Ionization of Liquids by Radiation: Measurement by a Clearing Field

Abstract. *A method has been developed for determining the yield of free ions formed by irradiation of a liquid with high-energy x-rays. Contrary to expectation, branched-chain paraffins produce many more free ions than straight-chain paraffins do, and the ether 1,4-dioxane produces only a third as many free ions as its hydrocarbon analog, cyclohexane.*

The yield of ions in an irradiated liquid, which escape initial recombination with no applied field, is important; first, for understanding the mechanisms of radiation-chemical reactions in liquids, and second, because it throws light on the poorly understood subject of the behavior of free electrons in liquids. Measurements of this yield (*1–3*) have involved determination of both conductivity and ionic mobilities in an irradiated liquid. A more direct method would be to apply a clearing field after terminating the irradiation—that is, a field great enough to pull all the ions to the electrodes so fast that negligible volume recombination occurs. We have successfully used this method to determine ion yields in a number of liquids at 23°C, by means of the circuit sketched in the insert to Fig. 1.

An auxiliary capacitor (200 picofarads) is connected between the parallel-plate measuring cell and ground. At the end of the x-ray pulse, high voltage (sufficient to give a field of 3 kv/cm in the cell) is applied at *A*, through a high-voltage triode (Eimac 25T). Since the auxiliary capacitance is 300 to 1000 times greater than that of the cell, nearly all the voltage drop occurs across the cell. After the drift of ions to the cell electrodes is complete, the high voltage is turned off. Point *A* then returns to ground potential, and, if there had been no ions in the cell, point *B* would return to ground potential also. Any charge collected from the cell during the period of high voltage will result in an exactly corresponding potential remaining at *B*. The switch *S* is then closed (within a few seconds of shutting off the high voltage), and the charge collected is read on the electrometer (Keithley Instruments, Type 610B). The purpose of the 5-megohm shunt is to build up the voltage on the plate of the triode and to discharge the circuit at the end of the high-voltage pulse. The rise time of the cell circuit (< 5 × 10^{-6} second) depends mainly on the 5000-ohm effective internal resistance of the triode.

Difficulties occurred because of contact potentials when commercial relays were used for switch *S*. Construction of Pt–Pt point-to-plate contact solved that problem.

Liquids were purified by conventional means, and then distilled in a vacuum over Na-K alloy and electrolyzed.

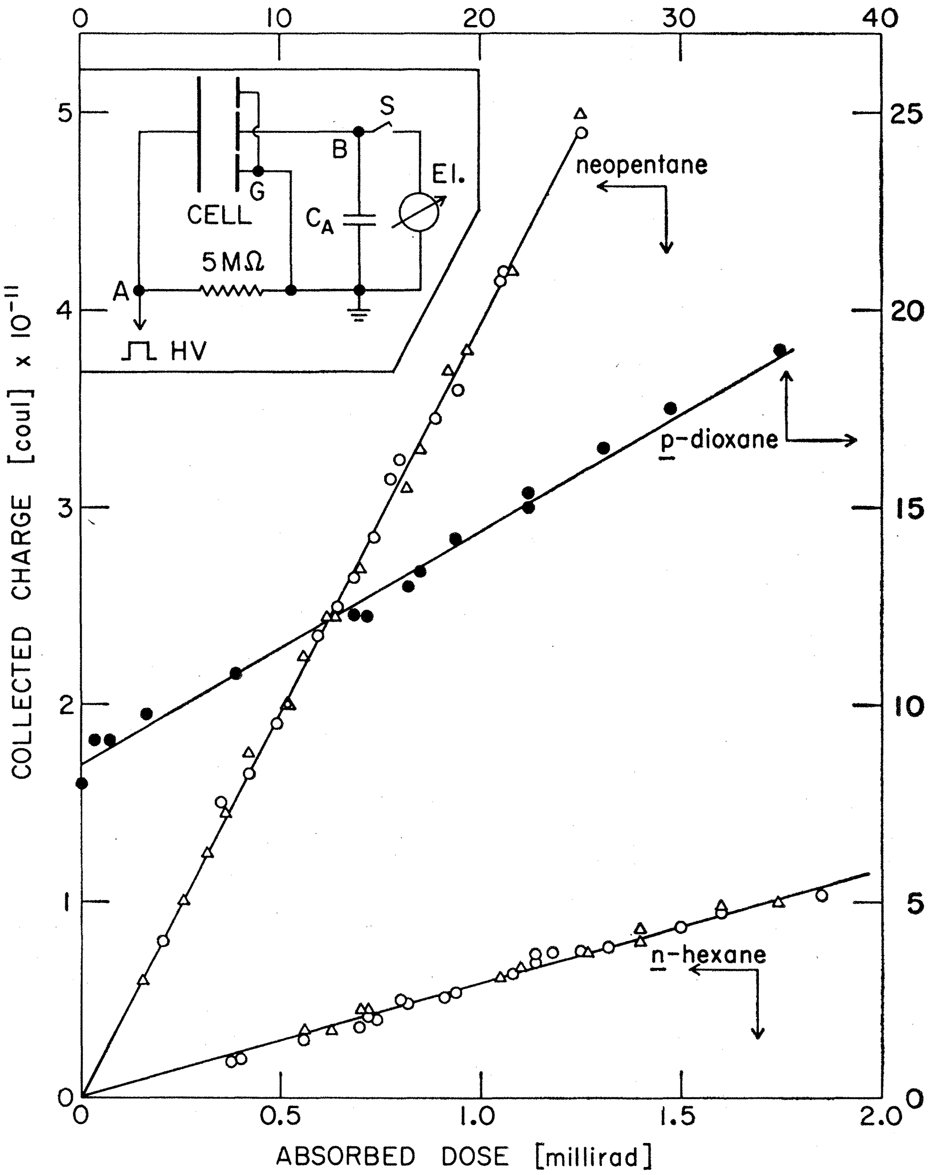

Fig. 1. Charge collected from an effective volume of 0.74 cm^3 as a function of radiation dose for *n*-hexane and neopentane (lower and left-hand scales) and 1,4-dioxane (upper and right-hand scales) at 23°C. Insert: Schematic circuit diagram. High-voltage polarity negative, ○; positive, △ or ●.

X-ray pulses were obtained from a Van de Graaff generator, with 1.6-Mev electrons on a gold target. Several parallel-plate measuring cells with different interelectrode spacings were used, all being of glass coated with tin oxide and having aluminum electrodes.

Typical data are given in Fig. 1, which shows the charge collected after an 0.5-msec pulse of 1.6-Mev x-rays, as a function of the radiation dose in millirads. The cell used to obtain these data had a collecting electrode 1.5 cm in diameter and a plate separation of 0.42 cm. At the doses used, the initial half-life of the ions varied from about 3 to 30 seconds. The collection time was only of the order of 0.1 second at

Table 1. Ion yields in various liquids at 23°C.

Liquid	G values (ion pairs per 100 ev)
1,4-Dioxane	0.047; 0.044; 0.042
n-Hexane	0.11_4; 0.12_9; 0.11_7; 0.11_7
3-Methylpentane	0.14
n-Pentane	0.14_3; 0.14_0; 0.15_3
Cyclohexane	0.14_0; 0.15_5; 0.14_7; 0.15_5; 0.16_2; 0.14_0; 0.13_4
2-Methylbutane	0.16_7
2,3-Dimethylbutane	0.20
2,2-Dimethylbutane (neohexane)	0.29_1; 0.29_5; 0.32_3; 0.30_4; 0.29_9; 0.29_9
2,2,4-Trimethylpentane	0.29_7; 0.33_3; 0.32_5; 0.33_1; 0.34_5
2,2-Dimethylpropane (neopentane)	0.74_0; 0.89_4; 0.85_2; 0.86_9; 0.80_5

a field of 3 kv/cm, so that ion recombination during the radiation pulse and ion collection was negligible, as shown by the linearity of the charge-dose curves.

The curves have an intercept which depends on the background conductivity κ; the intercept is negligible for hydrocarbons (κ about 10^{-17} ohm^{-1} cm^{-1}) but appreciable for 1,4-dioxane (about 10^{-14} ohm^{-1} cm^{-1}). The yield sought is proportional to the slope of the curve. The charge collected was independent of strength and time of application of the clearing field above 2 kv/cm and 0.5 second.

When the circuit was tried with an air ionization chamber of known volume, a value of 33 ± 1 was obtained for W, the number of electron volts to produce an ion pair in air, in good agreement with standard determinations (*4*). Ion yields from various liquids are shown in Table 1.

The precision of the method appears to be better than ± 10 percent. The value of G (ions of either sign formed per 100-ev input) for *n*-hexane is in fairly good agreement with the best previous values (*1, 3*), namely, 0.10 ± 0.01. The low value for 1,4-dioxane confirms determinations thought to be less accurate (*1, 2*). The remarkably high values for branched-chain hydrocarbons agree, at least qualitatively, with results obtained by Capellos and Allen (*5*) and with a value for 2,2,4-trimethylpentane obtained by extrapolation from the high-field conductivity data reported by Ladu and Pelicioni (*6*).

The probability of an ion pair escaping initial recombination is (*7*) $\exp(-e^2/\epsilon kTr)$ where e is electronic charge; k, Boltzmann's constant; T, absolute temperature; ϵ, the dielectric constant of the medium; and r, the distance between the two ions. This expression should hold for ionization produced by x-ray, with r the interionic distance at which the pair attains thermal energy; or, for ions formed in a group of several pairs, the distance between the last two ions remaining after all others have recombined. It has been assumed (*1, 2*) that r should depend mainly on the electron density of the medium, and that the ratio of observed G values for different liquids should be roughly predictable on this basis. If this were the case, all the G values in Table 1 should be the same within about ± 20 percent. The actual variation is by a factor of 20.

We conclude that the mean slowing-down distance for electrons r depends strongly on properties of the medium, the nature of which is far from obvious. Mozumder and Magee (*8*) relate values of r, and hence of G, to the cross sections for energy loss by the free electron, first to intramolecular and then to intermolecular vibrational modes in the liquid.

WERNER F. SCHMIDT
A. O. ALLEN

Chemistry Department,
Brookhaven National Laboratory,
Upton, New York 11973

References and Notes

1. A. Hummel, A. O. Allen, F. H. Watson, Jr., *J. Chem. Phys.* **44**, 3431 (1966).
2. G. K. Freeman and J. M. Fayadh, *ibid.* **43**, 86 (1965).
3. W. F. Schmidt, *Z. Naturforsch.* **23b**, 126 (1968).
4. *Intl. Committee Radiol: Units, Rep. 10b*, NBS Handbook 85 (U.S. Dept. of Commerce, Washington, D.C., 1964).
5. C. Capellos and A. O. Allen, *Science*, in this issue.
6. M. Ladu and M. Pellicioni, *Nucl. Instr. Methods* **39**, 339 (1966).
7. L. Onsager, *Phys. Rev.* **54**, 554 (1938).
8. A. Mozumder and J. L. Magee, *J. Chem. Phys* **47**, 939 (1967).
9. Research performed under the auspices of AEC.

30 January 1968; revised 12 March 1968

Ionization of Liquids by Radiation: Measurement by Charge Scavenging

Abstract. *Pulse radiolysis of dilute solutions of triphenylcarbinol in saturated hydrocarbon gives spectra of the triphenylmethyl free radical,* $(C_6H_5)_3C\cdot$, *and cation,* $(C_6H_5)_3C^+$. *The yield of the ion is independent of the carbinol concentration, and is thought to measure the yield of free ions generated in the solvent. The relative yields of ions thus found in cyclohexane and 2,2,4-trimethylpentane agree with measurements made by the clearing-field method.*

On pulse irradiation of dilute solutions of aromatic hydrocarbons in cyclohexane, aromatic ions are seen as transients (*1*), an indication that charge transfer occurs from the solvent to the aromatic molecule. Quantitative evaluation of the process has been difficult in that the ion spectra are often overlaid with absorptions coming from triplet states (*2*) and free radicals, and the ions themselves may be both positive and negative.

We now report on irradiation of di-

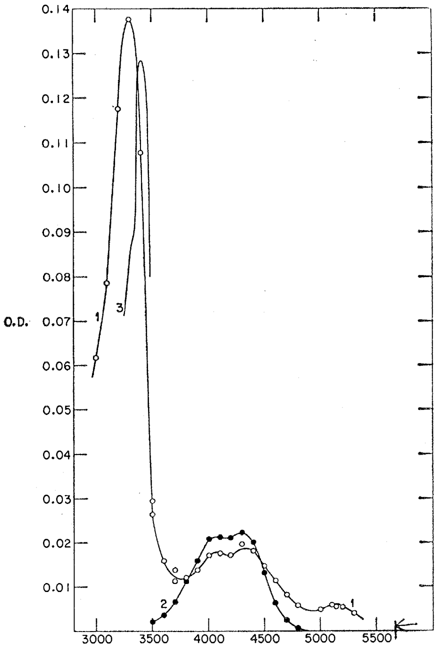

Fig. 1. Curve 1, spectrum obtained on pulse radiolysis of $10^{-3}M$ $(C_6H_5)_3COH$ in cyclohexane. Curve 2, spectrum of $(C_6H_5)_3COH$ dissolved in concentrated sulfuric acid. Curve 3, spectrum of neutral triphenylmethyl radical in toluene according to Chu and Weissman (*3*); they also show a weak many-peaked absorption near 5000 Å. Curves 2 and 3 are arbitrarily normalized.