12.2 Studies of Some Elementary Processes Involving Electrons in the Gas Phase by Pulse-radiolysis Microwave-cavity Technique

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Abstract The pulse radiolysis-microwave cavity technique has been employed for detection of free electrons in the gas phase. Presented are results of the observation of electron disappearance by attachment to molecules,the electron thermalization (energy loss) processes in the presence of an electron-attaching compound, and the formation of electrons by Penning ionization.

INTRODUCTION

Radiation effects on gaseous media involve a number of elementary reactions associated with reactive intermediates such as electrons, positive ions, free radicals, and atoms or molecules in electronically excited states. It is important to investigate these elementary reactions in order to clarify their specific roles in the chemical consequences of the radiation effects. The pulse radiolysis method has long been used for such purpose. Most intermediates can be detected by measurements of optical absorption or emission, but electrons are hard to be monitored by ordinary means. In order to observe the time variation of the electron density the microwave conductivity method has been combined with the pulse radiolysis and have been successfully applied to studies of electron attachment reactions, electron thermalization, and the Penning ionization process in the gas phase (Shimamori, 1991). The present work presents some new results on these elementary processes, which are brought through further improvement of the experimental and analytical procedures associated with the microwave cavity method.

EXPERIMENTAL

The details of the method and the apparatus were described elsewhere (Shimamori, Tatsumi, Ogawa, and Sunagawa, 1992 a, b). The gas sample in a microwave cavity was irradiated by 3 ns X-ray pulse from Febetron 706, and the change in the microwave conductivity was detected. The output signal from detectors in circuit, which is proportional to the shift of the resonant frequency of the cavity was amplified and fed to a digital oscilloscope. In the electron attachment measurement, the heating microwaves were additionally applied to the cavity in order to vary the mean electron energy.

RESULTS AND DISCUSSION

(i) Electron attachment

A trace amount of sample compound is added to 70 Torr of Xe, and the lifetime is measured for the first-order decay of electrons due to an attachment reaction. The two-body attachment rate constant is determined from the lifetime so obtained. Varying the heating power we can determine the rate constant as a function of the mean electron energy. The results are shown in Fig.1 for CCl_4, $CFCl_3$, and $CHCl_3$. It has been established that the data of rate constants as a function of the mean electron energy can be converted to the cross sections as a function of the electron energy by "unfolding" the rate constants. The details of the unfolding procedure was described elsewhere (Shimamori, Sunagawa, Ogawa, and Tatsumi, 1994).

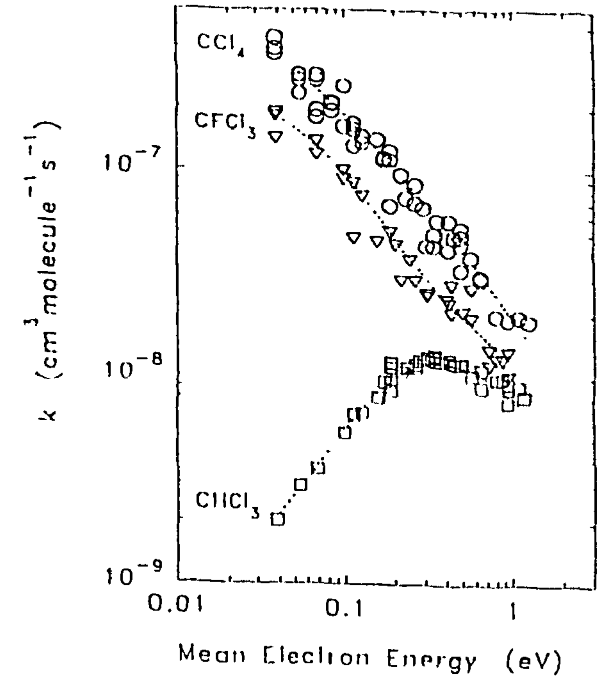

FIG. 1 Rate constants for electron attachment to CCl_4, $CFCl_3$, and $CHCl_3$ as a function of the mean electron energy.

Shown in Fig.2 are the cross sections for CCl_4, $CFCl_3$, and $CHCl_3$. Both CCl_4 and $CFCl_3$ show a peak at 0 eV, and the latter has another peak at 0.8eV. $CHCl_3$ exhibits a peak at 0.3eV. These compounds are known to undergo dissociative electron attachment, and the peaks at 0 eV correspond to the formation of Cl^- ion and that at 0.8eV in $CFCl_3$ to the production of Cl_2^-, which is in accord with the result of the electron-impact study (Illenberger, 1982). The peak at 0.3eV in $CHCl_3$ also corresponds to the Cl^- production. The cross sections

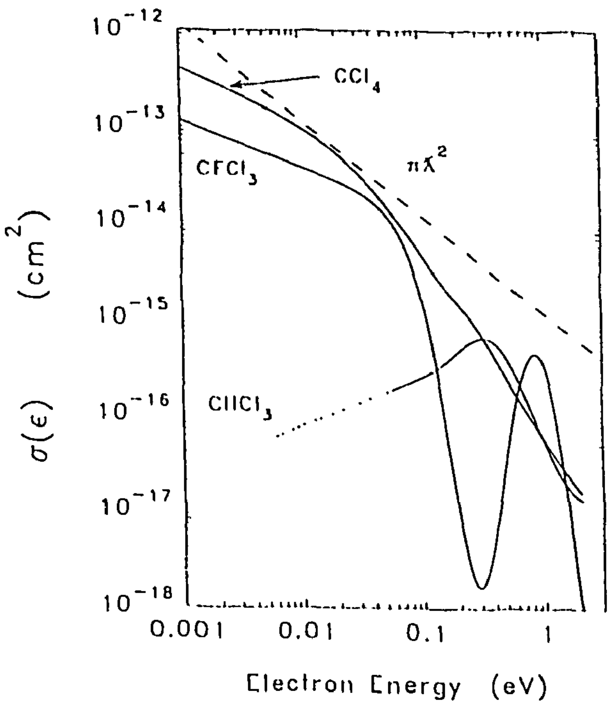

FIG.2 Cross sections for electron attachment to CCl_4, $CFCl_3$, and $CHCl_3$ (solid lines) and the s-wave maximum cross section (dashed line).

for CCl_4 are in good agreement with most previous data.

(ii) Electron thermalization in the presence of electron-attaching gas

Following pulsed X-ray irradiation of Ar atoms, high-energy electrons produced by ionization lose their energies by collisions with Ar atoms and are eventually thermalized. The electron thermalization during electron attachment to C_6F_6 in Ar buffer gas has been observed. Time profiles of the conductivity signals observed for pure Ar (70 Torr) and Ar (70 torr) containing C_6F_6 are shown in Fig.3(A). For pure Ar the signal increases slowly. This is ascribed to the presence of the Ramsauer minimum in the electron energy dependence of the momentum transfer cross section for Ar. When electrons are thermalized the signal becomes flat. The signals for mixtures with C_6F_6, on the other hand, show decreases by the electron attachment reaction. This reaction may be influenced by the electron thermalization process. The signals can be converted to the electron densities dependence on time, as shown in Fig.3(B). Generally the rate of disappearance of electron by attachment to a molecule is given by Eq.(1).

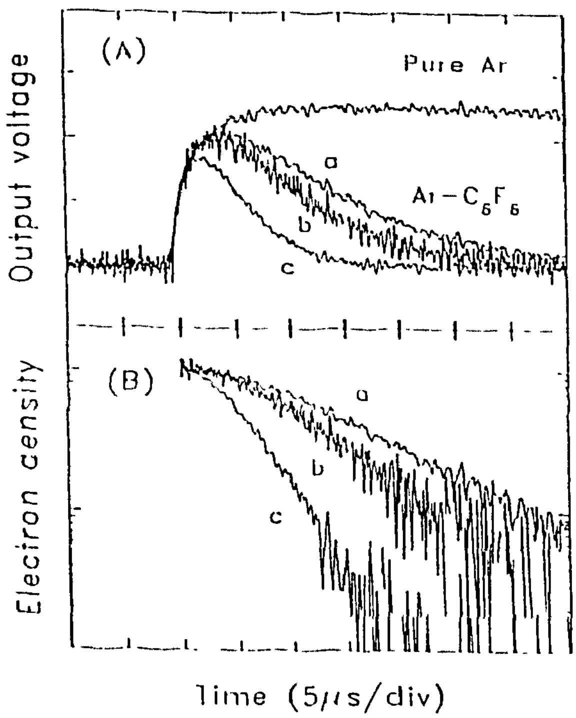

FIG.3 (A) Microwave conductivity signals for pure Ar (70 Torr) and those for mixtures containing C_6F_6 at different pressures, (a) 1.29 × 10^{-5} Torr, (b) 3.71 × 10^{-5} Torr, and (c) 9.08 × 10^{-5} Torr. (B) The electron density as a function of time

$$\frac{d\ \ln[e^-]}{dt} = -k(\langle\varepsilon\rangle)\,[C_6F_6] \quad (1)$$

where $[C_6F_6]$ is the concentration of C_6F_6, $k(<\varepsilon>)$ is rate constant as a function of mean electron energy, $<\varepsilon>$. If the results of electron densities dependence on time

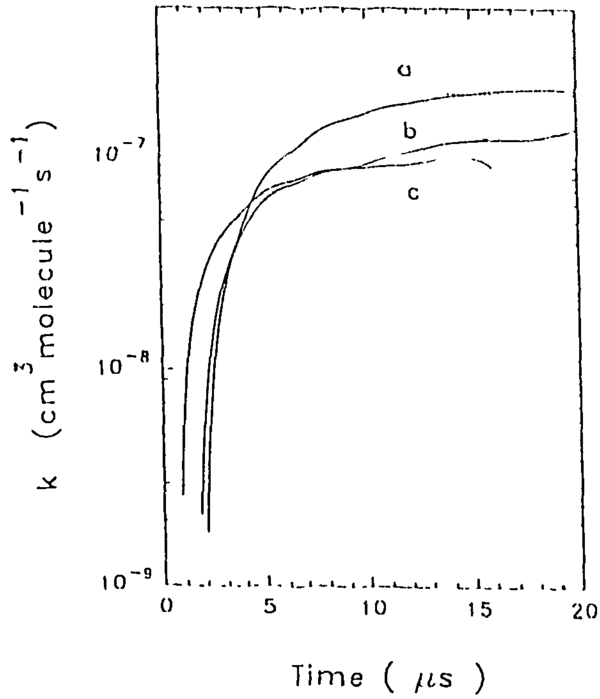

FIG.4 Rate constants for electron attachment to C_6F_6 as a function of time. The dotted line represents the value for thermal electrons

are the first-order decay, differential equation (1) can be solved to obtain the rate constants. Since, however, the decays are not of the first-order, the attachment rates must be dependent on time. Thus, we have differentiated the ln[e^-] vs t curve directly to obtain the derivative $-k(<\varepsilon>)[C_6F_6^-]$ at respective time. The rate constants as a function of time so obtained are shown in Fig.4. Since the rate constants of electron attachment to C_6F_6 as a function of mean electron energy is known (Shimamori, Sunagawa, Ogawa, and Tatsumi, 1994), the time-variation the rate constants can be converted to that of the mean electron energy, as shown in Fig.5. This shows that at a high concentration of C_6F_6 the electrons are captured before they are thermalized.

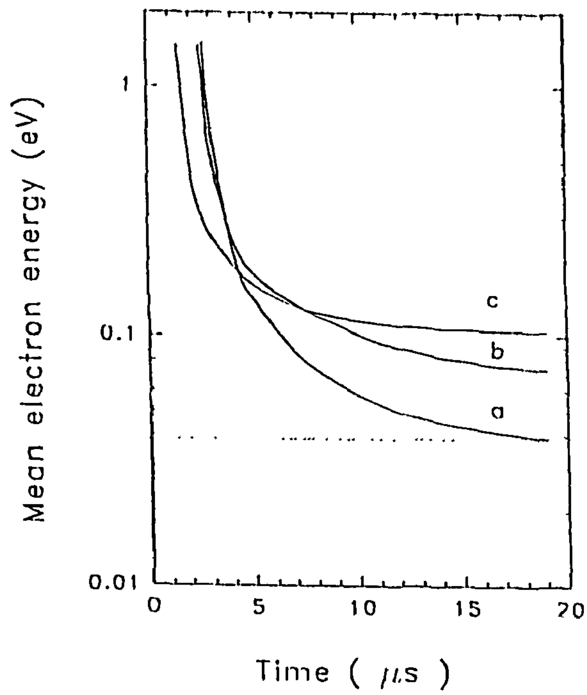

FIG.5 Mean electron energies vs time. The dotted line corresponds to the thermal energy.

Such behavior may be true of electron degradation process in the presence of other electron-attaching compounds.

(iii) Penning ionization

Penning ionization of neo-C_5H_{12} by metastable neon atom Ne^* has been investigated. The rate constant for this process has been obtained from an analysis of observed microwave conductivity signals representing the variation of electron density. The decay of Ne^* through de-excitation processes are as follows:

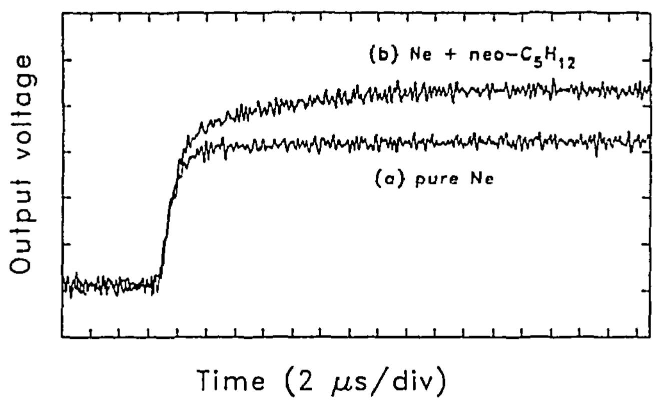

FIG.6 Microwave conductivity signals observed for (a) pure Ne 400 Torr and (b) 4.85×10^{-3} Torr neo-C_5H_{12} in 400 Torr Ne.

$$Ne^* + AB \rightarrow Ne + (AB)^+ + e^- \quad (2)$$

$$\rightarrow (Ne\,AB)^+ + e^- \quad (3)$$

$$\rightarrow Ne + A^+ + B + e^- \quad (4)$$

$$\rightarrow \quad Ne + A + B \qquad (5)$$

where Ne^* is a metastable neon atom, AB is neo-C_5H_{12}. The solution of differential equation representing the time-variation of electron density is.

$$[e^-] = [Ne^*]_0 \left(\frac{k}{k+k_5}\right)\{1-e^{-(k+k_5)[AB]t}\} \qquad (6)$$

where the brackets [ ] stand for the concentration, subscript 0 means the initial concentration immediately after pulse irradiation, and $k(=k_2+k_3+k_4)$ and k_5 are the rate constant for the ionization processes and the dissociation process, respectively. The microwave conductivity signals, which are proportional to electron density, as a function time is shown in Fig.6(a) for pure Ne (400 torr) and (b) for Ne (400 torr) containing neo-C_5H_{12}. The first-order growth rate is determined by analysis of the electron production process, which is obtained by subtracting the microwave conductivity signal (a) from that of (b). The slope of the plot of the growth rates against [neo-C_5H_{12}] gives $k+k_5=3.0 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. This value is rather lower than the known value (8.4×10^{-10}) for the Penning ionization of He metastable atoms by neopentane (Ueno, Yokoyama, Takao and Hatano, 1980). .

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