

TABLE III
VALUES OF $z_i(1 - H^{1/2})_{is}r_s$

z_i	0	0.25	0.50	0.75	1.00
K ⁺	0.40695	0.37672	0.34772	0.31981	0.29289
Li ⁺	.29289	.26603	.24010	.21504	.19072
Cl ⁻	.29289	.29370	.29391	.29362	.29289

mixture as compared with that in binary solution at the same J . From the resulting ionic quantities, the calculated $\Delta\lambda$ referred to earlier may be obtained at once.

For $J = 0.01$, $z_i = 0.5$, the calculated $\Delta\lambda_{K^+}$, $\Delta\lambda_{Li^+}$ and $\Delta\lambda_{Cl^-}$ are thus -0.315 , $+0.160$ and -0.006 unit, respectively, which may be compared with the observed values of Table II. Not much stress can be placed on the difference in sign for chloride, although the discrepancy is slightly greater than the apparent precision of the chloride data. For the cations, however, the differences between the calculated and observed $\Delta\lambda_i$ are greater than the most pessimistic estimate of the experimental error. What is unexpected is that the observed $\Delta\lambda_i$ are numerically greater than the calculated rather than less. The assumptions underlying the theory of the mixture effect are essentially those inherent in the familiar Limiting

Law for binary electrolytes, and for the alkali chlorides at these concentrations, the Limiting Law over—rather than underestimates—the effect of ionic interaction. It is of course possible that the assumption implicit here that the higher order terms are the same in the mixture as in binary solution is seriously in error, but at the moment no theory of a mixture effect for the higher order terms is available. However, these terms for all three ions in binary solution at $J = 0.01$ are of the order of 0.4 unit—roughly one-half the numerical value of the relaxation term of eq. 5 for Li⁺ and one quarter that for K⁺; hence, to account in this way for the discrepancy would require rather drastic changes percentually in their values.

One obvious conclusion is that further study, both experimental and theoretical, of the mixture effect is in order; a second is that when testing any theory dealing with ionic conductances, equivalent conductances *per se* can give little if any explicit information which is pertinent. Finally, we wish to express our thanks to the National Research Council of Canada for a grant in aid of this research and to Canadian Industries Limited for the award to G. S. K. of a fellowship.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY AND BROOKHAVEN NATIONAL LABORATORY]

A Comparison of the Decomposition of Hexane and Cyclohexane by Different Types of Radiation

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Hexane and cyclohexane have been irradiated with radiations having energy loss parameters from 0.02 to 5 e.v./Å. and the liquid products have been examined by gas chromatographic and infrared methods. In this preliminary study no change in over-all decomposition is observed which can be attributed directly to a variation in the linear energy transfer of the radiation.

At the present time there is a paucity of comparative data on the decomposition produced in liquid organic materials by different types of radiation. This situation is in marked contrast to the reasonably detailed understanding now available of the dependence of radiation effects on linear energy transfer (LET) in aqueous systems. The present studies represent a preliminary investigation into the effect of variation with LET of the over-all decomposition produced in two of the more simple hydrocarbons which have been the subject of previous work with fast electrons.^{3,4} Except for minor differences which appear to be attributable to changes in intensity, very similar yields are observed for the various types of radiations employed here.

Early experiments by Sworski and Burton⁵ on or-

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(3) H. A. Dewhurst, *J. Chem. Phys.*, **24**, 1234 (1956); *J. Phys. Chem.*, **61**, 1466 (1957); **62**, 15 (1958).

(4) H. A. Dewhurst and E. H. Windlow, *J. Chem. Phys.*, **26**, 969 (1957).

(5) T. J. Sworski and M. Burton, *THIS JOURNAL*, **73**, 3790 (1951).

matic systems which compared the relative yields of the formation of hydrogen and methane for reactor radiations and for γ -rays have indicated that the ratio of these products increased with increase of LET. McDonell and Gordon⁶ have compared the γ -ray radiolysis of methanol with previous studies of the decomposition produced by 28 mev. helium ions and have observed a difference in the yield for formation of ethylene glycol. More recent studies of the yield of hydrogen produced in the decomposition of cyclohexane by fast electrons and by cyclotron radiations have shown little difference between the effect of light and heavy particles (less than 10%).⁷ Investigations currently in progress on the determination of radical production by the iodine scavenging technique have shown a somewhat larger effect.⁸ All of these studies emphasize that meaningful interpretation of the effect of LET on radiation chemical reactions in hydrocarbon systems will result only from studies of the quantitative details of relatively small

(6) W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).

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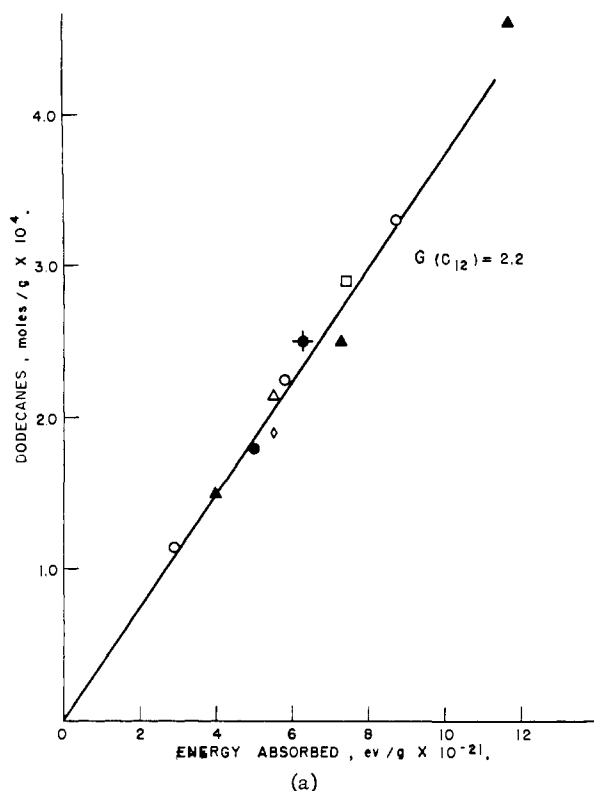


Fig. 1.—Formation of: (a) total isomeric dodecanes; (b) intermediate hydrocarbons (C_8-C_{11}); (c) unsaturated product in the radiolysis of *n*-hexane. Radiations used were: \bullet , cobalt-60 γ -rays; \circ , 800 kvp electrons from a resonant transformer; \bullet , 2 mev. electrons from a Van de Graaff; \square , 18 mev. cyclotron deuterons, \blacktriangle and \diamond , 35 mev. cyclotron helium ions (in the latter case the sample was stirred during irradiation); \triangle , 12 mev. cyclotron helium ions.

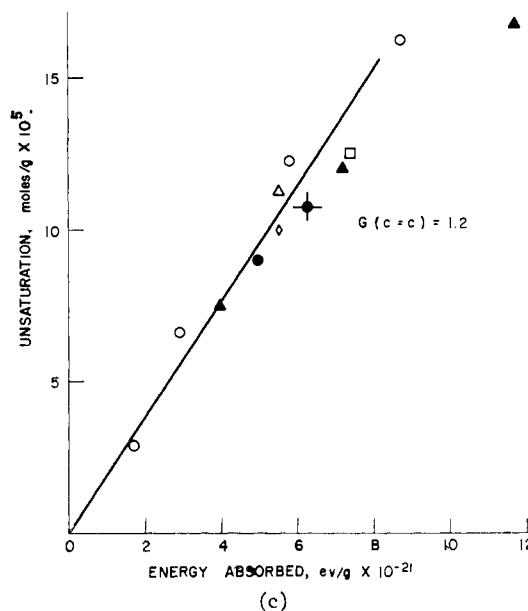
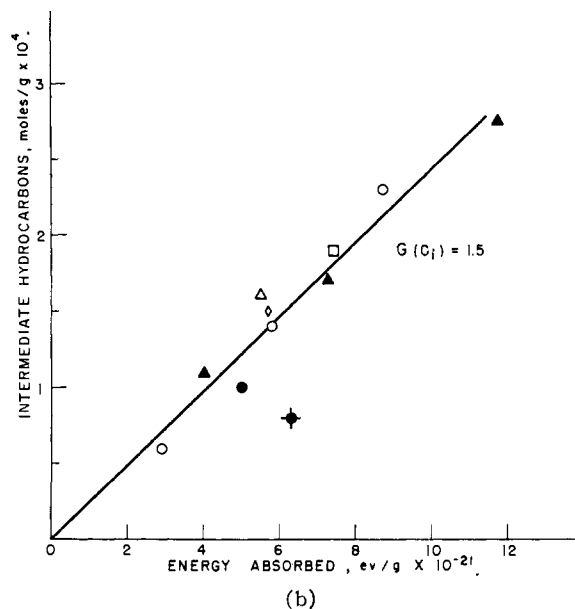
differences between the different radiations. More detailed studies are obviously very much in order.

Experimental

Materials.—Phillips Research Grade hydrocarbons were used for all experiments except those with the resonant transformer where purified pure-grade material was used. Samples were sealed in thin windowed glass irradiation cells after being degassed by repetitive freezing and pumping.

Irradiations. (a) Cobalt-60 γ -Rays.—Irradiations were carried out in Brookhaven cylindrical sources at an absorbed dose rate of 3.55×10^{15} e.v./g./sec. Samples were irradiated for approximately 20 days with the total absorbed energy corresponding to 6×10^{21} e.v./g. The absolute value of the absorbed energy was obtained by comparison with the Fricke Dosimeter ($G(Fe^{+++}) + 15.5$) assuming that absorption is proportional to the electron density of the material.

(b) Fast Electrons.—Electron beams from an 800 kvp. General Electric resonant transformer and from a 2 mev. Van de Graaff accelerator were used directly. In the former case the irradiation technique was as previously described.³ The entire sample was irradiated uniformly at a dose rate of 1.35×10^{19} e.v./g./sec. In the case of Van de Graaff electrons, energy absorption was determined by the charge input method.⁹ In these and the following measurements with cyclotron beams the inside surface of the irradiation cell was covered with a thin coating of "dag" which served to collect the current. Electron currents were of the order of 5 microamperes and energy dissipation rates in the irradiation zone were of the order of 10^{20} e.v./g./sec. The total volume irradiated was approximately 25 cc. Because of the rela-



tively high rate of energy dissipation (10 watts), appreciable heating on the sample occurred.

(c) Cyclotron Deuterons and Helium Ions.—Both 19 mev. deuteron and 35 mev. helium ion beams were used and the total absorbed energy was determined by the charge input method after appropriate allowances were made for current displacement.¹⁰ The energy of the heavy particles was determined by absorption techniques and in one experiment absorbers were used to reduce the energy of the helium beam to 12 mev. Positive ion currents were of the order of 0.1 microampere and energy dissipation rates (in the irradiated solutions) were in this case also of the order of 10^{20} e.v./g./sec.

Sample Analysis.—Irradiated samples were examined by gas chromatographic and infrared techniques as described in previous studies.³ All analyses were carried out under comparable conditions.

Results and Discussions

The gas chromatograms for the products produced in hexane by the different types of radiation were qualitatively identical to those already de-

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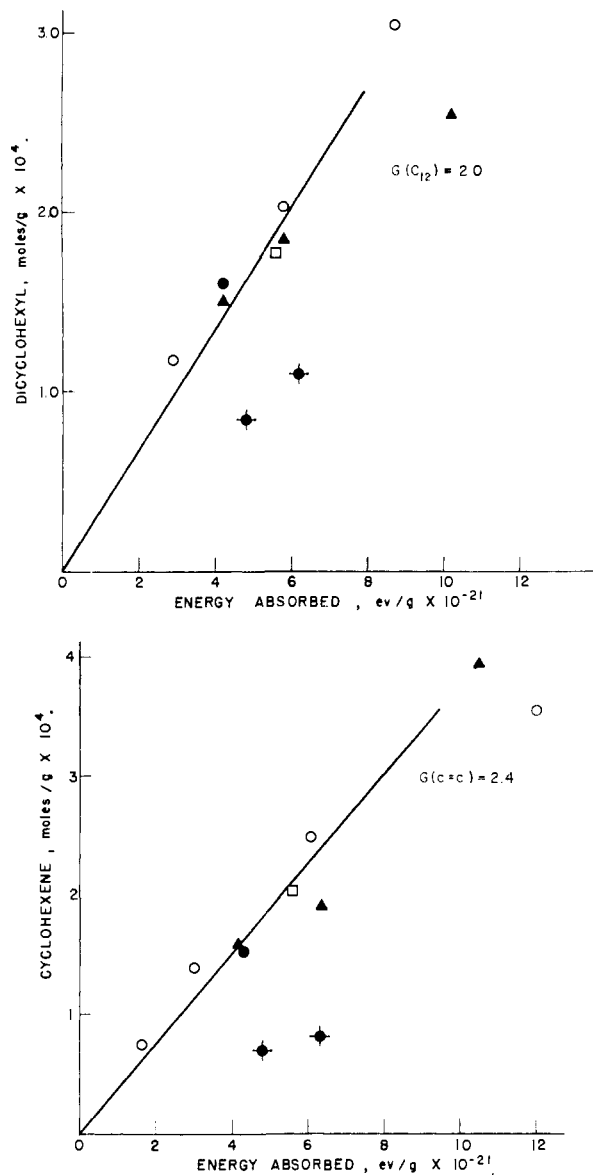


Fig. 2.—Formation of (a) dicyclohexyl and (b) cyclohexene in the radiolysis of cyclohexane. Radiations used were: ●, cobalt-60 γ -rays; ○, 800 kVp electrons; ●, 2 MeV electrons; □, 18 MeV cyclotron deuterons; ▲, 35 MeV cyclotron helium ions.

scribed.³ The formation of dodecanes and of intermediate molecular weight products as a function of absorbed energy is shown in Fig. 1. The distribution of individual components among the isomeric dodecanes was found to be the same for each of the radiations studied. The total yield of intermediate molecular weight material was also the same for all radiations except cobalt-60 γ -rays where a somewhat lower yield was observed. The previous suggestion that this difference represents a dose rate dependence⁴ appears to be further confirmed by the present studies. In Fig. 1C the yield of *trans*-vinylene unsaturation determined by infrared measurements shows no significant difference among the various types of radiation.

Gas chromatographic analysis of the products produced in the radiolysis of cyclohexane by heavy particle radiations also shows a qualitative similarity to the previous work with fast electrons. In this case dicyclohexyl and cyclohexene are the major liquid products, the formation of each being given in Fig. 2 as a function of the absorbed energy. In the case of the γ -irradiation studies, each of these compounds is produced with a significantly lower yield. Comparison of the γ -ray and fast electron results shows that this decrease is an effect of intensity and not of LET. Recently Nixon and Thorpe¹¹ have observed the formation of unsaturated polymeric material from γ -irradiated cyclohexane. Such polymeric material was not found in the 800 kVp. electron irradiation and may well reflect an important effect of dose rate. The particle beam experiments all give the same yields for each of these predominant products.

It is seen in general that for the fast-electron, deuteron and helium ion radiolysis of liquid *n*-hexane and cyclohexane at dose rates of the order of 10²⁰ e.v./g./sec. very similar product yields are observed. This contrasts with the very marked differences observed in water radiolysis particularly where the molecular products become extremely important for irradiations carried out with heavily ionizing radiations. Apparently, as one might suspect, the reactions competing with track recombination processes are very much more complex in organic systems.

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