THE IONIZATION OF OXYGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS

By T. R. Hogness and E. G. Lunn

Abstract

Using an apparatus previously described, in which ions formed by impact of electrons of definite energy are analyzed by Dempster's positive ray method, the relative numbers of O_1^+ and O_2^+ are measured at different pressures and electron energies. Over a range of pressure from $<10^{-5}$ to 10^{-2} mm of mercury in pure oxygen, and over a large range of partial pressures of oxygen in mixtures with helium and with argon, the ratio O_2^+/O_1^+ remains practically constant. Evidence is thus given that O_2^+ and O_1^+ are formed by independent primary processes and, therefore, that an impact electron of sufficient energy can either ionize the molecule and form O_2^+ or dissociate the molecule forming O_1^+. The ionization potentials were determined: $O_2 = O_2^+ + \epsilon$; 13 volts and $O_2 = O_1^+ + O + \epsilon$; 20 volts. The latter, together with the ionizing potential of atomic oxygen, gives 6.5 volts (150,000 cal. per mol) for the heat of dissociation of oxygen. Both molecular and atomic negative ions were found. The above results are correlated with band-spectra data, with the recent theory of Franck on dissociation by absorption of radiation, and with the structure of the oxygen molecule.

THE following paper discusses experiments on oxygen made with the previously described[1,2,3] method for the positive ray analysis of the products of electron impact ionization in gases.

Experimental Details

The apparatus was that previously employed, except that the slits were narrowed to permit the use of higher pressures in the ionization tube, and to increase the resolving power. The increased resolving power was necessitated by the impossibility of freeing the oxide-coated platinum filament from all traces of residual gases, and the consequent appearance of peaks due to these impurities; these peaks, though small, would, with lower resolution, merge into the oxygen peaks and vitiate the measurements of their intensity. The ions of these impurities are presumed, from their specific charges, to be: Hg^+, CaO^+, CO_2^+, 30 = ?, 29 = ?, N_2^+, 20 = ?, 19 = ?, H_2O^+, OH^+, O^+, 15 = ?, N^+ and C^+. With the slits narrowed to 0.28 mm these peaks are sharp and well separated. The mercury peak disappears after liquid air has been on the traps for some days, while the other peaks either disappear or become negligibly small after prolonged heating of the filament. Judging from the peak intensities obtained in previous

work with very low pressures of hydrogen[2] and nitrogen,[3] the partial pressures of the above impurities were $<10^{-6}$ mm of mercury, except in those experiments in which the highest filament temperatures were employed.

The oxygen was prepared by electrolysis of aqueous barium hydroxide and was dried with phosphorus pentoxide. Before entering the ionization tube it passed through a liquid air trap.

Positive ions. As shown by the figure, the relative intensity of the ions O_1^+ and O_2^+, as measured by the ratio of the peak intensities, remains practically constant over a range of pressure from $<10^{-5}$ to 10^{-2} millimeters of mercury. Evidence is thus given that O_1^+ and
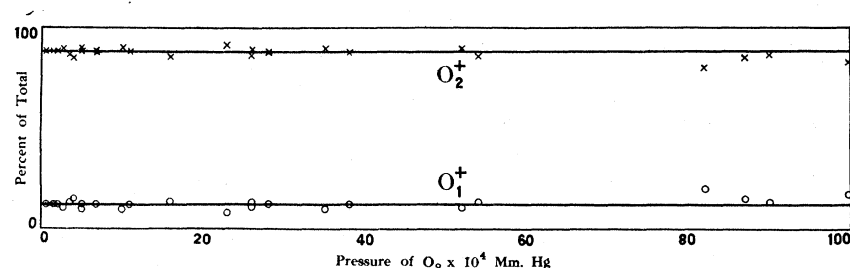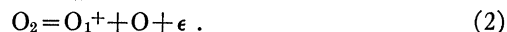

Fig. 1. Precentage of O_1^+ and O_2^+ as a function of pressure.

O_2^+ are formed by independent processes, and hence that an impact electron of sufficient velocity can either produce an O_2^+ ion which does not dissociate on collision with gas molecules:

$$O_2 = O_2^+ + \epsilon , \qquad (1)$$

or it can dissociate the molecule and ionize one atom as the primary process:

$$O_2 = O_1^+ + O + \epsilon . \qquad (2)$$

The slight increase in the percentage of O_1^+ at the higher pressures is probably due to the formation of these ions from the impurities, for, owing to a specific inhibiting effect of oxygen on the emission of electrons from an oxide-coated filament,[4] it was necessary to raise the filament to a high temperature and hence to increase the concentration of those foreign gases which, on ionization, produce O_1^+-ions.

The relative intensities of O_1^+ and O_2^+ were found to be nearly independent of other experimental conditions, such as the partial

[1] Hogness and Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924).

[2] Hogness and Lunn, Phys. Rev. **26**, 44 (1925).

[3] Hogness and Lunn, Phys. Rev. **26**, 786 (1925).

[4] Koller, Phys. Rev. **25**, 671 (1925).

pressure of oxygen in mixtures with helium and with argon, and the speed of the positive ions in the ionization chamber.

In mixtures of oxygen with helium and with argon the percentage of O_1^+ was found to be only slightly larger than in pure oxygen, and this slight increase is probably caused by O_1^+ ions from the impurities due to the high filament temperature made necessary by the small partial pressure of the oxygen. With argon in the tube, peaks of specific charges 40 and 36 (referred to $O = 16$) appeared, thus confirming Aston's[5] evidence on the isotopy of argon.

The relative intensities of O_1^+ and O_2^+ are practically independent of the energy of the impact electron from 50 to 200 volts; above 200 and up to 600 volts, increasing this energy gradually decreases the percentage of O_1^+. Similarly, varying the speed of the positive ions in the ionization chamber by changing the field V_3 from 0 to 31 volts does not change the intensity ratio appreciably.

Ionization potentials. The ionization potentials for the formation of O_2^+ and O_1^+ were determined by comparing their disappearing potentials with that of helium in essentially the manner previously described.[2] Oxygen was mixed with helium in the reservoir until the "saturation" intensities of He^+ and O_2^+ were the same, and the disappearing potentials compared; the concentration of oxygen was then increased until the He^+ and O_1^+ "saturation" intensities were equal, and the disappearing potentials of these ions were then measured. Taking 24.5 volts as the ionization potential of helium,[6] the mean of six determinations gave 13 volts as the ionization potential for the formation of O_2^+ and 20 volts for the formation of O_1^+.

Negative ions. On reversing the magnetic field and the electrical fields V_3 and V_4, the negative ions O_2^- and O_1^- were observed. These had previously been found by J. J. Thomson.[7] The atomic ion was the more intense under all conditions studied; but the intensities of both O_1^- and O_2^- were so small as to preclude the possibility of their formation being related to the positive ion process.

DISCUSSION

The ionization of oxygen has been studied by McHenry[8] and by Smyth.[9] McHenry used Thomson's positive-ray apparatus and hence

[5] Aston, Phil. Mag. **39,** 611 (1920).

[6] Lyman, Science **56,** 167 (1922).

[7] J. J. Thomson, Rays of Positive Electricity, p. 71.

[8] McHenry, Phil. Mag. **45,** 433 (1923).

[9] Smyth, Proc. Roy. Soc. **105 A,** 116 (1924).

experimental conditions that make difficult any comparison of his results with those above. The present results differ somewhat from those of Smyth. His published curves show a larger percentage of O_1^+ than was found above; this is perhaps due to the presence of N_1^+ and other impurities not resolved by his apparatus. The ion of apparent $m/e = 8$, which Smyth observed, was probably not O^{++}. In the present work its peak appeared as a very broad one of small height— indicative of formation by some secondary process, such as the disruption of an O_2^+-ion which had fallen through the full analyzing field.[10] The above experiments show no evidence of the discontinuity in the ionization curves at 450 volts found by Smyth. His measurements gave 15.5 and 23.0 volts as the ionization potentials. We believe Smyth's values for these ionization potentials to be in error, owing, perhaps, to incorrect initial velocity corrections; but their difference $(23.0 - 15.5 = 7.5$ volts) agrees well with that (7 volts) found above.

Of the several determinations of the ionizing potentials of oxygen[11] only that of Mackay[12] shows ionization as low as 13 volts; he found two potentials at 12.5 and 16.1 volts. Studying low voltage arcs in oxygen, Lockrow and Duffendack[13] found critical potentials at 16.1 and 19.5 volts. The lower, that at which the arc broke, they ascribed to the formation of O_2^+; the upper, a critical potential for changes in the spectrum, was attributed to the formation of O_1^+ by the process $O_2 = O_1^+ + O + \epsilon$. The lower potential of Mackay and the upper one of Lockrow and Duffendack are thus in good agreement with those found above for the formation of O_2^+ and of O_1^+ respectively.

From the evidence based on the magnetic and chemical properties of oxygen, G. N. Lewis[14] has given $:\ddot{O}: :\ddot{O}:$ as the schematic structure of the oxygen molecule—a molecule then with two unpaired electrons. Now Saunders[15] has pointed out that atoms with unpaired electrons have low ionizing potentials, the tendency of electrons to pair resulting then in the observed alternation in the value of the ionization potentials of the elements with increase in atomic number; Mulliken[16] and Birge[17] have suggested an analogy between the energy levels of atoms and of

[10] See Smyth, Phys. Rev. **25,** 452 (1925).

[11] For a summary of these see Compton and Mohler, Bull. Nat. Res. Council, vol. 9, part 1, *Critical Potentials.*

[12] Mackay, Phys. Rev. **24,** 319 (1924).

[13] Lockrow and Duffendack, Phys. Rev. **25,** 110 (1925).

[14] G. N. Lewis, Chemical Reviews **1,** 231 (1924); J. Am. Chem. Soc. **46,** 2027 (1924).

[15] Saunders, Science **59,** 47 (1924).

[16] Mulliken, Phys. Rev. **26,** 561 (1925).

[17] Birge, Nature **117,** 300 (1926).

molecules. It might therefore be anticipated that, because of the two unpaired electrons in the oxygen molecule, the ionization potential of oxygen would be lower than that of nitrogen. Experiment shows this to be the case. It might be expected, too, that oxygen, containing, as it does, three distinct kinds of electrons (bonding, unpaired—non-bonding, and paired—non-bonding) would have two ionization potentials in addition to that for the disruption of the molecule. Now Mackay[12] did find two lower ionization potentials. From this point of view the lower one (12.5 volts) perhaps corresponds to the ejection of an unpaired electron, the upper one (16.1 volts) to the ejection of a paired—non-bonding electron.*

The difference in the processes by which the atomic ions are formed in the ionization of oxygen and of nitrogen suggests correlating these processes with the recent theory of Franck[18] on the dissociation of molecules by the absorption of radiation. Franck assumes that the absorption of a light-quantum results only in an electron transition and that the nuclear separation remains unchanged at the moment of this transition. With the electron in a new energy level the nuclei then find themselves held together by a different binding energy; this different binding energy gives rise to a different amplitude and hence, a different frequency of vibration. He further assumes that there is a limiting distance of approach of the nuclei, beyond which there will be sufficient repulsion to cause disruption, and as the binding force is weakened, i. e., as the equilibrium positions of the nuclei are more widely separated, this limiting distance of approach becomes greater. If then, as the result of an electron transition, the equilibrium positions of the nuclei are suddenly at a greater distance apart than before, the two nuclei may, at the moment of transition, be beyond the limiting distance of approach and hence disruption will follow. Dymond[19] found this to be the case in iodine, and Birge and Sponer[20] have recently found this to be true of oxygen as well. Professor Birge has informed us that ionized oxygen in the excited state corresponding to about 20 volts energy has a much slower vibration frequency than

---

* The O_2^+ (20 volts) which spontaneously breaks down into O and O^+ may be regarded as being either an O_2^+ with a remaining electron excited, or an O_2^+ with a different kind of electron (bonding) removed from that produced at 13 volts. In our work on nitrogen[3] the latter view was assumed, while Sponer has since suggested the former. The evidence favoring Dr. Sponer's suggestion is that but one series limit for the electron levels in nitrogen is known. Naturwiss. **13,** 275 (1926).

[18] J. Franck, Trans. Faraday Soc., 1925.

[19] Dymond, Zeits. f. Physik **34,** 553 (1925).

[20] Birge and Sponer Abst. 13, Stanford Meeting; Birge, Abst. 14, *ibid.*; Birge and Sponer (to be published in full).

the normal state; this means that the equilibrium positions are at greater nuclear separation. Very probably then, the mechanism assumed by Franck for dissociation by absorption of radiation and by electron impact applies to this case of dissociation. Nitrogen does not show this same difference in vibration frequencies in the normal and ionized states, so that the nitrogen nuclei would not be beyond the limit of closest approach in the N_2^+ ion produced at 24 volts[3] and no spontaneous dissociation would follow.

It may be recalled that in the case of hydrogen[2] and nitrogen[3] the measurement of the ionization potentials for the formation of H_1^+ and N_1^+ respectively could give only upper limits to the heats of dissociation as the atomic ions are formed by secondary processes. In the case of oxygen, however, since O_2^+ is formed by a direct process, the heat of dissociation of oxygen can be calculated unambiguously. For

$$O_2 = O_1^+ + O + \epsilon; \quad 20 \text{ volts} \tag{3}$$
$$O = O_1^+ + \epsilon \quad ; \quad 13.5 \text{ volts}^{21} \tag{4}$$
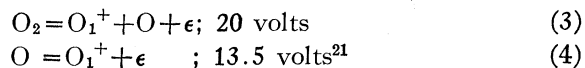
which, by subtraction, gives 6.5 volts or 150,000 calories per mol as the heat of dissociation of oxygen. The possible limits for the heat of dissociation of oxygen as set by critical potential measurements have been discussed by Wulf. [22] Owing to a lack of interpretation of those measurements the limits were rather wide—56,400 and 137,400 cal. per mol. The latter agrees within the experimental error with that found above, and the new limits are set by the limits of accuracy of the determination of the ionization potential. No claim is made for great accuracy in the above critical potential measurements. As previously done we might make a conservative estimate of ±1 volt, although the maximum deviation of our few values from the above means was 0.4 volt. Born and Gerlach,[23] following a suggestion of Franck and Grotrian, and utilizing Warburg's[24] measurement of the long wave-length limit for the formation of ozone, have calculated the heat of dissociation of oxygen to be 162,000 cal. per mol. Since we obtained our value of 6.5 volts, Birge and Sponer have calculated the heat of dissociation from data derived from band-spectra. The concordance of their value of 7.05±0.03 volts (162,600±700 cal.) with those of two such very different experimental methods suggests strongly

[21] Hopfield, Phys. Rev. **21**, 710 (1923).

[22] Wulf, J. Am. Chem. Soc. **47**, 1944 (1925).

[23] Born and Gerlach, Zeits. f. Physik **5**, 433 (1921).

[24] Warburg, Sitzungsber. d. preus. Akad. d. Wiss., Math-phys. Kl. 1914, p. 872.

the fundamental correctness of the assumptions underlying these methods.

Throughout the above paper it has been tacitly assumed that the ion of $m/e = 16$ was O_1^+ and not O_2^{++}. It is now seen that the chief justification for this assumption is that it is consistent with the spectroscopic observations of Lockrow and Duffendack,[13] and that it leads to a consistent value for the heat of dissociation of oxygen. Professor Birge has sufficient data to assure us that the energy of formation of O_2^{++} is greater than 20 volts. The ion appearing at 20 volts can therefore be only O_1^+.

In conclusion, the authors wish to express their thanks to Prof. R. T. Birge and Dr. H. Sponer of the Department of Physics for making available a large amount of unpublished results, as well as for their kindly interest in the progress of this work.

DEPARTMENT OF CHEMISTRY,
    UNIVERSITY OF CALIFORNIA,
        March 23, 1926.