

ATOMIC AND MOLECULAR PROCESSES IN THE GAS PHASE AS STUDIED BY A PULSE RADIOLYSIS METHOD

Y. Hatano, K. Shinsaka, A. Yokoyama¹⁾, Y. Kokaku²⁾, N. Suzuki, M. Toriumi, A. Nishikawa, and H. Koizumi

Department of Chemistry, Tokyo Institute of Technology, Meguro-ku, Tokyo 152.

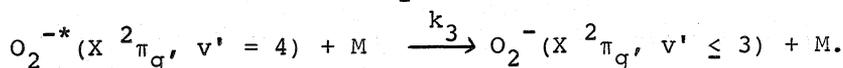
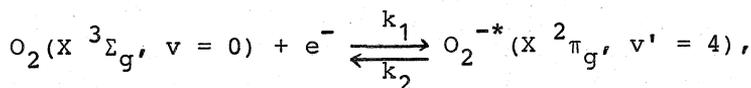
1. Introduction

We have been studying the thermal electron attachment to an oxygen molecule by a pulse radiolysis-microwave cavity technique³⁾, and the de-excitation processes of excited rare gas atoms by time-resolved spectroscopy, using a relatively light versatile electron pulse accelerator, Febetron 706. We report here some application of the accelerator by the recent results of our experiments on the thermal electron attachment in some O₂-hydrocarbon mixtures and the de-excitation of excited rare gas atoms.

2. Thermal electron attachment in some O₂-hydrocarbon mixtures

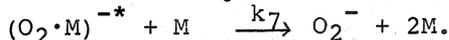
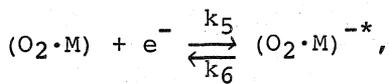
The sample gas was introduced into a cylindrical X-band microwave cavity and was irradiated by a X-ray pulse from Febetron 706, which produces a 600 keV electron beam pulse of triangular time profile with a half width of several nanoseconds (≈7000 Å). The microwave circuit which is the Pound type frequency discriminator including two Magic Tees and two detector diodes was used for the measurements. Differentially amplified signal between the diodes is accurately proportional to the shift of the cavity resonant frequency, in the result, to electron concentration.

Thermal electron attachment to O₂ in the presence of third body molecule (M) at low pressures has been explained by the Bloch-Bradbury (B-B) mechanism⁴⁾:



With increasing the pressure of M, the effective two body rate constant of electron attachment, k_{eff} , continues to increase and exceeds the limiting value k_1 which is expected by the B-B mechanism as shown in Fig. 1.

This excess part of electron attachment process has been ascribed to electron attachment to van der Waals molecule (O₂·M)⁴⁾:



The rate constant of the initial electron attachment to (O₂·M) is found about two orders of magnitude larger than that for O₂ itself as given in Table 1 (cf. $k_1 = (4.8 \pm 0.6) \times 10^{-11} \text{ cm}^3/\text{sec}$)^{3,4)}.

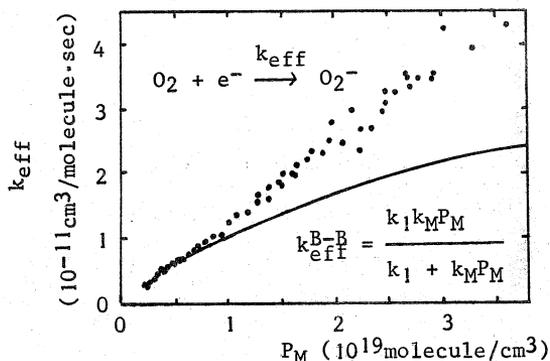
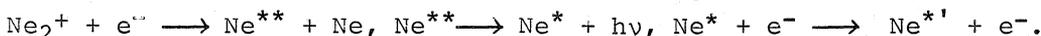


Fig. 1. Effective rate constant for O₂-C₂H₆ mixtures as a function of density of C₂H₆. Solid curve shows the contribution of the B-B mechanism.

3. De-excitation of excited rare gas atoms

3.1 Time-resolved optical absorption⁶⁻⁹⁾ of excited neon atoms Ne ($3P_1$, $3P_0$, $3P_2$) has been measured after the irradiation of pulsed electron beam from Febetron 706 upon Ne-M mixtures. At high electron densities the decay rates of neon 1s states are affected by thermal electrons as shown in our observation of optical emission accompanying 1s states (Ne^*) from higher energy states (Ne^{**}) through a dissociative recombination of Ne_2^+ with e^- , and also in the observation of collisional mixing between 1s states:



The addition of a small amount of SF_6 was effective in suppressing the effect due to thermal electrons. The obtained rate constants for Ne are given in Table 2 showing only two examples, due to the limited space, of among twelve compounds examined.

3.2 Energy transfer from Ar ($1P_1$, $3P_0$, $3P_1$, $3P_2$) to N_2 ($C\ 3\pi_u$, $v' = 0, 1, 2, 3$) has been also studied by measuring both the time-resolved optical absorption of each argon excited state (Ar^*) and optical emission of N_2 ($C\ 3\pi_u \rightarrow B\ 3\pi_g$). The effect of thermal electrons was also removed by the addition of a small amount of SF_6 . Energy transfer rate constants from Ar^* to N_2 and SF_6 were determined as in Table 3.

Table 2. $Ne^*(3P_J)$ de-excitation rate constants and cross sections

M	J	$k(10^{-10}cm^3s^{-1})$	$\sigma(\text{\AA}^2)$
N_2	2	0.65 ± 0.05	8.6
	0	0.67 ± 0.09	8.9
	1	0.81 ± 0.06	11
SF_6	2	2.3 ± 0.2	38
	0	3.1 ± 0.2	52
	1	4.2 ± 0.3	70

Table 1. Initial electron attachment rate constant

M	k_5
$(O_2 \cdot M) + e^- \xrightarrow{k_5} (O_2 \cdot M)^{-*}$	
$(10^{-11} cm^3 s^{-1})$	
C_2H_6	800
C_3H_8	200
n- C_4H_{10}	2000
C_2H_4	500

Table 3. Ar^* de-excitation rate constants

M	Ar^*	$k(10^{-11}cm^3s^{-1})$
N_2	$1P_1$	5.8 ± 0.6
	$3P_0$	2.4 ± 0.4
	$3P_1$	3.9 ± 0.5
	$3P_2$	2.9 ± 0.2
SF_6	$1P_1$	98.9 ± 6.0
	$3P_0$	34.7 ± 0.7
	$3P_1$	61.9 ± 1.6
	$3P_2$	33.0 ± 0.9

1) Present address: Japan Atomic Energy Research Institute, Tokaimura, Ibaraki 319-11.

2) Present address: Prog. Eng. Res. Lab., Hitachi, Totsuka-ku, Yokohama 244.

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