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# Hydrogen Iodide Production in Radiolysis of Organic Liquids Containing Dissolved Iodine: Cyclohexane, *n*-Hexane, Benzene<sup>1</sup>

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### 1. INTRODUCTION

Efforts to find significant HI production in  $\gamma$ -ray radiolysis of cyclohexane containing dissolved iodine have been repeatedly unsuccessful; G(HI) has been found by various investigators to be < 0.5 (1), < 0.3 (B. Besancon, private communication), and "negligible" (2). Consequently, a view has developed that H atoms are clearly *not* produced in radiolysis of any organic liquids. Speculations regarding the mechanism of radiolysis, of methanol (3) for example, have been complicated by the necessity of inclusion of this view. On the other hand, studies by Dewhurst (4) on the radiolysis of liquid *n*-hexane almost certainly require the assumption that H-atom production is involved in one of the elementary decomposition processes. The studies reported herein were performed in order to establish conditions of observable HI production; they show that illusorily low values of G(HI) may result from reactions both during and after irradiation.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

Cyclohexane (Eastman Kodak spectro grade) was used without further purification. n-Hexane (Phillips pure grade) was subjected successively to passage through a silica gel column, azeotropic distillation with methanol, extraction of methanol with water and finally passage through silica gel. Benzene (Merck ACS reagent grade) was recrystallized three times prior to use.

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The 20-ml samples of the various substances in Pyrex vessels (ca. 60-ml capacity) were completely degassed in successive distillations prior to exposure in an underground source (5).

## 2.2. Irradiation and Dosimetry

Irradiation by Co<sup>60</sup>  $\gamma$ -rays followed the techniques conventional in this laboratory except as otherwise noted. The dose rate for cyclohexane irradiation was 6.70  $\times 10^{20}$  ev liter<sup>-1</sup> min<sup>-1</sup>; for *n*-hexane 5.74  $\times 10^{20}$  ev liter<sup>-1</sup> min<sup>-1</sup>; and for benzene 7.65  $\times 10^{20}$  ev liter<sup>-1</sup> min<sup>-1</sup>. Dosage was determined by Fricke dosimeter technique (6) using the value  $G(\text{Fe}^{+++}) = 15.6$  (6–8) with appropriate corrections for the electron densities.

In all the cases studied in this work, iodine was added to the liquid at known concentration before the radiolysis.

## 2.3. Determination of Hydrogen Iodide

Determination of hydrogen iodide resultant from radiolysis involved extraction into water and employment of pH or ultraviolet absorption techniques. In a typical set of runs, samples were cooled to liquid nitrogen temperature immediately after irradiation, distilled water was added to the solid samples, and the samples were melted while being shaken. The HI was completely removed by successive extraction with water (total 100 ml) in a separatory funnel. Thereafter, any iodine introduced into the water in that process was extracted by three successive extractions with cyclohexane, thus destroying all  $I_3^-$  and leaving only I<sup>-</sup> in the water. An unirradiated solution was treated in the same way to yield a reference solution. The I<sup>-</sup> ion production was determined by ultraviolet absorption at 226 m $\mu$  ( $\epsilon =$ 14,000 at 25°C) (9, 10).

In the case of benzene, direct ultraviolet determination of I<sup>-</sup> was compared with a determination of I<sub>3</sub><sup>-</sup>. In that case a small amount of I<sub>2</sub> was added to the final aqueous solution (after extraction with cyclohexane), and the amount of I<sup>-</sup> was calculated from [I<sub>2</sub>] ( $\epsilon = 746$  for 460 mµ at 25°C) and [I<sub>3</sub><sup>-</sup>] ( $\epsilon = 26,400$  for 353 mµ at 25°C) by use of the known equilibrium constant (10). The agreement between I<sup>-</sup> directly determined and I<sup>-</sup> determined from [I<sub>2</sub>] and [I<sub>3</sub><sup>-</sup>] was good; the inference is that any C<sub>6</sub>H<sub>6</sub> left in the aqueous extract after extraction with cyclohexane was without effect on the ultraviolet absorption by I<sup>-</sup> at 226 mµ.

In a few cases in which the HI production was relatively high, a direct pH determination with a Beckman Model G pH meter gave results in good agreement with those obtained by ultraviolet absorption spectrometry (see Table I).

The principal point of departure from past procedures involves the technique of extraction with water. We have established that the observed yield of HI is sensitive to the time interval between irradiation and extraction. All efforts were made to reduce this interval to zero. It is apparent in Section 3 that the ideal situation

Sample	Time		
	0	1 hr	3 days
Cyclohexane	0.99	0.86	0.27
	$1.05^{a}$		
n-Hexane	1.36	1.10	1.13
	1.34*		

TABLE I Apparent G(HI) as a Function of Time after 1-Hour Irradiation  $([I_2] = 2 \times 10^{-2} M)$ 

<sup>a</sup> Ultraviolet absorption.



FIG. 1. Apparent G(HI) as a function of irradiation time; solutions of  $2 \times 10^{-2} M I_2$  in *n*-hexane and cyclohexane,  $4 \times 10^{-2} M I_2$  in benzene. The double circles in each case represent irradiations with water present (~0.15 ml of H<sub>2</sub>O per 20-ml sample).

involves an extrapolation to zero interval succeeding zero time of irradiation. Indications of the extraction technique are consequently given with the results.

## 3. RESULTS

Table I shows that the apparent G(HI) decreases with increase of the time interval between irradiation of samples (cyclohexane, *n*-hexane) and aqueous extraction. During that time interval the samples were maintained under vacuum so that the effects were not attributable to secondary contamination. In these experiments,



FIG. 2. HI production as a function of irradiation time; solutions as in Fig. 1



FIG. 3. Rate of HI production as a function of its concentration; solutions as in Fig. 1

hydrogen iodide was determined by pH measurement unless otherwise indicated. In the two cases noted in the table, the values determined from pH were checked by ultraviolet absorption.

Figure 1 shows the results of some studies of the effect of time of irradiation on

apparent G(HI) from solutions in all three solvents. In each case extraction followed immediately on irradiation. The apparent G(HI) decreases with irradiation time in all cases; in *n*-hexane and benzene the decrease seems to be toward a limiting value at higher irradiation time. The rough extrapolated values of G(HI) at zero irradiation time for cyclohexane, *n*-hexane, and benzene are, respectively, about 2.1, 2.5, and 0.9. Also shown in Fig. 1 are three values of G(HI) obtained on 5minute irradiation of solutions saturated with water (i.e., about 0.15 ml of water had been added and shaken into the hydrocarbon solution). Doubtless, presence of the water interferes with disappearance of HI by some secondary reaction.

Figure 2 shows increase of HI concentration in the samples as a function of time of irradiation. Figure 3 shows the tangents to the curves of Fig. 2 at various times, d[HI]/dt, plotted as a function of HI concentration. As is indicated also by Fig. 1, the apparent rates of HI production in *n*-hexane and benzene become constant after an initial period of irradiation; in cyclohexane the rate decreases linearly with HI concentration.

Figure 4 shows the effects of  $I_2$  concentration on apparent G(HI) in the three systems. For this series of studies 20-ml samples were irradiated for 5 minutes in the presence of about 0.15 ml of water. Plotted in the same figure as a function of  $I_2$  concentration are the values of  $-\Delta G(H_2)$ ; i.e., the decreases in  $G(H_2)$  resultant



FIG. 4. Variation of G(HI) with iodine concentration in three liquids which contain about 0.15 ml of H<sub>2</sub>O per 20-ml sample. The single circles of large size represent 5-minute irradiations; the double circles represent 20-minute irradiations. Included in the figure are small circles representing  $-\Delta G(\text{H}_2)$  for *n*-hexane  $\bullet$  (4) and cyclohexane  $\bigcirc$  (1). The dashed line represents  $-\Delta G(\text{H}_2)$  in cyclohexane.

from addition of  $I_2$  to cyclohexane (1) and *n*-hexane (4). The latter points fit the G(HI) curve fairly well.

### 4. DISCUSSION

In these experiments the amount of  $I_2$  consumed was in all cases less than 4% of the amount initially present. Thus, a reasonable assumption is that in all cases the rate of the process represented by

$$Sample \longrightarrow HI \tag{1}$$

is invariant during the course of the reaction. Figure 3 means, then, that in n-hexane and benzene rates of HI disappearance become constant after attainment of a certain concentration of HI and that in cyclohexane the rate of such disappearance becomes first order in HI concentration.

## 4.1. n-Hexane

We write in addition to reaction 1

 $Sample \longrightarrow X \tag{2}$ 

$$HI + X \longrightarrow P \tag{3}$$

where X is some product which can react with HI to yield P, a stable product. If the reaction rates may be represented by  $r_1 > r_2$  and if  $r_3$ , represented by

$$r_3 = k_3 [\text{HI}] [\text{X}] \tag{4}$$

is fairly rapid, HI accumulates with irradiation time until  $r_3$  eventually equals  $r_2$ . But

$$d[\mathrm{HI}]/dt = r_1 - r_3 \tag{5}$$

so that, when  $r_3 \rightarrow r_2$ ,

$$d[\mathrm{HI}]/dt \to r_1 - r_2 \tag{6}$$

and is constant if, as indicated for  $r_1$ ,  $r_2$  is also fairly constant during the course of the reaction.

In this picture X is an unsaturated entity and reaction 3 is merely the addition of HI to that entity. According to Dewhurst (4), for *n*-hexane G(unsaturates)averages 1.19 as determined in the presence of several scavengers other than I<sub>2</sub>. Figures 1 and 4 clearly indicate G(HI) > 2. Thus  $r_1 > r_2$ , as required by the suggested mechanism, and HI addition is generally considered to be fairly rapid (11, 12). In correspondence to equation 6

$$G_s(\mathrm{HI}) = G_1 - G_2 \tag{7}$$

where the G's are for HI production in the steady state and in reactions 1 and 2 respectively. From Fig. 3  $G_s(\text{HI})$  is calculated to be 1.29, and, since  $G_2$  can be taken to be Dewhurst's value of 1.19, it follows that  $G_1 = 2.48$ , in good agreement with

the zero irradiation value of  $\sim 2.5$  extrapolated from Fig. 1 or the value of  $\sim 2.3$  which may be estimated from Fig. 4.

#### 4.2. Benzene

The similarity of the curves for *n*-hexane and benzene in Fig. 3 suggests a similar process so far as HI production is concerned. If we assume the same schemes,  $G_2$  (i.e., the 100-ev yield of X which can react with HI) is calculated from equation 7, by introducing data obtained from Fig. 1 and Fig. 3, to be  $0.9 - 0.23 \approx 0.7$ .

### 4.3. Cyclohexane

In cyclohexane HI disappearance seems to become first order in HI concentration after attainment of a certain concentration of HI. Thus, in this region

$$d[\mathrm{HI}]/dt = r_1 - k[\mathrm{HI}] \tag{8}$$

The slope of the straight line in Fig. 3 gives  $k = 1.61 \times 10^{-2} \text{ min}^{-1}$ . A clue to the interpretation of the first-order dependence shown in equation 8 may be afforded by the fact that the rate of HI disappearance was found to be much greater during irradiation than afterward. This fact means that during irradiation HI may be reacting with some intermediate species or that some intermediate species may be catalyzing the HI disappearance reaction.

The conclusion,  $G(\text{HI}) \sim 2.1$  in cyclohexane solution, is (as seen from Fig. 4) very close to the value  $-\Delta G(\text{H}_2) \sim 2.2$  formerly given for the effect of iodine on hydrogen yield (1). A reasonable inference, based on this result alone, is that HI is formed by reaction of atomic H with iodine and that  $-\Delta G(\text{H}_2)$  in this case represents a simple scavenging reaction. If this view should prove correct, the mechanism of cyclohexane radiolysis previously suggested (1) could be greatly simplified.

#### 5. SUMMARY

Radiolysis of cyclohexane, *n*-hexane, and benzene solutions containing dissolved iodine gives hydrogen iodide with initial G(HI) estimated to be, respectively, about 2.1, 2.5, and 0.9. Low yields of HI previously observed are attributed in part to rapid reactions of HI with intermediate products during irradiation. In the case of cyclohexane, an alternative possibility is HI disappearance catalyzed by some intermediate. In addition, in all cases, postirradiation disappearance of HI also occurs. The kinetics are examined, and a tentative interpretation is offered. In benzene,  $G_2 \sim 0.7$  is, in the scheme suggested, the 100-ev yield of a species which can react rapidly with HI.

These results may lead to modification of previously expressed views (1) of the mechanism of cyclohexane radiolysis.

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#### REFERENCES

- 1. M. BURTON, J. CHANG, S. LIPSKY, and M. P. REDDY, Radiation protection in cyclohexane. Radiation Research 8, 203-213 (1958).
- R. W. FESSENDEN and R. H. SCHULER, On the use of iodine as a radical detector in hydrocarbon radiolysis. J. Am. Chem. Soc. 79, 273-276 (1957).
- G. MESHITSUKA and M. BURTON, Radiolysis of liquid methanol by Co<sup>60</sup> gamma-radiation. Radiation Research 8, 285-297 (1958).
- H. A. DEWHURST, Radiation chemistry of organic compounds. II. n-Hexane. J. Phys. Chem. 62, 15-20 (1958).
- M. BURTON, J. A. GHORMLEY, and C. J. HOCHANADEL, Design of an inexpensive highintensity gamma source. Nucleonics, 13, No. 10, 74-77 (1955).
- R. M. LAZO, H. A. DEWHURST, and M. BURTON, The ferrous sulfate radiation dosimeter. J. Chem. Phys. 22, 1370-1375 (1954).
- C. J. HOCHANADEL and J. A. GHORMLEY, A calorimetric calibration of gamma ray actinometers. J. Chem. Phys. 21, 880-885 (1953).
- R. H. SCHULER and A. O. ALLEN, Yield of the ferrous sulfate radiation dosimeter. J. Chem. Phys. 24, 56-59 (1956).
- H. FROMHERZ and W. MENSCHICK, Ueber die Lichtabsorption der Alkalihalogenide in waesserigen Loesungen. Z. phys. Chem. (Leipzig) B7, 439-467 (1930).
- 10. A. D. AWTREY and R. E. CONNICK, The absorption spectra of  $I_2$ ,  $I_3^-$ ,  $I^-$ ,  $IO_3^-$ ,  $S_4O_6^-$ , and  $S_2O_3^-$ . Heat of the reaction  $I_3^- = I_2 + I^-$ . J. Am. Chem. Soc. **73**, 1842–1843 (1951).
- 11. P. KARRER, Organic Chemistry 54 (1950).
- S. F. O'CONNOR, L. H. BALDINGER, R. R. VOGT, and G. F. HENNION, Solvent effects in addition reactions. I. Addition of hydrogen bromide and chloride to cyclohexane and 3-hexane. J. Am. Chem. Soc. 61, 1454-1456 (1939).