

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 Pellicioni (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 dis-

tance 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.

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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-

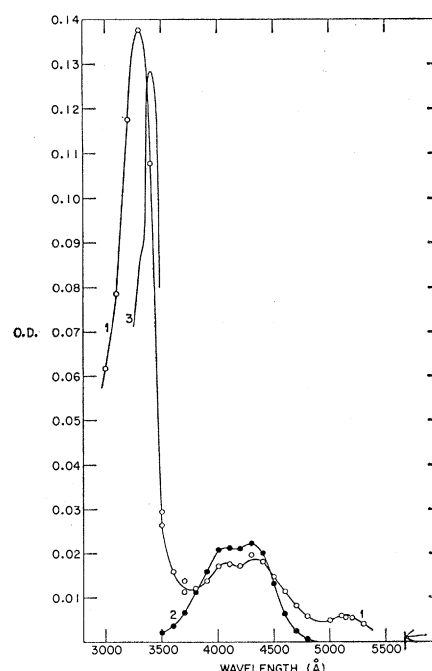


Fig. 1. Curve 1, spectrum obtained on pulse radiolysis of $10^{-3}M$ $(C_6H_5)_3COH$ in cyclohexane. Curve 2, spectrum of $(C_6H_5)_3COH$ dissolved in concentrated sulfuric acid. Curve 3, spectrum of neutral triphenylmethyl radical in toluene according to Chu and Weissman (3); they also show a weak many-peaked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

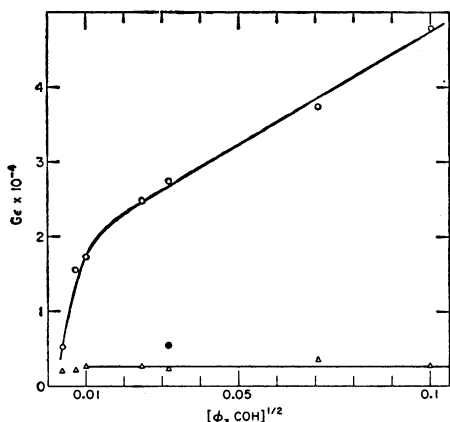


Fig. 2. Yields of triphenylmethyl radical (○) and ion (Δ) (multiplied by the respective peak extinction coefficients) in cyclohexane and of the ion in 2,2,4-trimethylpentane (●), versus the square root of the molarity of triphenylcarbinol. Each point is an average of four determinations.

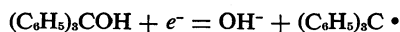
lute solutions in saturated hydrocarbons of triphenylcarbinol, $(C_6H_5)_3COH$. This alcohol forms triphenylmethyl-carbonium ion $(C_6H_5)_3C^+$ by proton transfer from acidic solvents and is related to the unusually stable triphenylmethyl free radical $(C_6H_5)_3C\cdot$.

The spectrum of the transient absorption produced by an 8- μ sec pulse of 2 Mev electrons (dose, 0.5×10^{17} ev/ml) in a $10^{-3}M$ solution of triphenylcarbinol in cyclohexane, and the spectra of the ion $(C_6H_5)_3C^+$ (a solution of the carbinol in H_2SO_4) and of the radical in toluene (3) show (Fig. 1) that the radiation-produced absorption is the sum of absorptions due to the radical and the ion; no other components are of any importance.

From the maximum optical densities at the peaks of the radical and ion absorptions, and the energy input, we calculated the product $G\epsilon$ (molecules formed per 100 ev input $\times$ molar optical extinction coefficient) for the ion and radical separately (Fig. 2). Small corrections were made for decay during the pulse and for the absorption of light by the radical at the ion-peak wavelength. Both species show clean second-order decay; with a typical dose (1300 rad), the first half-life of the ion was 3.0×10^{-5} second. The radical was somewhat longer-lived.

The linear increase in radical yield with the square root of the carbinol concentration above $10^{-4}M$ carbinol suggests that these radicals are produced in the initial recombination of ions

formed in pairs close together, if charge transfer from the solvent ion to the carbinol has occurred prior to neutralization. Approximate linear dependence on the square root of solute concentration is expected for this mechanism (4). The radical yield seen at lower concentrations arises from other processes, perhaps in part from electron capture by the carbinol:



The most striking feature is that the yield of the carbonium ion is independent of concentration down to $10^{-4}M$, and is almost as great at $10^{-5}M$. The ion presumably arises by proton transfer to the carbinol from the free solvent ions which escape initial recombination. This reaction is almost complete in a few microseconds at $10^{-5}M$ carbinol, and therefore occurs at every or nearly every encounter between the reacting molecules. It is reasonable to assume that practically every ion of the solvent is converted to $(C_6H_5)_3C^+$.

The ratio of $G\epsilon$ in 2,2,4-trimethylpentane and in cyclohexane should give the ratio of the ion yields, since the optical properties of the ion are expected to be the same in all nonpolar solvents. The ratio from Fig. 2 is 2.1, whereas the clearing-field method gave for the pure solvents an ion yield ratio of 2.2, identical within experimental error (5). This confirms one of the unexpected results obtained by the clearing-field method.

With $G\epsilon$ in cyclohexane about 2760, if we take G from the clearing-field measurements as about 0.147, we find ϵ about 18800. In H_2SO_4 solution, $\epsilon = 38000$. The change by a factor of 2 is not surprising, since one solvent is extremely polar and acidic, while the other is entirely nonpolar.

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Proton Radiography

Abstract. Energetic protons from an accelerator may be used to produce radiographs showing unusually high contrast but relatively poor spatial resolution.

Energetic protons from an accelerator may be used to produce radiographs showing unusually high contrast but relatively poor spatial resolution. Figure 1 is a proton radiograph of a stack of aluminum absorbers, 18 g/cm² in thickness, with a piece of aluminum foil 0.035 g/cm² thick inserted at a depth of 9 g/cm². Although the foil represents an increment of only 0.2 percent in the total thickness of aluminum, its outlines are quite clear. The fuzziness of the edges, caused by multiple small-angle scattering of protons in the aluminum, is estimated to extend 0.15 cm from each side of the true edge.

In order to produce a wide, uniform proton beam to illuminate the object to be radiographed, I have used a scatterer of lead, 7.4 g/cm² thick, in the external beam of the Harvard cyclotron (1). The beam striking the lead scatterer has a diameter of approximately 2 cm. Protons are reduced in energy from 160 to 137 Mev by the lead, but 3 m downstream, at the point where the radiographs are made, the proton flux is nearly uniform to a radius of 10 cm from the beam line. The measured percentage of this proton flux penetrating to various depths in aluminum is shown

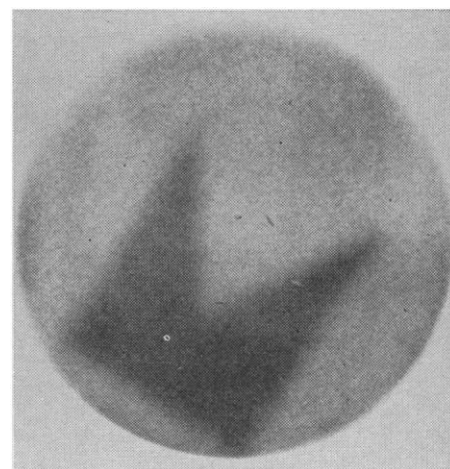


Fig. 1. Proton radiograph of aluminum absorber 7 cm in diameter and 18 g/cm² thick, with an additional thickness of 0.035 g/cm² aluminum foil, cut in the shape of a pennant, inserted at a depth of 9 g/cm². The addition of 0.2 percent to the total thickness produces a substantially darker area on the film.