The Estimation of Free Ion Life Time by Pulse Electrical Conductivity Measurement

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Hitherto the electrical conductivity measurements of liquid under the ionizing radiation have been reported in many compounds[1-5] to investigate the mechanism of free ion generation, however less attention had been paid for their life times.[2a,4] Nevertheless, the determination of free ion life time seems to be required in relation to active species of radiation-induced ionic reaction, especially polymerization.[6]

The life time of free ion, τ, was proved to be given by following equation,

$$\tau = \frac{\varepsilon}{4\pi\sigma} = 2.8\times10^{-13}\frac{\varepsilon}{\pi\sigma} \qquad (1)$$

and to depend only on the steady state specific conductance, σ,[4] where ε represents a dielectric constant. The measured life times are known to be fairly long for radiation-induced intermediates at room temperatures,[2a,4] for instance in *n*-hexane, 120 msec at the dose rate of 10^{14} eVcm^{-3}sec^{-1} or 2.6 R sec^{-1},[5] though such a long life time may be understood in terms of extremely diluted steady state concentration of free ions (in above instance, roughly 10^{-11} M). In order to confirm the previously reported free ion life times,an estimation was made by a completely different method from the steady state conductance method using Eq. (1).

When reaction intermediates generated by photo-illumination disappear through bimolecular reaction, it is widely known that its steady state life time is estimated by the method of "intermittent illumination" or "rotating sector."[7] On the other hand, in our systems under investigation, a bimolecular decay of charged species through a neutralization between positive and negative ions has been established by the square root dependence of specific

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2) a) G. R. Freeman, *ibid.*, **39**, 988 (1963); b) G. R. Freeman and J. M. Fayadh, *ibid.*, **43**, 86 (1965).

3) R. W. Ahrens, B. Suryanarayana and J. E. Willard, *J. Phys. Chem.*, **68**, 2947 (1964).

4) K. Hayashi, Y. Yamazawa, T. Takagaki, F. Williams, K. Hayashi and S. Okamura, *Trans. Faraday Soc.*, **63**, 1489 (1967).

5) K. Hayashi T. Takagaki, K. Takada, K. Hayashi and S. Okamura, *Ann. Repts. Japanese Assoc. Rad. Res. on Polymers*, **8**, 79 (1966–67).

6) F. Williams, K. Hayashi, K. Ueno, K. Hayashi and S. Okamura, *Trans. Faraday Soc.*, **63**, 1501 (1967).

7) H. W. Melville and G. M. Burnett, " Technique of Organic Chemistry," Vol. VIII: Investigation of Rates and Mechanisms of Reactions, ed. by S. L. Friess and A. Weissberger, Interscience Publishers, New York, N. Y. (1953), p. 113.

conductance on dose rate[1a,1b,2a,4,5] and decay behavior of cell current after an interruption of irradiation.[1a,1b,4] So as to apply the "intermittent illumination" method into the life time determination of free ion, Van de Graaf electron accerelator was modified for a repeated pulse irradiation and measurements of time-averaged ion currents were carried out.

Experimental

Distilled cyclohexane (Merk, spectrograde) was degassed in a vacuum line and dried through repeated contacts with sodium-potassium alloy. Then it was vacuum-distilled into a glass cell with stainless steel parallel plate electrodes of 30 mm diameter situated in a distance of 5 or 9 mm and sealed off under 10^{-5} mmHg. The details of electrical conductivity measurement were described elsewhere.[4] For the direct reading of average iron current under pulse irradiation, digital electrometer was connected to the output of vibrating reed electrometer. Measurements were carried out at room temperatures (15±1°C).

Van de Graaf electron accerelator (High Voltage Corp.) was modified for the pulse irradiation applying pulsed negative voltage to a plate which is located just outside of filament. Only four kinds of pulses were available. Their repetition times are 10, 31, 120 and 250 msec. Synchroscopic traces of each pulse pattern were shown in Fig. 1. Except for superimposed a.c. signals on each top of pulses, which seems to give no influence on ion current on average, they all are consisted of rectangular wave. Irradiation ratio, a ratio of an irradiation interval of one pulse to the pulse repetition time, β, was maintained in all pulses to be 0.42, which is determined by the limitation of pulser.

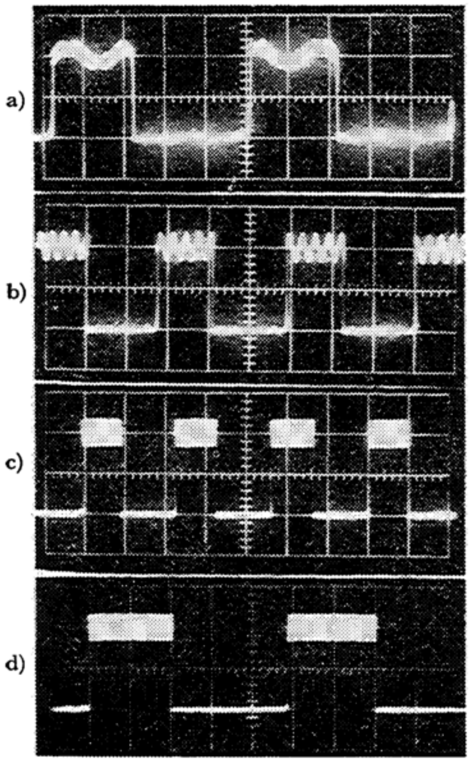

Fig. 1. Synchroscopic traces of Van de Graaf electron pulses ($\beta=0.42$).
Repetition times are; a) 10 msec (2 msec/div.), b) 31 msec (10 msec/div.), c) 120 msec (50 msec/div.), d) 250 msec (50 msec/div.).

Results

Cell current ratios, $i/\sqrt{\beta}i_s$, are shown in Fig. 2 for four kinds of pulses keeping the dose rate of each series invariable. Here, i and i_s represent an average cell current under pulse irradiation and that under the steady irradiation operated to have the same peak beam current as the corresponding pulses, respectively. It is valid that the cell current ratios gradually decrease at longer pulse repetition time and the three curves corresponding to the different dose rates are similar in their shape; at lower dose rate, the curve moves to the direction of slower pulse. These results qualitatively agree with the expected consequence from the ordinary kinetics of intermittent illumination,[7] indicating a bimolecular disappearence of charge carriers.

However, at the pulses of 120 and 250 msec, all the experimental curves show negative deviations from the kinetically calculated curve for $\beta=0.42$, given with a broken line in Fig. 2, and consequently considerable amounts of errors on the free ion life times are introduced since life times are determined through appropriate overlapping of experimental curves onto the kinetically calculated one. Such a negative deviation was always observed irrespective to the electrode distance, applied voltage or the effect of electrodes irradiation.

With no regard for such deviations, the free ion life times are roughly estimated at several dose rates and at various field strengths as shown in Fig. 3. Vertical lines above and below the each point show a

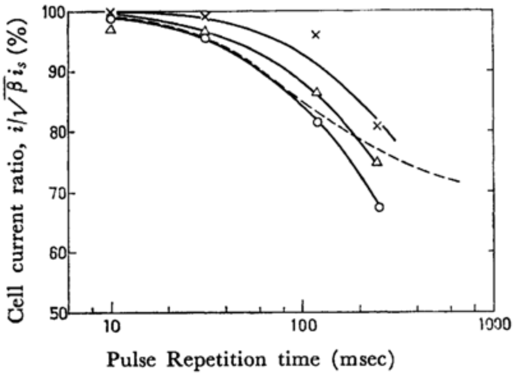

Fig. 2. Pulse repetition time *vs.* cell current ratio in cyclohexane at several dose rates; ○ 3.7×10^{14}, △ 1.5×10^{14}, × 3.7×10^{13}, eV cm^{-3} sec^{-1}. Applied voltage; 400 V. The distance between electrodes, 0.89±0.05 cm. Broken line denotes the theoretical curve for $\beta=0.42$ drawn to fit lowest experimental curve.

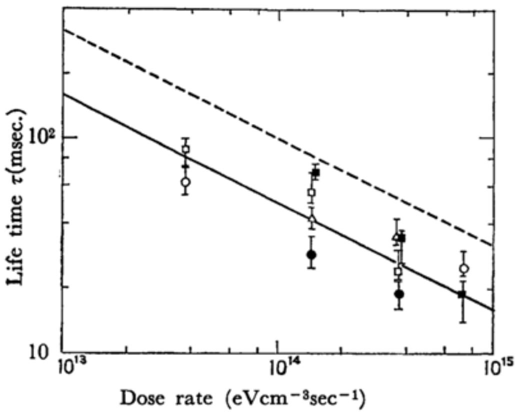

Fig. 3. Dose rate *vs.* estimated life time in cyclohexane at various field strength; ○; 800; ●; 440, □; 400, ■; 165, △; 40 Vcm^{-1}. Broken line denotes the life time calculated by steady state conductivity.

probable limit of error which may be introduced by the overlapping procedure of curves. Though the estimated life times scatter so much at a fixed dose rate, no systematic variation due to the field strength can be recognized. Thus estimated life time, as shown with solid line in Fig. 3 agreed with the calculated one by steady state conductance, dotted line, within a factor of two. The difference between the life times obtained through two independent methods may be attributed to the incompletion of both methods as the life time determination method. Even in steady state conductance measurements, the results from three independent experiments do not show so good agreements each other.[1a,2b,5]

Discussion

As reasons for the deviation of experimental curves from the kinetically calculated one, at first a deformity of pulse shape, an inhomogenity of ionic concentration to the direction perpendicular to the electric field attributed to an insufficient penetration of radiation and a competitive unimolecular decay of ions due to discharge at the electrodes are considered. However, corrections to the ordinary kinetics of intermittent illumination[7] indicate that such effects cannot account for the negative deviation at long repetition time pulses. If there were to be a distribution in the free ion life time, the observed deviation would be positive. Another possibility is an inhomogenity of ionic concentration to the direction of the electric field, which arises from a translational motion of ions along the field.

In the dark period between the pulses, there appear space-charge regions where positive or negative ions are exclusively present in neighborhood of anode and cathode respectively, since ions move toward the oppositely charged electrode all the time when a diffusional motion of charges is disregarded. Namely, the influence of the space-charge region on an average cell current should be considered from the both points of view *i.e.* the decrease of the space-averaged ionic concentration and the decrease of field strength in bulk region. A modified kinetics of intermittent illumination taking account of the space-charge regions under the assumption of the uniform field strength along the electrode distance[8] indicates that the deviation from the ordinary kinetics in cell current ratio-repetition time curve is negative and is proportional to the dark period or repetition time. Moreover, in the dark time, the observed cell current is expected to become smaller because of the decreasing field strength of bulk regions with time. In consequence, the deviation from the ordinary kinetics is negative and proportional to several powers of the pulse repetition time, which is consistent with our results; negative deviation at longer repetition time pulses, especially at the longest repetition time pulse.

At all events, pulse irradiation effect on cell current ratio was observed at the repetition time between 10 and 250 msec, the same range as the free ion life times estimated by steady state conductivity measurement. It confirms the validity of the free ion life time estimation method by steady state conductivity measurement.

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