

ELECTRON TRANSPORT, ELECTRON ATTACHMENT AND ELECTRON-ION
RECOMBINATION IN NONPOLAR LIQUIDS AND SOLIDS AS STUDIED
BY A X-RAY PULSE CONDUCTIVITY METHOD

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Thermal electron behavior in nonpolar liquids and solids has been one of the most interesting subjects in radiation chemistry¹⁾, and has been studied using some physical methods such as infrared spectroscopy²⁾, microwave-power absorption technique³⁾ and electron conductivity method^{4,5)}. The electron conductivity method is more sensitive than the others for detecting electrons in nonpolar media and may be most suitable for the above purpose. This method has been carried out in many different ways depending on combination of methods of quasifree electron formation and its observation technique.

There are several ways to generate quasifree electron in condensed samples. First is by making use of α , β and γ -rays from radioactive isotopes as an external or internal radiation source⁶⁾; second, by photo-irradiation⁷⁾; third, by irradiation of charged particles accelerated by different types of accelerator²⁾ and fourth, by X-ray irradiation^{4,5,8)}.

We have demonstrated that Febetron 706 is a very attractive electron-pulse accelerator with respect to conductivity method^{1,5,9)}. The X-ray pulse obtained from electron pulse of Febetron 706 has very short pulse width of a few nsec with very high dose rate. The dose rate can be controlled easily by setting Pb plate in front of the accelerator window. The X-ray from Febetron can generate quasifree electron uniformly in condensed samples within a very short pulse-width. These features of Febetron can give us a new way to investigate electron-ion recombination as well as electron mobility and electron attachment.

The electron current in neopentane-n-hexane mixtures, produced by a few nsec X-ray pulse, in the presence of external electric field, has been observed in the nsec- μ sec range. The experimental apparatus is shown in Fig.1. The form of the time dependence of the electron current has been shown to vary with dose per pulse and is analysed accordingly. The electron mobilities, μ_e , are thereby determined in the mixtures. The rate constant for electron scavenging, k_s , by CCl_4 varies with μ_e ; k_s for $\text{C}_2\text{H}_5\text{Br}$ shows a maximum for a mixture with the mole fraction of n-hexane, $x_h=0.48$. The results for k_s obtained for the mixtures agree with those for various neat hydrocarbons reported by other research group⁸⁾.

We have applied the same method to the investigation of electron behavior in solid neopentane, which is known as a typical plastic crystal. A very peculiar effect of the addition of a small amount of n-butane on temperature dependence of electron mobility has been found in solid neopentane. In pure neopentane at its melting point a steep increase in the value of μ_e with decreasing temperature has been observed, whereas in the presence of a small amount of impurity n-butane (0.1-2%) the increase in the value of μ_e has been clearly suppressed. In the liquid phase, however, addition of such a small amount of n-butane cannot make any appreciable difference in μ_e . The impurity effect might be quite valuable for better understanding electron transport phenomena in nonpolar media.

The rate constant of electron-ion recombination, k_r , is proportional to μ_e over the wide range of μ_e in both liquid and solid neopentane and in liquid mixtures of neopentane and n-hexane as shown in Fig.2. This shows that the electron-ion recombination is diffusion-controlled in condensed nonpolar hydrocarbons.

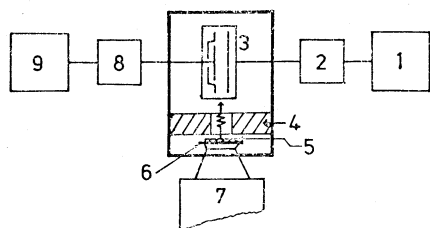


Fig.1. Schematic representation of the apparatus
 (1) high voltage power supply
 (2) 8kHz low pass filter
 (3) conductance cell
 (4) lead brick of 5cm thickness
 (5) lead plate of 0 to 8mm thickness
 (6) tungsten foil
 (7) Febetron 706 accelerator
 (8) 1MHz amplifier (if necessary)
 (9) 60MHz or 150MHz oscilloscope

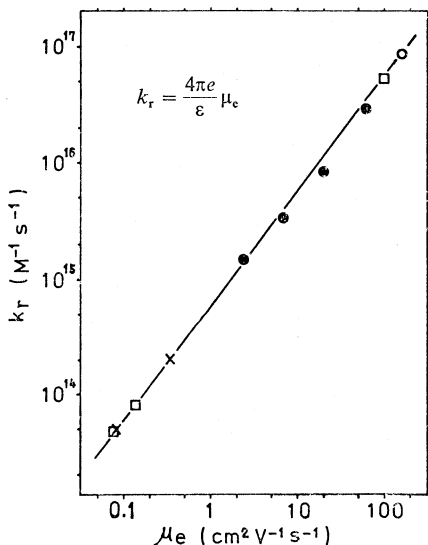


Fig.2. The rate constants of electron-ion recombination, k_r , as a function of the electron mobilities, μ_e , in the liquid neopentane-n-hexane mixtures (●) and in solid neopentane (○). The k_r in neat hydrocarbons and tetramethylsilane measured by other groups (×), (□) are listed in the same figure. The solid line is calculated from the reduced Debye equation.

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- 1) Int. Conf. on Electrons in Fluids, Banff, Canada (1976)
- 2) Baxendale, Bell and Wardman, *J. C. S. Faraday I*, **69**, 776 (1973)
- 3) Warman, de Haas and Hummel, *Chem. Phys. Lett.*, **22**, 480 (1973)
- 4) Schmidt and Allen, *J. Chem. Phys.*, **52**, 4788 (1970)
Dodelet and Freeman, *Can. J. Chem.*, **50**, 2667 (1972)
- 5) Wada, Shinsaka, Namba and Hatano, *Can. J. Chem.*, **55**, 2144 (1977)
- 6) Shibamura, Hitachi, Doke, Takahashi, Kubota and Miyajima, *Nucl. Instr. and Meth.*, **131**, 249 (1975)
- 7) Minday, Schmidt and Davis, *J. Chem. Phys.*, **50**, 1473 (1969)
- 8) Allen, Gangwer and Holroyd, *J. Phys. Chem.*, **79**, 25 (1975)
- 9) Namba, Wada, Shinsaka and Hatano, 19th Conf. Jpn. Soc. Rad. Chem., Kyoto (1976) and 20th Conf. Jpn. Soc. Rad. Chem., Sapporo (1977)