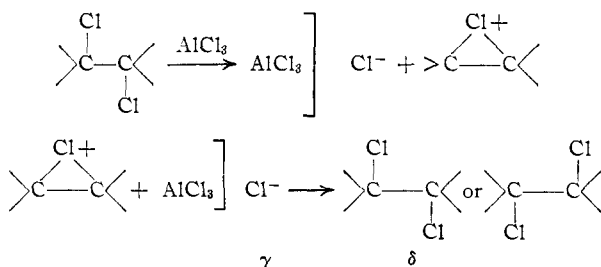


Although no pure δ -HCC was recovered, the evidence for the presence of this isomer is fairly conclusive. The absence of all other HCC isomers has not been established.

It is impossible to give a simple mechanism for the formation of the δ -HCC at this time; however, two possibilities can be discussed. First, it is possible that δ -HCC is formed from the α -HCC previously produced from the γ -HCC by the "flipping over" of chlorine 4. It is also possible that the delta isomer is formed from the gamma directly. When one of the 2,6-biaxial chlorines is removed, chlorine 1 is in the proper *trans* position to form a bridge between carbons 1 and either 2 or 6.¹³ A chlorine ion may then be picked up in either of two positions as illustrated



Thus, either gamma or delta or mixtures of the two may result. It is, of course, possible that both mechanisms suggested occur.

In spite of the tendency for isomerization to occur in the chlorine exchange reaction between lindane and AlCl_3 sufficient quantities of labeled gamma isomer were obtained for use in tracer studies. The reaction is being studied further in an effort to ar-

(13) S. Winstein, *Colloq. intern. Montpellier*, **18**, 55 (1951).

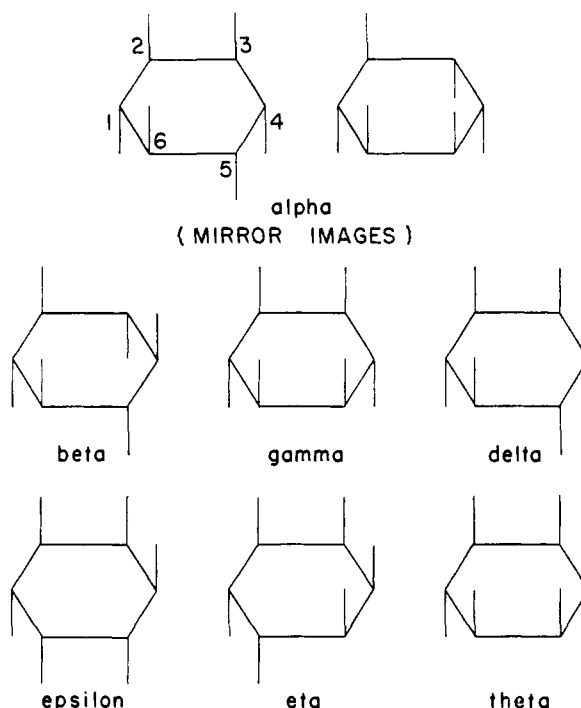


Fig. 1.—Linear models of 1,2,3,4,5,6-hexachlorocyclohexane.

rive at conditions where isomerization can be kept to a minimum. Reagents other than AlCl_3 are also being considered as exchange media.

Acknowledgment.—The authors wish to thank Dr. D. S. Noyce, University of California, who helped with nomenclature and clarified some of the ideas on mechanism presented.

SAVANNAH, GEORGIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

On the Use of Iodine as a Radical Detector in Hydrocarbon Radiolysis¹

BY RICHARD W. FESSENDEN^{2a} AND ROBERT H. SCHULER^{2b}

RECEIVED AUGUST 23, 1956

The effects of radiation on solutions of iodine in cyclohexane have been studied over the iodine concentration range of $5 \times 10^{-6} M$ to $5 \times 10^{-2} M$. The yield for the formation of alkyl iodide in deaerated solution is independent of iodine concentration from $10^{-5} M$ to $5 \times 10^{-3} M$ but is somewhat higher at higher concentrations. In the lower concentration region the radiation yield, $G(\text{RI})$, is found for both Co^{60} γ radiation and 2 Mev. Van de Graaff electrons to be 5.6 molecules of alkyl iodide produced per 100 e.v. absorbed by the system. Aerated solutions of iodine in cyclohexane have lower yields than the corresponding deaerated solutions. For aerated solutions $G(\text{RI})$ is proportional to the iodine concentration at low concentrations and the kinetics indicate a simple competition between iodine and dissolved oxygen. The yield of uptake of radio-iodine to form stable alkyl iodides has been found to be equal to the yield of iodine disappearance, showing that the production of hydrogen iodide and hydrolyzable iodides is negligible.

The kinetics of the radiation-induced reaction between iodine and various hydrocarbons have previously been investigated³⁻⁵ and it has been

(1) Research performed under the auspices of the U. S. Atomic Energy Commission. Presented at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 13, 1956.

(2) (a) Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts. (b) Department of Radiation Research, Mellon Institute, Pittsburgh, Pa.

(3) R. H. Schuler and W. H. Hamill, *THIS JOURNAL*, **74**, 6171 (1952).

(4) P. F. Forsyth, E. N. Weber and R. H. Schuler, *J. Chem. Phys.*, **22**, 68 (1954).

(5) E. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research*, **3**, 68 (1955).

shown that the radiation yield is independent of temperature from 25 to 75° and of iodine concentration in the range $0.5 \times 10^{-3} M$ to $5 \times 10^{-3} M$. These observed kinetics indicate that the formation of organic iodides can be taken as a measure of radical production in the substrate. Further work over a wider range of concentration is however clearly desirable and is the subject of the present investigation.

In the above-mentioned studies the extent of reaction of iodine was determined by spectrophotometric measurement of the decrease in iodine con-

centration. The initial stages of the reaction can be better followed by measurement of the production of organic iodides. This is conveniently done here by using radio-iodine and by determining the uptake of activity by the organic material. By adjusting the specific activity of the iodine to an appropriate level, approximately the same sensitivity can be maintained in the analysis over a wide range of concentrations.

Experimental

Sample Preparation.—All hydrocarbons used were Phillips Research Grade except for certain of the experiments on air saturated cyclohexane where triply recrystallized material was used. Radio-iodine in the form of molecular iodine was obtained by exchange of inactive iodine with an evaporated deposit of the carrier-free activity.⁶ Solutions of known composition were then made up from this material: at high concentrations from weighed iodine samples and at low concentrations by spectrophotometric determination of the iodine concentration or by dilution of a known sample. Where desired the sample was degassed by successively freezing, pumping and sealing. It was shown that this procedure did not result in loss of iodine. For a number of solutions, samples were carried through the entire processing including the degassing operation and the blank reaction was shown to be negligibly small. Pick-up of radio-iodine in the organic fraction was found to be 0.04–0.08% at concentrations above 10^{-3} M, 0.5% at 10^{-4} M, and 0.8% at 5×10^{-5} M.

Irradiation.— γ -Irradiations were carried out inside the cylindrical Co⁶⁰ source described by Schwarz and Allen⁷ in 14 mm. i.d. Pyrex irradiation tubes 150 mm. long. The observed rates of reaction after correction for decay of the source have been compared to the observed rate of 8.75 μ moles/l./min. (as of June 1, 1955) for the oxidation of ferrous ion in the Fricke dosimeter. The rate of energy dissipation in the cyclohexane, 2.64×10^{16} e.v./cc./min., and absolute radiation yields (*G* values) have been calculated on the basis $G(\text{Fe}^{+++}) = 15.5$ assuming that energy is absorbed proportional to the electron density of the material irradiated.

Fast electron irradiations were carried out using the Brookhaven 2 Mev. Van de Graaff generator. Absolute yields were directly determined by the power input method and corrections applied as in the calibration of the Fricke dosimeter.⁸ The electron beam current was collected from the all glass irradiation cell which had an external coating of graphite to ensure that there would be no loss of current to ground through electrical paths external to the current integrator. The solutions were stirred during the irradiations by the use of a glass enclosed magnetic stirrer similar to that employed in the previous work on aqueous systems.³

Reaction Measurement.—The extent of reaction was determined from the initial concentration of iodine and the fraction of iodine converted to organic iodide. This latter quantity was measured by extracting the molecular iodine from the sample and determining the ratio of the organic activity to the total activity. At the lower concentrations inactive carrier was added to the sample after irradiation to reduce the specific activity of the iodine and facilitate extraction. In the most dilute solutions an appreciable fraction of the iodine was found adsorbed on the walls of the irradiation vessel. This was taken into account in the concentration and yield calculations. Activity measurements were made in an annular jacketed Geiger counter. Where necessary, corrections were applied for dead time loss in the counter. In general at least 10,000 counts were accumulated in each of the measurements.

In the fast electron experiments, the irradiation cell assembly included as a side arm a spectrophotometer cell in which the concentration of iodine could be followed during intermittent irradiation by measurement of the optical density of the solutions. Radio-iodine was used and after the irradiation series was completed the samples were extracted and measured as in the γ -ray experiments.

(6) I¹³¹ obtained through U. S. Atomic Energy Commission, Oak Ridge, Tenn.

(7) H. A. Schwarz and A. O. Allen, *Nucleonics*, **12**, #2, 58 (1954).

(8) J. Saldick and A. O. Allen, *J. Chem. Phys.*, **22**, 438 (1954); R. H. Schuler and A. O. Allen, *ibid.*, **24**, 56 (1956).

Results and Discussion

The data for the γ -ray induced reaction between iodine and cyclohexane in degassed solutions are given in Table I. It is seen that the extent of reaction is proportional to the dose and that the yield is independent of iodine concentration below 5×10^{-3} M. At higher concentrations, the reaction between iodine and cyclohexane has a somewhat increased yield. For the very concentrated de-aerated solutions prolonged irradiation produced a second phase which was deep brown in color. It was shown that this hydrocarbon insoluble material contained little non-extractable iodine ($\sim 1\%$ of the organic yield). This second phase was not found in the corresponding concentrated aerated solutions although the yield in those experiments was only slightly less than in de-aerated solutions.

TABLE I

REACTION BETWEEN IODINE AND CYCLOHEXANE INDUCED BY γ -RADIATION^a

I ₂ concn., M $\times 10^4$	Irradiation period, ^b min.	Organic activity, %	Relative yield, moles/l./ min. $\times 10^6$	G(RI)
473	3910	13.0	1.57	7.30
431	966	3.78	1.68	7.70
431	5036	18.5	1.59	7.30
239	229	1.42	1.48	6.80
239	724	4.35	1.43	6.54
98	80	0.97	1.19	5.44
98	724	8.73	1.18	5.40
55.1	40	0.95	1.32	6.04
55.1	200	4.75	1.31	6.00
9.3	41	5.61	1.27	5.82
9.3	200	25.4	1.18	5.40
7.42	124	20.3	1.21	5.62
4.65	7.0	1.89	1.25	5.74
4.65	50	14.30	1.33	6.12
0.92	30	40.1	1.22	5.60
.30	2.0	8.60	1.28	5.88
.30	5.0	20.2	1.20	5.52
.093	1.0	13.8	1.28	5.90
.093	3.0	38.2	1.18	5.42
.031	1.0	35.0	1.08	4.96

^a Degassed samples. ^b Energy is observed in cyclohexane at the rate of 2.64×10^{16} e.v./cc./min.

In Table II the data from two experiments with Van de Graaff electrons are given. During these irradiations the iodine concentration was followed spectrophotometrically and found, as in the previous X-ray experiments,^{4,5} to decrease by an amount proportional to the dose. The yields of reaction as determined from iodine disappearance and from uptake of radio-iodine are the same. This demonstrates that there is negligible forma-

TABLE II

REACTION BETWEEN IODINE AND CYCLOHEXANE INDUCED BY 2 MEV. ELECTRONS^a

I ₂ concn., M $\times 10^4$	Irradiation dose, ^b e.v. $\times 10^{-19}$	Fraction iodine reacting measured by		G(RI)
		Iodine ^c disap- pearance	Activity uptake	
5.91	9.15	0.283	0.287	5.62
5.91	15.65	.480	.486	5.60

^a Degassed samples. ^b Delivered to 25.1-ml. sample. ^c Measured optically at 520 m μ .

tion of substances such as hydrogen iodide or hydrolyzable iodides which would result in iodine disappearance but not in the formation of organic soluble activity.

In Fig. 1 the radiation yields for the various determinations are given along with the previous measurements with 120 pkv X-rays. The agreement between the present results and the previous work is about as good as can be expected in view of the indirect dosimetry involved in the X-ray experiments. The agreement between the Co^{60} γ -ray and Van de Graaff electron results shows that the reaction is intensity independent over a very wide range of intensities.

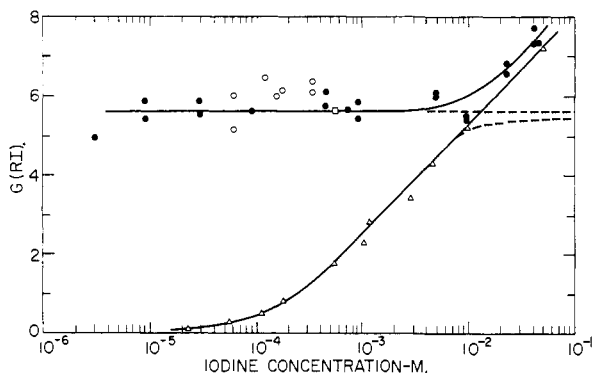


Fig. 1.—Concentration dependence of radiation-induced reaction between iodine and cyclohexane: degassed solutions ●, irradiated with Co^{60} γ -radiation; ○, with 120 PKV X-radiation; □, with 2 Mev. Van de Graaff electrons; aerated solutions Δ, irradiated with Co^{60} γ -radiation; sigmoid curve corresponds to $G(\text{RI})/[5.6 - G(\text{RI})] = 0.83 \times 10^3 [\text{I}_2]$.

The data for air-saturated cyclohexane are also given in Fig. 1. The extent of reaction in these studies was approximately 10% in all cases so that the iodine concentration was essentially constant during the irradiation. Except at high iodine concentration the yield of iodine uptake is considerably lower than for the corresponding degassed solutions. The quantity $G(\text{RI})/[5.6 - G(\text{RI})]$ is proportional to the iodine concentration as is shown in Fig. 2. This indicates that a simple competition is taking place between iodine and the dissolved oxygen for the radicals produced by the radiation. It appears that radicals which are removed by reaction with oxygen are not capable of reacting further with iodine. The iodine concentration at which the yield is one-half of the aerated value occurs at $1.2 \times 10^{-3} M$ in cyclohexane whereas in *n*-heptane the corresponding concentration was observed to be $0.3 \times 10^{-3} M$.⁴ Since for air-saturated samples containing small amounts of dissolved iodine the yield of reaction is proportional to the iodine concentration, the fractional reaction is independent of concentration and is proportional only to the dose given the system.

The independence of yield upon a wide variation in concentration for concentrations below $5 \times 10^{-3} M$ appears to justify the use of iodine as a scavenger for free radical determination at these concentrations. However, work currently in progress on the radiation-induced reaction between

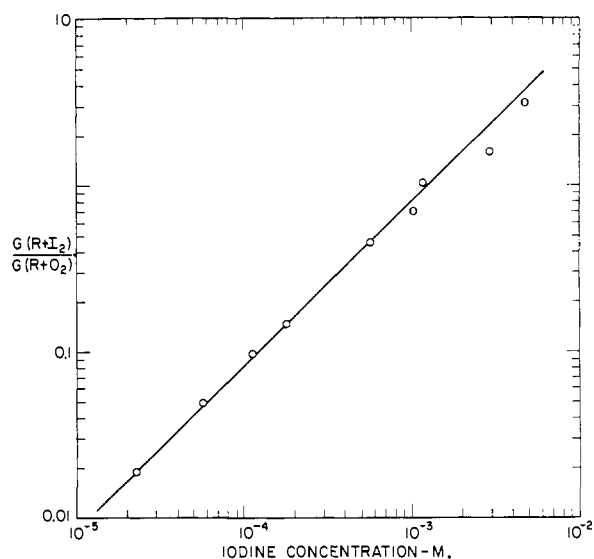
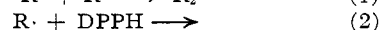
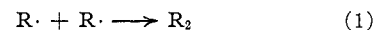


Fig. 2.—Competition between iodine and dissolved oxygen. Solid curve represents unit slope corresponding to $G(\text{RI})/[5.6 - G(\text{RI})] = 0.83 \times 10^3 [\text{I}_2]$.

iodine and benzene indicates that the situation is considerably more complicated in aromatic systems so that caution is in order in the use of these scavenger techniques.

At concentrations above $5 \times 10^{-3} M$ the yield for formation of stable organic iodides increases. Although it has been shown previously⁹ that small amounts of iodine ($<10^{-3} M$) do not affect the hydrogen yield, at these higher concentrations the yield of this gas is now known to decrease.¹⁰ It appears that the radiation chemical processes which are responsible for the ultimate chemical reactions are affected by the presence of high concentrations of scavenger in the substrate. The independence of hydrogen yield upon iodine concentration at the lower concentrations indicates, as previously discussed,⁴ that the presence of iodine at these low concentrations does not complicate the physical processes resulting from the radiolysis.

In discussion of the use of diphenylpicrylhydrazyl free radical (DPPH) as a radical scavenger in the radiolysis of hydrocarbons, Chapiro has proposed that the drop in yield observed at low concentrations ($<10^{-3} M$) results from a competition between reaction of the radicals with each other and with the scavenger.¹¹



It is seen from the present work with scavenger iodine that the yield is constant to concentrations below $10^{-5} M$ and therefore reaction 1 cannot be effective in the iodine-containing solutions. As most of the studies of Chapiro and co-workers were with air-saturated systems^{12,13} the competition between oxygen and the scavenger is probably a

(9) C. C. Schubert and R. H. Schuler, *J. Chem Phys.*, **20**, 518 (1952).

(10) To be published.

(11) A. Chapiro, *J. chim. phys.*, **51**, 165 (1954).

(12) A. Prevost-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, *Disc. Faraday Soc.*, **12**, 98 (1952).

(13) A. Chapiro, J. W. Boag, M. Ebert and L. H. Gray, *J. chim. phys.*, **50**, 488 (1953).

complicating factor in the observations. Since the yield falls off only at DPPH concentrations of the order of $10^{-4} M$ in air-saturated solutions it would appear that DPPH is a more efficient scavenger than iodine and that its presence in solution in any

appreciable concentration would effectively eliminate reaction 1. It would seem, therefore, that the drop in yield observed at low DPPH concentrations is not due to radical-radical combination. UPTON, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

Isotopic Fractionation in the System Iodine Cyanide/Cyanide by a Combined Equilibration-Precipitation Process¹

BY F. E. JENKINS AND G. M. HARRIS

RECEIVED AUGUST 17, 1956

The equilibrium constant for the reaction $\text{CNI} + \text{C}^{14}\text{N}^- \rightleftharpoons \text{C}^{14}\text{NI} + \text{CN}^-$ as predicted by statistical thermodynamics is $K = 1.05$ at 30° . The experimental values obtained by examination of the activity of precipitated silver cyanide are always larger than the predicted value, and vary with the composition of the dioxane-water solvent used. The results can be interpreted quantitatively in terms of a combination of isotope effects in the equilibration and precipitation reactions.

A recent study has shown that the exchange reaction $\text{CNI} + \text{C}^{14}\text{N}^- \rightleftharpoons \text{C}^{14}\text{NI} + \text{CN}^-$ takes place very rapidly in a variety of media.² The predicted thermodynamic equilibrium constant for the reaction, K , is 1.05 at 30° ,³ and the present study began as an attempt to confirm this value experimentally. It was planned to determine K by comparison of the specific activities of cyanide ion before and after exchange equilibration, A_0 and A_e , respectively. Then

$$K_{\text{exp}} = a/b (A_0 - A_e)/A_e \quad (1)$$

where a and b are the molar concentrations of cyanide and iodine cyanide, respectively. This relation assumes that no isotopic fractionation results from the reactant separation process. Much larger K_{exp} values than expected were obtained, and can be explained quantitatively in terms of a combination of isotope effects in the equilibration and precipitation reactions involved.

Experimental

The reagents were prepared and purified as described elsewhere.² Iodine cyanide and carbon-14-labeled sodium cyanide were equilibrated in solutions containing various proportions of water and dioxane. Inorganic cyanide was completely precipitated from suitable aliquots with silver nitrate dissolved in the same water/dioxane solvent; the silver cyanide was transferred by alcohol slurry technique to a metal planchet and dried. The badly rimmed samples so prepared were dissolved in pyridine added to the planchet; when the pyridine was evaporated slowly under an infrared lamp, smoothly uniform microcrystalline deposits remained which gave activity counts with a gross reproducibility of better than 0.7% by standard end-window G/M tube assay technique.⁴

Results and Discussion

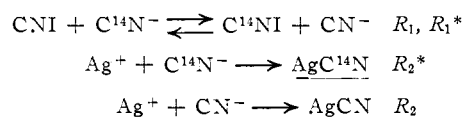
The values of K_{exp} obtained for a number of solvent compositions and a/b ratios are summarized in Table I. The reactions involved are

(1) A preliminary report was made of this work in THIS JOURNAL, **77**, 4439 (1955).

(2) F. E. Jenkins and G. M. Harris, to be published.

(3) D. R. Stranks and G. M. Harris, THIS JOURNAL, **75**, 2015 (1953).

(4) It was found impossible to achieve this high a degree of reproducibility by means of the zinc cyanide precipitation procedure used by Adamson and co-workers (*ibid.*, **73**, 4786 (1951); **74**, 1590 (1952)).



where the R 's are the various reaction rates. The differential equations describing the system are

$$\frac{d(\text{C}^{14}\text{NI})}{dt} = R_1 \frac{(\text{C}^{14}\text{N}^-)}{(\text{CN}^-)} - R_1^* \frac{(\text{C}^{14}\text{NI})}{(\text{CNI})}$$

and

$$\frac{d(\text{AgC}^{14}\text{N})}{d(\text{AgCN})} = \frac{R_2^*}{R_2} \frac{(\text{C}^{14}\text{N}^-)}{(\text{CN}^-)}$$

Explicit solution of the problem is possible for two limiting cases:

(1) If equilibrium is established in the CNI/CN⁻ system prior to separation, and R_2 (and R_2^*) $\gg R_1$ (and R_1^*), the $(\text{C}^{14}\text{N}^-)/(\text{CN}^-)$ ratio is the

TABLE I

EXPERIMENTAL AND CALCULATED APPARENT EQUILIBRIUM CONSTANTS FOR THE REACTION $\text{CNI} + \text{C}^{14}\text{N}^- \rightleftharpoons \text{C}^{14}\text{NI} + \text{CN}^-$ AT 30.6°

Vol. % di- oxane in sol- vent	Reactant ratio $f = a/b$	No. of de- ter- mina- tions	(av. \pm std. dev.) K_{exp}	$K_{\text{calcd.}}$	Reac. rate ratio $\frac{R_1^*}{R_2}$
0	0.9	12	1.08 ± 0.02	1.08^b	0.15^b
20	.9	22	$1.15 \pm .02$	1.15^b	0.75^b
28	.9	22	$1.18 \pm .03$	1.18^b	1.25^b
40	.1	8	$1.15 \pm .10^a$	1.23^c	Large
40	.9	40	$1.28 \pm .02$	1.29^c	Large
40	12.2	12	$1.63 \pm .14^a$	1.58^c	Large
60	0.9	22	$1.29 \pm .03$	1.29^c	Large

^a Errors greater in these instances since determination is much less precise for f values far from unity. ^b From Fig. 1, curve E. ^c Calculated by eq. 2.

same in the precipitate as in the original equilibrated aliquot of solution. Then K_{exp} as determined by eq. 1 is in fact the true equilibrium constant $K = R_1/R_1^*$.

(2) If R_1 (and R_1^*) $\gg R_2$ (and R_2^*), equilibrium is continuously maintained during precipi-