X—4

THERMAL ELECTRON ATTACHMENT TO O_2 AS STUDIED BY A MICROWAVE CAVITY TECHNIQUE COMBINED WITH PULSE RADIOLYSIS

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The low-energy electron attachment to O_2 has extensively been studied using an electron swarm or a beam technique. Its mechanism has been considered to be a three-body process which proceeds in two stages as was first proposed by Bloch and Bradbury (B-B), that is initial electron capture of O_2 resulting in the formation of a vibrationally excited O_2^{-*} and subsequent stabilization of O_2^{-*} by collision with another O_2 or with a foreign molecule M.

$$e^- + O_2 \longrightarrow O_2^{-*} \qquad (1)$$
$$O_2^{-*} \longrightarrow O_2 + e^- \qquad (2)$$
$$O_2^{-*} + O_2 \longrightarrow O_2^- + O_2 \qquad (3)$$
$$O_2^{-*} + M \longrightarrow O_2^- + M \qquad (4)$$

The details of the B-B mechanism, however, have not been fully understood. On the autoionization lifetime of O_2^{-*} which is known to be in the excited vibrational level of v'=4, the order of 10^{-10} sec has been suggested theoretically, while about 10^{-12} sec has been proposed using an electron swarm method. Furthermore, the mechanism of the collisional stabilization of O_2^{-*} by third bodies has not been clarified.

In this study a microwave cavity method combined with pulse radiolysis has been used to observe the disappearance of thermal electron directly with fast response by attachment to O_2.[1-4] The experimental apparatus is shown in Fig. 1. Microwave power from a klystron(9V54) is transmitted in an X-band waveguide via a variable attenuator, an isolator and a magic tee to a brass cylindrical microwave cavity(loaded Q=5000) which has a resonant frequency of 9536 MHz and is operated in the TE_{011} mode. Incident microwave power to the cavity is about 50 μwatt. For a vacuum seal a 0.3 mm mica foil with epoxy cement is inserted into a part of the waveguide. Electrons are produced by irradiation of a nsec X-ray pulse from a 0.1 mm tungsten foil attached to the pulser window of a Febetron 706. For uniform X-ray exposure the cavity is located 50 cm away from the pulser window. Since the dose is about 20 mR per pulse, the electron concentration in the cavity is estimated to be of the order of 10^5 cm^{-3} for the gas pressures used. In order to observe exclusively the electron attachment process, we made experiments at relatively high pressures and the time-scale was restricted to within about 100 μsec, in which the electron loss by diffusion to the cavity wall could entirely be neglected. The effect of electron-ion recombination could also be neglected because of the very low dose of X-rays used.

Various compounds such as rare gases, diatomic molecules, hydrocarbons and alcohols have been used as third bodies. For almost all third bodies the electron attachment obeys the B-B mechanism. In the case of N_2, C_2H_4 and CO_2 as third bodies, however, some multi-body processes have an important contribution to the attachment mechanism in addition to the simple B-B mechanism.

The rate constant of initial electron capture has been found to be $(4.8 \pm 0.6)\times10^{-11} cm^3 s^{-1}$. Three-body rate constants have been obtained for various third bodies (Table 1). The difference in these values is correlated with the smallest vibrational energy level spacing of third-body molecules and is ascribed to the difference in the efficiency of collisional stabilization of O_2^{-*}, which is classified into two cases depending on whether the vibrational relaxation is effected by V-T or V-V transitions. Conventional theories have failed to explain the magnitudes of V-T transition probabilities obtained here. The lifetime of $O_2^{-*}(v'= 4)$ has been estimated to be $(1.0 \pm 0.3)\times10^{-10}$ s.

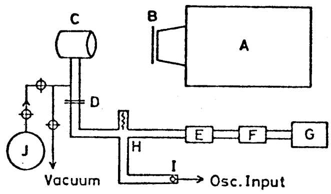

Fig.1. Schematic representation of the appratus.
A, Febetron 706
B, 0.1 mm tungsten foil
C, microwave cavity
D, 0.3 mm mica
E, isolator
F, attenuator
G, klystron
H, magic tee
I, crystal diode
J, gas cell

Table 1. Three-body rate constants at about 300 K($\times10^{-30}$ cm^6 s^{-1})

M	k_M
He	0.033 ± 0.003
Ne	0.023 ± 0.003
Ar	0.05 ± 0.01
Kr	0.05 ± 0.01
Xe	0.085 ± 0.005
H_2	0.48 ± 0.03
D_2	0.140 ± 0.005
N_2	0.085 ± 0.005
O_2	2.3 ± 0.2
CH_4	0.34 ± 0.01
C_2H_6	1.7 ± 0.1
C_2H_4	2.7 ± 0.5
C_3H_8	3.3 ± 0.2
n-C_4H_{10}	5
n-C_5H_{12}	7.9 ± 0.4
neo-C_5H_{12}	8.0 ± 0.7
n-C_6H_{14}	8.1 ± 0.4
CH_3OH	11 ± 2
C_2H_5OH	18
CO_2	3.4 ± 0.2

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