with high values of γ show a greater tendency towards the formation of clusters.

On the other hand, for gases with similar values of γ the tendency towards polymerisation is determined by the critical constants. Oxygen ($T_c = -119°C$, $p_c = 50$ atm, $\gamma = 1.40$) exhibits a greater tendency towards the formation of clusters than nitrogen ($T_c = -147°C$, $p_c = 33.5$ atm, and $\gamma = 1.40$). In experiments with compressed air the formation of the dimers $(N_2)_2$, N_2O_2, and $(O_2)_2$ in the proportions 1 : 0.3 : 1.6 was observed. The concentration of clusters increases rapidly with increase of gas pressure in the reservoir, reaches a distinct maximum, falls, and then increases again.

Green and Milne[20] also observed the formation of oxygen cluster molecules during the supersonic flow of oxygen under analogous conditions. In 1972 Golomb and Good[21] demonstrated mass-spectrometrically the formation of dimers, trimers, and oligomeric clusters (up to molecules with a mass of 600) in the supersonic adiabatic flow of a number of gases into a vacuum. The maximum concentration of the oxygen dimer was observed at an O_2 pressure in the reservoir-source of 200 torr and a temperature of 400 K.

The clusters thus detected have come to be regarded as condensation "embryos" in the supercooled gas. This view is supported by the finding that gases with high values of T_c, p_c, and γ, i. e. with a considerable tendency towards condensation, show a greater tendency towards the formation of clusters.

Thus the existence of the oxygen dimers (O_2) in the gas under the usual conditions and also of clusters with a high molecular weight in the stream during the supersonic adiabatic flow of the gas must now be regarded as firmly established.

III. OXYGEN CLUSTER IONS

A considerable proportion of studies on the equilibria and rates of formation and decomposition of negative cluster ions were made using instruments consisting of a

combination of a drift tube and a mass-spectrometer[22-25]. A potential difference is applied between two electrodes in a tube 2.5 cm in diameter; these define the drift region (usually 2.5–3 cm long). The primary negative ions are formed by electron impact at the beginning of the drift tube[26]. The electron source is a heated filament or a photocathode. The ions pass from the drift tube to the mass analyser through an aperture of small diameter (25–250 μm) in the centre of the anode. Such devices sometimes operate under pulsed conditions, the ions and electrons being admitted into the drift space in pulses lasting between 1 and 20 μs, which amount to about 1% of the drift time[27,28].

Another type of instrument used in the study of reactions of oxygen cluster ions, in particular positive ions, is the high-pressure mass-spectrometer. Positive ions are obtained by a pulsed electron beam with energies up to 4 keV. The ions drift from the field-free space in the ion source to the inlet aperture in the mass analyser. At pressures up to 10 torr the reaction time reaches some hundreds of microseconds[29]. The use of such a device with pulsed operation for the study of reactions in the absence of a field was first described by Tal'roze and Frankevich[30]. The duration of the electron pulse was usually 10 μs, the time during which the inlet to the mass analyser is open also being 10 μs; the period between the pulses (2 ms) is sufficiently long for the ion current due to the preceding pluse to disappear completely.

The instrument makes it possible to record the time variation of the current due to each ion investigated. In continuous-operation devices the ion–molecule reaction takes place in a field where ions have a kinetic energy exceeding by 1–3 orders of magnitude the thermal energy corresponding to the temperature of the walls of the ionisation chamber. The reaction velocities obtained in such apparatus must be extrapolated to zero field. Such extrapolation involves errors, since the variation of the reaction rate with field strength is not always simple. Pulsed operation devices make it possible to avoid these complications.

A series of studies were made on equilibria involving positive cluster ions of oxygen in low-pressure mass-spectrometers using tritium as the source of ionising radiation[31]. In such apparatus the reaction time is about 1 ms and the time resolution achieved by the amplifier is better than 1 μs.

Reactions involving the formation of heteromolecular oxygen cluster ions and the exchange reactions of the neutral molecule in the cluster were studied using flow apparatus in a stream of carrier gas (helium, argon, etc.). Such flow apparatus makes it possible to investigate the reactions at temperatures from 80 to 600 K and pressures up to 10 torr. Oxygen is ionised by electron impact in the ion source located at the beginning of the tube through which the stream of gas is flowing. The reaction products are detected with a quadrupole mass analyser.

IV. THE O_4^- ION

The early attempts to detect the O_4^- ion in oxygen at 300 K and a pressure in the range 0.6–3 torr using a drift tube[32-34] were unsuccessful, although in analogous experiments at 77.4 and 87.6 K Voshall et al.[35] detected the O_4^- ion and estimated its dissociation energy as 0.06 ± 0.006 eV (1.4 ± 0.2 kcal mole^{-1}) from the temperature variation of the equilibrium constant for the formation and decomposition of O_4^-. On the basis of their results, the authors[35] concluded that the O_4^- ion cannot be detected in the drift tube above 195 K. However, theoretically it was to be expected that the O_4^- ion should be approximately as stable as the O_4^+ ion investigated previously ($\Delta H = -9.6$ kcal mole^{-1}).[36]

Using a high-pressure mass-spectrometer and titanium tritide as a 2 c source of ionising radiation, Conway and Nesbitt[37] detected the O_4^- ion and determined the equilibrium constant for the reaction $O_2^- + O_2 \rightleftharpoons O_4^-$ at temperatures from 273.2 to 352.8 K and oxygen pressures of 6.9 and 12 torr. The equilibrium constants (K, torr^{-1}) for the formation of O_4^- are listed below

T, °K	6 torr	9 torr	12 torr	K_{av}
273.2	9.46 *	10.6 *	10.7	10.3
293.0	1.58	1.55	1.61	1.58
313.4	0.323	0.344	0.335	0.334
333.0	0.102	0.106	0.102	0.103
352.8	0.0323	0.0341	0.0368	0.0344

* Determined for a flow reaction.

ΔH°_{298} for the formation of O_4^-, calculated from the above equilibrium constants, is −13.55 ± 0.16 kcal mole^{-1} (0.59 eV).

Using an improved drift tube, McKnight and Sawina[28] obtained curves relating the relative concentrations of O_4^- and O_2^- ions to drift time in oxygen at 310 K and pressures from 0.5 to 4 torr and found that the equilibrium constant for the formation of O_4^- is 0.5 torr^{-1} (1.6×10^{-17} cm^3), which virtually agrees with the above data of Conway and Nesbitt[37]. McKnight and Sawina[28] measured for the first time the rate of the termolecular reaction involving the formation of O_4^-:

$$O_2^- + 2O_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_4^- + O_2 \ .$$

The rate constant k_1 for this reaction is 3×10^{-31} cm^6 mol.$^{-2}$ s^{-1} at 310 K. The rate constant for the reverse reaction was found from the rate constant for the forward reaction and the equilibrium constant: $k_2 = 2 \times 10^{-14}$ cm^3 mol.$^{-1}$ s^{-1}.

Pack and Phelps[38] studied recently the reactions of negative oxygen ions on apparatus consisting of a combination of a drift tube and a quadrupole mass analyser and found that the rate constants for the forward and reverse reactions in the formation of the O_4^- ion are $k_1 = 4 \times 10^{-31}$ cm^6 mol.$^{-2}$ s^{-1} and $k_2 = 2.7 \times 10^{-14}$ cm^3 mol.$^{-1}$ s^{-1} respectively, which agrees well with McKnight and Sawina's data[28]. Thus the reaction of O_2^- with O_2 is fairly rapid, the system reaching equilibrium with a time constant of 1 ms at an oxygen pressure of 1 torr.

The detection of O_4^- ions with the aid of the mass-spectrometer is difficult, since their content at equilibrium is smaller by a factor of 2 than that of O_2^- ions at 310 K and 1 torr and the time constant for equilibration increases with decrease of pressure. In the presence of traces of CO_2 the O_4^- ion is converted into CO_4^- as a result of the reaction $O_4^- + CO_2 \xrightarrow{k} CO_4^- + O_2$ ($k = 4.3 \times 10^{-10}$ cm^3 mol.$^{-1}$ s^{-1}), which masks still further the O_4^- ion (at a CO_2 partial pressure of 10^{-5} torr the time constant for this reaction is 10 ms).[39]

Lecuiller et al.[40] detected the O_4^- ion in the zone of the corona discharge between the surface of an aqueous $FeSO_4$ solution and a negatively charged knife edge (2–30 kV) together with the negative oxygen ions O^-, O_2^-, and O_3^-; they found that the relative concentrations of O_3^- and O_4^- ions depend greatly on the discharge current (0–70 μA). O_4^- ions should be present in the atmosphere, since at a height of 40 km they are formed as a result of the reaction between O_2^- and O_2 with a time constant less than 10 ms;

the presence of CO_2 and H_2O in the troposphere promotes the conversion of O_4^- into water and carbon dioxide clusters followed by their reactions[28].

It is of interest to compare the rates of formation of O_4^- and O_4^+. Durden et al.[29] found that the rate constant for the formation of O_4^+ is 2.8×10^{-30} cm^6 s^{-1} at 298 K and also determined the dissociation energy of the O_4^+ ion as 0.4 eV, while, as stated above, the dissociation energy of the O_4^- ions is 0.58 eV.[37] Thus the rate of formation of the negative cluster ion is smaller by an order of magnitude than the rate of formation of the positive ion, although the bond energy in the negative ion is greater than in the positive ion. Apparently it does not necessarily follow that the higher the bond energy the higher the rate of formation of the cluster ion. The properties of the O_4^- ion investigated show that the ion plays a major role in systems involving negative oxygen ions, for example in the reactions of electrons in the lower layers of the atmosphere.

V. THE O_4^+–O_{18}^+ OXYGEN CLUSTER IONS

In 1964 Yang and Conway[36] determined the equilibrium constant for the reaction $O_2^+ + 2O_2 \rightleftharpoons O_4^+ + O_2$ at temperatures from 239 K to 344 K and oxygen pressures from 1 to 9 torr with the aid of a high-pressure mass-spectrometer and titanium tritide as a 400 mc source of ionising radiation in oxygen. These data are presented in Table 1.

Table 1. The equilibrium constants (K, torr^{-1}) for the reaction $O_2^+ + O_2 \rightleftharpoons O_4^+$.

T, °K	p_{O_2}, torr	K, torr^{-1}	T, °K	p_{O_2}, torr	K, torr^{-1}
259	1.00	3.8	320	1.00	0.097
259	2.00	4.8	320	2.00	0.094
259	9.00	5.7	320	4.00	0.106
			320	9.00	0.121
273	1.00	1.30			
273	2.00	1.49	344	1.00	0.036
273	4.00	1.61	344	2.00	0.035
273	9.00	1.76	344	4.00	0.037
			344	9.00	0.045
293	1.00	0.41	—	—	—
293	4.00	0.56	—	—	—
293	9.00	0.81	—	—	—

The familiar relation

$$\Delta F_{T_2} - \langle \Delta C_p \rangle_{av} \left(\Delta T - T_2 \ln \frac{T_2}{T_1} \right) = \Delta F^\circ_{T_1} - \Delta S^\circ_{T_1} \Delta T, \qquad (1)$$

where $\Delta F^\circ_{T_1}$ is the Gibbs free energy of reaction under standard conditions linked to the equilibrium constant K (Table 1) by the relation $\Delta F^\circ_{T_1} = -RT_1 \ln 760 \times K$ and $\langle Cp \rangle_{av} = 2.8$ cal mole^{-1} deg^{-1} is the average change in heat capacity in the above temperature range, was used to determine the thermodynamic characteristics of the reaction. The estimate was based on the assumption that O_4^+ is a rigid linear complex with a distance of 3.0 Å between the centres of O_2 and O_2^+; it was also assumed that the distance between the centres of the atoms in O_2^+ is equal to the corresponding distance in O_2; $\Delta S^\circ_{T_1}$ is the standard entropy of reaction at a temperature T_1. Graphical solution of Eqn. (1) gave $\Delta S^\circ_{293} = -20$ e.u. and $\Delta F^\circ_{293} = -3.56$ kcal mole^{-1}. Hence $\Delta H^\circ_{293} = -9.60$ kcal mole^{-1} (0.416 eV).

In 1965 Conway and Yang[41] estimated mass-spectrometrically the equilibrium constants for the formation of positive homomolecular oxygen cluster ions ($O_{2n}^+ + O_2 = O_{2n+2}^+$ with $n = 2$–5) at a low temperature (Fig. 2).

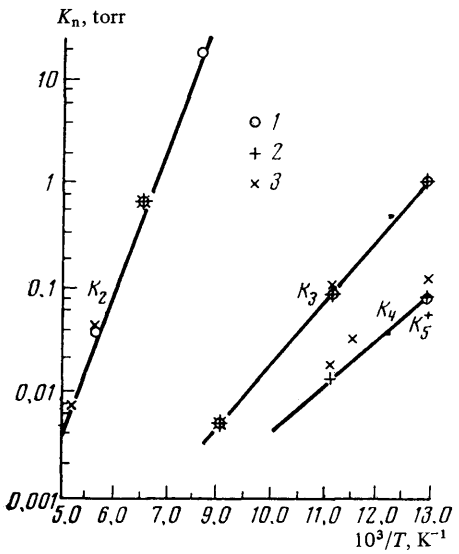


Figure 2. Temperature variation of the equilibrium constants K_n of reactions of the type $O_{2n}^+ + O_2 = O_{2n+2}^+$; oxygen pressure (torr): 1) 1; 2) 2; 3) 4.

In 1970 Conway and Janik[42] repeated the previous study and refined the results for the O_4^+–O_{18}^+ cluster ions, using a somewhat improved research technique. Table 2 lists the observed equilibrium constants for the formation of the cluster ions by the reaction $O_2 + O_{2n}^+ \rightleftharpoons O_{2n+2}^+$.

Table 2. The equilibrium constants K_n for the reactions $O_{2n}^+ + O_2 \rightleftharpoons O_{2n+2}^+$.

n	T, °K	p_{O_2}, torr				Multiplier
		1,55	3,09	6,15	9,14	
3	77.3	1.07	1.10	1.18	1.26	·100
3	90.1	1.03	1.02	1.06	1.16	·10^{-1}
4	77.3	8.02	8.21	9.37	10.78	·10^{-2}
4	90.1	—	0.79	1.03	1.31	·10^{-2}
5	77.3	4.50	4.47	5.21	5.95	·10^{-2}
5	90.1	—	—	8.48	9.30	·10^{-3}
6	77.3	—	—	2.77	3.30	·10^{-2}
7	77.3	—	—	1.90	2.40	·10^{-2}
8	77.3	—	—	—	1.70	·10^{-2}

The standard enthalpies and entropies of formation of the cluster ions by the reaction $O_2 + O_{2n}^+ = O_{2n+2}^+$ and the corresponding bond energies were calculated from the observed low-temperature equilibrium constants (77–90 K) and the models adopted for the ions (Table 3).

Conway[43] calculated the energies of the O_4^+ and O_4^- ions (together with N_4^+) by a somewhat modified MO-SCF method for structures with C_2 symmetry as a function of the angles $\theta = \theta'$ and the distance R between the interacting species (Fig. 3). The equilibrium dissociation energies D_3 for the equilibrium distances R_e and angles θ_e are listed below:

Ion	D_e, kcal mole^{-1}	R_e, Å	θ_e, deg	D(expt.), kcal mole^{-1}
O_4^+	11.66	2.03	—67	10,8
O_4^-	8.49	2.08	—71	13,6
N_4^+	34.7	2.04	0	11,5

Table 3. Thermodynamic characteristics of the reactions $O_2 + O_{2n}^+ = O_{2n+2}^+$.

n	ΔS, e.u.	$\Delta H°$, kcal mole^{-1}	$D_0(O_2-O_2^+)$	$D_e(O_2-O_2^+)$*
1	—25.01±0.2	—10.84±0.05	10.53±0.10	11.58±0.11
2	—31.78±0.3	—6.87±0.06	6.51±0.07	7.72±0.13
3	—19.8(—0.3+1.0)	—2.54(—0.03+1.0)	2.56(+0.16—0.06)	2.88(+0.07—0.71)
4	—23.9(—0.5+2.1)	—2.46(—0.05+0.18)	2.43(±0.06—0.09)	2.81(+0.01—0.30)
5	—17.0(—3.0+9.2)	—1.84(—0.3+0.7)	2.00(±0.4—0.6)	2.13(+0.4—1.0)

* $D_e(O_2 - O_2^+)$ is the dissociation energy corresponding to the minimum in the potential energy curve.

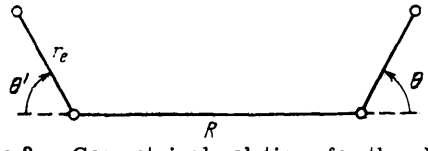


Figure 3. Geometrical relations for the planar ion–molecule complex.

Durden et al.[29] also determined the rate constants for the formation of the O_4^+ ion and its dissociation energy using a high-pressure mass-spectrometer with a pulsed electron beam having an energy of 4 keV as the source of ionising radiation. They succeeded in following the decrease of the concentration of O_2^+ ions and the increase of the concentration of O_4^+ ions in oxygen after the electron pulse (at an oxygen pressure of 3–4 torr) before the equilibrium concentrations of these ions were reached. Equilibrium was attained 60 μs after the pulse at 298 K and after 20–30 μs at 341 K. The rates of formation of O_4^+ were also determined in other investigations[29,44,46,47] and in a study by Joung and Falconer[45]. Using the mass-spectrometric method for the study of reactions in a stream of carrier gas (helium), Adams et al.[46] investigated at 200 K and an overall pressure of 1.767 torr the equilibrium in the following reaction involving a cluster ion:

$$O_2^+ + O_2 + He \rightleftarrows O_4^+ + He \ .$$

The rate constants for the formation and decomposition of the O_4^+ ion are listed in Table 4.

It is interesting to note that the rate constant for the formation of the cluster ion O_4^+, equal to 2.8×10^{-30} cm^6 mol.$^{-2}$ s^{-1}, is almost a factor of 30 smaller than the rate constant for the corresponding reaction of nitrogen[29] ($N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$), which is 8.57×10^{-29} cm^6 mol.$^{-2}$ s^{-1}.

Table 4. The rate constants for the formation (k_1) and decomposition (k_2) of the O_4^+ ion.

Reaction	°K	k_1, cm^6 mol.$^{-2}$ s^{-1}	k_2, cm^3 mol.$^{-1}$ s^{-1}	Refs.
$O_2^+ + 2O_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_4^+ + O_2$	298	$2.8 \cdot 10^{-30}$	$2.8 \cdot 10^{-13}$	29
»	298	$2.4 \cdot 10^{-30}$	—	44
»	298	$1.5 \cdot 10^{-30}$	—	45
$O_2^+ + O_2 + He \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_4^+ + He$	200	$2.45 \cdot 10^{-30}$	$3 \cdot 10^{-17}$	46,47
	200	$2 \cdot 10^{-31}$	$1 \cdot 10^{-14}$	48

VI. REACTIONS OF HETEROMOLECULAR OXYGEN CLUSTER IONS

Adams et al.[46] measured the rate constants for trimolecular reactions involving the association of O_2^+ with H_2, N_2, O_2, CO_2, NO_2, and SO_2 in a stream of helium as the carrier gas and the third body at temperatures below 300 K, which proceed via the general mechanism

$$A^\pm + B + M \rightarrow A^\pm B + M \ .$$

The rates of association of O_2 with N_2, O_2, and CO_2 at 200 K were also measured.

Since the bond energy and the rate constant for the termolecular reaction vary in the same sense (in agreement with theoretical concepts), the authors[46] found that the molecules can be arranged in the following sequence in order of increasing energy of the bond with the O_2^+ ion: $H_2 < N_2 < O_2 < N_2O < SO_2 < H_2O$. For O_2^-, the stability of the ionic clusters increases in the sequence $N_2 < O_2 < H_2O < CO_2 < NO$. The rates of formation of cluster ions such as $O_2^+.N_2.N_2$, $O_2^+.O_2.N_2$, etc. were also estimated.

Reactions of another type involving the formation of heteromolecular ionic clusters in a stream which have been investigated are the bimolecular exchange reactions of the neutral molecule in the cluster:

$$A^\pm \cdot B + C \rightarrow A^\pm \cdot C + B \ ,$$

where A = O_4^-, O_2^+, O_2^-, or O^- and B and C = O_2, N_2, N_2O, SO_2, H_2O, CO_2, NO, or CO. The rate constants for these reactions were measured at 80, 200, and 300 K. In certain cases the exchange reactions of the neutral molecule in the cluster ion are only weakly exothermic, so that the reverse reaction takes place; it is then possible to estimate the free energies of these reactions (from the equilibrium constants). Since the entropy changes in these reactions should be small, their free energies $\Delta F° = -RT \ln K$ are close to the enthalpies of reaction ΔH. The latter values are approximately equal to the differences between the bond energies of the initial molecules and the resulting cluster ion. This has been confirmed to some extent by data for the equilibrium in the reaction $O_2^- . O_2 + CO_2 \rightleftharpoons O_2^- . CO_2 + O_2$.

It was found that the free energy of this reaction, and hence the approximate difference ΔD between the association energies of $O_2^-.CO_2$ and $O_2^-.O_2$, is 0.26 eV. Pack and Phelps[49] found that the energy of the dissociation of the $O_2^-.CO_2$ ion into O_2^- and CO_2 is 0.8 ± 0.08 eV. On the basis of this value and the value of 0.59 eV obtained by Conway and Nesbitt[37] for the $O_2^- - O_2$ bond energy, we find ΔD = 0.21 eV. Within the limits of experimental error, this agrees with the above value of 0.26 eV.

The data presented for the chemistry of oxygen cluster ions show that much experimental information has already been accumulated in this field and that theoretical studies are being made in order to refine the ideas concerning the nature of the interaction forces in these ions; the results of the two lines of research supplement one another. Evidently in the future research in this field will develop vigorously in connection with the growing interest in the chemistry of the ionosphere, the radiation chemistry of gases, etc.

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