

THE POLYMERIZATION OF ETHYLENE SENSITIZED BY ETHYL IODIDE¹

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ABSTRACT

The polymerization of ethylene sensitized by the thermal decomposition of ethyl iodide in the presence of mercury vapor has been studied at 250° , 275° , and 300° C. C¹⁴-labelled ethyl iodide was used in a number of experiments. The increase in the rate of decomposition of ethyl iodide in the presence of ethylene and the formation of butyl iodide are accounted for by equilibrium processes of the type RI+Hg = R+HgI. The important features of the reaction were established from the identity, quantity, and activity of the various products. The predominant formation of olefins is attributed to the isomerization and decomposition of large radicals. Very little of the butane is formed by the combination of ethyl radical. Radical disproportionation is the most important chain termination step.

The decomposition of the lower alkyl iodides has been studied extensively (10) and it is generally agreed that in both the thermal reaction and in the photolysis in the region of the continuum (*ca.* 2600 Å) the primary process consists in the formation of alkyl radicals and iodine atoms. The quantum yields of the photochemical process are low because of the back reaction but can be greatly increased by trapping the iodine atoms with mercury or silver. The thermal or photochemical decomposition of alkyl iodides in the presence of ethylene and either mercury or silver should therefore afford a convenient method for studying the free radical sensitized polymerization of ethylene.

Jungers and Yeddanapalli (5) have studied the polymerization of ethylene sensitized by the photolysis of methyl, ethyl, *n*-propyl, and isopropyl iodides in the presence of mercury at temperatures in the range 130° to 275° C. Under conditions likely to yield low radical concentrations, viz. low iodide concentrations, high ethylene concentrations, and low light intensities, they found that the "yield", defined as the ultimate pressure decrease on prolonged irradiation divided by the initial pressure of iodide, reached maximum values which were in the approximate ratio 3.5 : 3.0 : 2.5 for methyl, ethyl, and the propyl iodides, respectively. They concluded from this that the final polymer had approximately the same molecular weight in each case and that for steric reasons the growing radicals formed by the successive addition of ethylene molecules underwent chain termination when they reached a more or less common critical size. According to their mechanism all the products should be saturated, for at low radical concentrations they assumed that chain termination would take place by the reactions

$$R + C_2 H_5 I = R H + C_2 H_4 I$$
^[1]

$$C_2H_4I = C_2H_4 + I,$$
 [2]

while at high radical concentrations they assumed that it would occur by

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radical combination. Radical disproportionation would also be expected to occur, in the light of more recent work (9).

Although Jungers and Yeddanapalli did not analyze their products their conclusions appeared to be well founded. However, because of the fundamental importance of polymerization reactions it seemed desirable to make a further study of the problem taking advantage of fractionation methods and infrared spectra as analytical tools. In the present work the polymerization of ethylene was initiated by the thermal decomposition of ethyl iodide in the presence of mercury. In order to obtain as much information as possible about the reactions of the ethyl radicals a number of experiments were performed using ethyl iodide labelled in the methylene group with C¹⁴.

EXPERIMENTAL

The Reaction System

The reaction vessel used in most of the experiments consisted of a Pyrex cylinder having a volume of approximately two liters. The cylinder was mounted vertically and a cooling thimble was placed in the connecting tubing at the point where it emerged from the furnace. By passing compressed air through the thimble the mercury which distilled from the pool at the bottom of the cell was condensed and allowed to drop back into the cell. A mercury cutoff served to isolate the cell during an experiment and this was used as a manometer to give a rough measure of the amount of reaction taking place.

The initial ethyl iodide was measured accurately as a gas, using a separate calibrated volume and a modified Pearson gauge. It was then frozen into the cell by placing liquid air in the thimble. Ethylene was measured and admitted in the same way. The cell was filled at room temperature, and since the reaction was allowed to proceed from $4\frac{1}{2}$ to 38 hr. rapid heating was not considered essential. At the end of an experiment the temperature was lowered by cutting off the current and blowing air through the furnace. When the cell had cooled to approximately room temperature the final pressure was measured and corrected to 25° C.

For the experiments with ethylene and ethyl iodide in the absence of mercury and those with ethyl iodide and mercury in the absence of ethylene a special cell having a volume of 720 cm.³ was used. The reagents were measured as described above and condensed into the cell by immersing it in liquid air. It was then sealed off and placed in the furnace. At the end of an experiment it was sealed to the apparatus at a breakoff valve.

Reagents

The ethylene used had a rated purity of 99.5%. It was treated with 2 N ammoniacal silver nitrate to remove traces of acetylene, dried over Drierite and phosphorus pentoxide, and subjected to a number of trap-to-trap distillations.

The inert ethyl iodide was distilled in an 18 plate column and thoroughly degassed before being placed in a storage vessel isolated with a mercury cutoff. The active ethyl iodide, labelled with C¹⁴ in the methylene group, was

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obtained from Tracerlab. The original 0.3 gm. sample had an activity of one millicurie. It was immediately diluted to 2 gm. with inert ethyl iodide and the portion of this used in the experiments was condensed into a storage bulb and isolated with a mercury cutoff. Both the active and inactive iodides were kept frozen with dry ice to avoid decomposition.

In preparing a sample of active ethyl iodide for an experiment suitable amounts of the active and inactive materials were removed from the storage bulbs, measured in the gas burette, and mixed. An aliquot of this material was then used to obtain the activity of the material to be used in the experiment. In a number of cases aliquots were distilled to remove any active material other than ethyl iodide which might have been present in the original sample. Since no such products could be found the distillation was subsequently eliminated.

Distillation of the Products

Ethylene and ethane were removed by distillation at -168° to -170° C. (7). Since no acetylene could be found the second fraction was taken off at an initial pressure of 1.0 mm. (*ca.* -100° C.), the cut being made at 0.2 mm. (*ca.* -50° C.). The second fraction and the residue remaining in the still were separately treated to remove iodides as described below and then redistilled into a number of fractions using initial and final takeoff pressures of the order of 0.2 and 0.05 mm., respectively. Only for the smaller fractions did the final takeoff temperature exceed the initial by as much as four or five degrees.

Separation and Analysis of the Iodides

A study of the infrared spectrum of the products showed that both ethyl and *n*-butyl iodide were present, although the initial material was free from the latter. Because of their different vapor pressures a fairly complete separation of the two was achieved in the fractionation referred to above. The iodides were removed from the fractions containing them in two ways. In the first method the fractions were frozen onto an aqueous paste of silver metanitrobenzoate which was then allowed to warm to room temperature and stand overnight, resulting in the formation of the ethyl or butyl ester and silver iodide. The residual wet gas was frozen onto solid potassium hydroxide and finally dried for 12 hr. in contact with phosphorus pentoxide. The infrared spectrum of the dried gas showed that the iodides were completely removed by this method.

To determine the amount of ethyl or butyl iodide the mixture of the ester and silver iodide was treated with warm concentrated nitric acid and then diluted with water and centrifuged. The supernatant liquid was then removed. The residual silver iodide was further extracted with 50% aqueous ethanol, filtered, dried, and weighed. Tests on known mixtures of hexane and ethyl iodide showed the method to be accurate to about 2%.

In some of the experiments with active ethyl iodide the silver metanitrobenzoate method was used in an attempt to obtain the activities of the two iodides. In this case the esters were extracted from the silver iodide with petroleum ether. After evaporating the solvent the esters were hydrolyzed

with 2 N sodium hydroxide; the resulting alcohols were then converted to barium carbonate as described below. However, it was found that the silver metanitrobenzoate reagent also removes quantitatively compounds with terminal unsaturation, although it does not remove other olefins to any degree. Although it was apparent that the method could not be used for the determination of the activities of the iodides it was used to remove terminally unsaturated olefins, and this made it possible to determine the activities of the remaining 2-alkenes.

The method ultimately used to determine the activities of the iodides involved their reaction with hexamethylenetetramine in chloroform solution. The resulting quaternary salt is insoluble in chloroform and was filtered off and burned for the activity determinations.

Infrared Gas Analysis

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A Perkin-Elmer model 12-C instrument was used, but because of the small samples obtainable the optical arrangement was modified. The glow bar was removed from its normal position to a point on the same optical axis but about 80 cm. from the light chopper. Between the two was placed the cell, consisting of a Pyrex tube 70 cm. long and 15 mm. in diameter. The end near the glow bar was flanged out to about 40 mm. Sodium chloride windows were sealed to each end of the cell and a stopcock and cold finger were sealed to the flanged end for freezing the gas into the cell and for obtaining the blank trace. Despite the very poor optical properties of this arrangement there was an appreciable net improvement in the accuracy with which small samples of gas could be analyzed.

In setting up the quantitative analysis scheme for the hydrocarbons the spectra of a number of standard samples obtained from the United States Bureau of Standards were taken at various pressures. Because of their small extinction coefficients at usable analytical wave lengths the amount of paraffin in a sample was usually determined by subtracting the amount of olefin from the total pressure. These results were checked by taking the spectrum of the residue from the treatment of the olefin-paraffin mixture with mercuric acetate, described below.

Activity Determinations

Samples for combustion were condensed into a gas burette consisting of a number of connected bulbs, one of which contained a cold finger which could be filled with liquid air. After measuring the volume of the gas oxygen was allowed to mix with it by opening a stopcock at the top of the burette. By slowly raising the mercury in the burette the mixture was fed into a continuous stream of pure oxygen which flowed through a conventional microcombustion tube. The carbon dioxide formed was bubbled through saturated barium hydroxide solution. The barium carbonate was collected and washed on a filter paper held in a Tracerlab E-8A precipitation apparatus. Carbon numbers calculated from the weights of dried barium carbonate were usually a few per cent low, presumably because of incomplete trapping of the carbon dioxide in the barium hydroxide solution.

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The C¹⁴ activity of the ethyl iodide used in any particular experiment was arbitrarily given a value A = 1, and the activities of the various products were measured relative to this on a molar basis. To obtain A the measured number of counts per minute, C_{obs} , was first corrected for the background count C_b . A correction for self-absorption was then made using the data of Yankwick *et al.* (12). For a constant area of barium carbonate precipitate (2.83 cm.², compared to our value of 2.82 cm.²) having various weights per unit area X, they obtained a function J(X) such that $(C_{obs}-C_b)/J(X)$ is equal to the number of counts per minute corrected for background and selfabsorption. To allow for any variation in the sensitivity of the geiger tube the count on the sample was always followed by one, C^* , taken on a standard reference sample of barium carbonate using the same geometry. A quantity S, proportional to the specific activity of the sample, was then obtained,

$$S = \frac{(C_{\rm obs} - C_{\rm b})/J(X)}{(C^* - C_{\rm b})W},$$

in which W is the weight of barium carbonate in the sample. The molar activity of the sample relative to that of the ethyl iodide used, referred to in the text simply as molar activity, is then given by

$$A = (S_s/S_i) N/2,$$

in which the subscripts s and i refer to the sample and to the iodide, respectively, and N is the number of carbon atoms in a molecule of product. A typical result, found for the hexane obtained in one of the experiments, is illustrated in Table I. The value of the molar activity of the hexane indicates that it contains, on the average, one ethyl radical derived from ethyl iodide.

	TABLE I							
_	DETERMINATIO	N OF	THE	MOLAR	ACTIVITY	OF	HEXANE	
		X,	-		$C_{\rm obs} - C_{\rm b}$,	$\overline{C^* - C_b}$,	

Material	W, mgm.	<i>X</i> , mgm./cm. ²	J(X)	$C_{obs} - C_b,$ c.p.m.	<i>C</i> * — <i>C</i> _b , с.р.т.	S	<u>A</u>
Initial ethyl iodide Hexane	$\begin{array}{c} 20.6\\ 31.48 \end{array}$	$7.32 \\ 11.18$	$0.421 \\ 0.300$	$\begin{array}{c} 12570 \\ 4350 \end{array}$	$\begin{array}{c} 4370\\ 4410 \end{array}$	$\begin{array}{c} 0.331 \\ 0.1045 \end{array}$	1.00 0.95

Separation of Olefins from Paraffins

To determine the molar activity of a paraffin it was necessary to separate it from the unsaturated compounds present in the same fraction. This was accomplished by an adaptation of the hydroxy-mercurial method (8). The gas was frozen into a 100 ml. flask containing 20 ml. of saturated aqueous mercuric acetate and 10 ml. of 3% hydrogen peroxide which had previously been degassed. The flask was then warmed to room temperature and shaken, intermittently, over a period of 12 hr. The residual gas and 1 or 2 ml. of the liquid were then distilled onto solid potassium hydroxide. After several hours the contents were cooled with dry ice and the hydrocarbons distilled back into the system and measured. For compounds of higher molecular weight than bu-

tane the final drying was made with phosphorus pentoxide rather than dry ice. The infrared spectra showed complete removal of olefins by this method. Analysis of synthetic mixtures showed the method to be quantitative for mixtures of ethane and ethylene. For other olefin-paraffin mixtures there was a slight loss of paraffin; in these cases the quantity of paraffin was estimated by the infrared method.

Nonvolatile Products

After a series of experiments in which ethylene, ethyl iodide, and mercury had been used the nonvolatile material in the reaction vessel was extracted with carbon tetrachloride. The absence of an appreciable residue on evaporating the solvent indicated that no diiodoethane was present. Except for the mercury, the nonvolatile material was completely soluble in aqueous potassium iodide. Chemical tests showed the presence of mercurous iodide. The absence of diiodoethane was also confirmed in the experiments with ethyl iodide and mercury alone.

RESULTS

Products

In Table II are shown the results of pairs of experiments done at 250°, 275°, and 300°C. The amounts of the products are given in mm. pressure in the reaction vessel at 25°C. The values of $-\Delta P/-\Delta C_2 H_5 I$, analogous to the

	-	PRODUCTS O	F THE REACT	TON		
	250)°C.	275°C.		300)°C.
Experiment No. Initial C_2H_3I Initial C_2H_4 Time, hr. $-\Delta C_2H_3I$ $-\Delta C_2H_4$	$\begin{array}{r} 23 \\ 10.4 \\ 139.6 \\ 25 \\ 8.8 \\ 30.9 \end{array}$	2733.2154.32429.361.4	$ \begin{array}{r} 21 \\ 11.2 \\ 143.5 \\ 19 \\ 10.6 \\ 41.3 \end{array} $	$\begin{array}{r} 22\\ 34.9\\ 143.6\\ 17.5\\ 34.1\\ 76.0 \end{array}$	$ \begin{array}{r} 28 \\ 11.3 \\ 146.2 \\ 7 \\ 10.8 \\ 46.4 \end{array} $	$\begin{array}{r} 25\\32.0\\152.5\\8\\30.8\\78.0\end{array}$
Ethane Propane <i>n</i> -Butane Hexane Total paraffin obs. Total paraffin calc.	$\begin{array}{c} 0.64 \\ \\ 0.89 \\ 1.5 \\ 3.0 \\ 3.6 \end{array}$	$2.04 \\ 0.2 \\ 2.9 \\ 3.7 \\ 8.8 \\ 12.2$	$\begin{array}{c} 0.5 \\ - \\ 2.2 \\ 2.8 \\ 5.5 \\ 5.0 \end{array}$	$3.6 \\ 0.37 \\ 6.3 \\ 4.5 \\ 14.8 \\ 16.6$	$\begin{array}{c} 0.9 \\ 0.38 \\ 2.3 \\ 2.4 \\ 6.0 \\ 5.4 \end{array}$	$3.6 \\ 1.5 \\ 7.0 \\ 4.9 \\ 17.0 \\ 15.4$
Propylene Butene-1 trans-Butene-2 2-Methyl butene-1 Hexene-1 trans-Hexene-2 C ₇ and higher Total olefin obs. Total olefin calc.	$\begin{array}{c} 0.54\\ 1.87\\ 0.48\\ 1.22\\ 0.42\\ 0.47\\ 5.5\\ 10.5\\ 9.9 \end{array}$	$\begin{array}{c} 0.67\\ 2.1\\ 0.35\\ 0.67\\ 2.1\\ 1.5\\ 11.5\\ 18.9\\ 15.5 \end{array}$	$1.73 \\ 2.5 \\ 0.62 \\ 1.8 \\ 0.54 \\ 0.90 \\ 4.9 \\ 13.0 \\ 13.5 \\ 1.7$	$2.0 \\ 3.2 \\ 0.9 \\ 1.1 \\ 1.4 \\ 2.1 \\ 13.0 \\ 23.7 \\ 21.9$	3.7 3.1 1.3 1.9 1.0 1.7 4.5 17.2 17.8	5.2 5.2 1.7 1.7 3.3 7.2 26.2 27.8
Butyl iodide $-\Delta P$ $-\Delta P/-\Delta C_2 H_3 I$ Olefin/paraffin obs. Olefin/paraffin calc.	$1.7 \\ 25.5 \\ 2.9 \\ 3.5 \\ 2.7$	$5.0 \\ 59.5 \\ 2.4 \\ 2.1 \\ 1.3 $	$0.6 \\ 32.9 \\ 3.1 \\ 2.4 \\ 2.7$	$1.0 \\ 69.3 \\ 2.0 \\ 1.6 \\ 1.3$	$0.0 \\ 33.5 \\ 3.1 \\ 2.9 \\ 3.3$	$\begin{array}{c} 0.0 \\ 65.6 \\ 2.1 \\ 1.5 \\ 1.8 \end{array}$

"yield" of Jungers and Yeddanapalli (5), are seen to be sensitive to the initial iodide pressure but relatively insensitive to temperature, in agreement with their observations. The value of approximately three for low iodide pressures is identical with their value for low ethyl radical concentrations. However, instead of the products being all saturated, as they predicted, it is seen that there is considerably more olefin than paraffin. The proportion of olefin is greater for low than for high ethyl iodide concentrations, and even in the latter case the amount is greater than could be accounted for by disproportionation.

Qualitative infrared analysis of the fraction listed in Table II as " C_7 and higher" showed it to be composed of hydrocarbons containing the groups CH_2 =C-R and CH_2 =CHR, in which R and R' are saturated radicals. The

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amount of this fraction was determined as the difference between the total final pressure and the sum of remaining individual product pressures. From the carbon balance of the reagents and products the average carbon number of this fraction was found to be approximately nine.

After treating the C₆ fraction with mercuric acetate it was possible to identify a hydrocarbon having an important band at 10.10 microns. Because of the small amount present it could not be positively identified, although the spectrum strongly resembled that of methyl cyclopentane. It was estimated that it could have amounted to 10 to 20% of the C₆ "paraffin".

Since the only products formed were alkanes, mono-olefins, cycloparaffins, and butyl iodide, it follows that the amount of paraffin produced must be equal to one half of the difference between the amount of ethyl iodide consumed and the amount of butyl iodide formed. The values of "Total paraffin calc." listed in Table II were obtained in this way; "Total olefin calc." was obtained by difference.

No evidence could be found for either methane or hydrogen. Pentane, if formed, did not exceed 5% of the sum of butane and hexane. The maximum amounts of pentene-1, cyclopentane, or cyclohexane that could be present were estimated to be less than 0.1 mm. The amount of *cis*-butene-2 could not exceed 20% of the *trans* isomer. The maximum amount of hydrogen iodide was estimated to be less than 0.01 mm.

Isotope Effect in the Decomposition of Ethyl Iodide

An appreciable carbon isotope effect has been observed in the thermal decomposition of a number of organic compounds (4) in which the decomposition has involved the rupture of C—C bonds. In the present instance a rupture of a C—I bond is involved. In most of the experiments a large part of the ethyl iodide was decomposed and hence, even if there were an isotope effect, the proportion of C¹⁴ in the ethyl radicals formed would be approximately the same as in the original ethyl iodide. However, the proportion of inactive ethyl radicals might be greater at the beginning of an experiment when the ethyl radical concentration is higher and the instantaneous value of the

"yield" is lower. Erroneous conclusions might therefore be drawn from the final measured activities of the products. To ascertain if the isotope effect were significant experiments were performed in which considerably different amounts of active ethyl iodide were decomposed in the presence of mercury but in the absence of ethylene. The results are shown in Table III. The acti-

TABLE III DECOMPOSITION OF C¹⁴-LABELLED ETHYL IODIDE IN THE PRESENCE OF MERCURY

Experiment No. Temperature, °C.	$31 \\ 250$	32 300
Initial ethyl iodide, mm.	38.6	39.2
Final ethyl iodide, mm.	36.2	24.0
Time, hr.	11	4.5
Ethylene formed, mm.	0.8	1.8
Ethane formed, mm.	1.2	7.1
Butene formed, mm.		0.4
Butane formed, mm.		1.6
S for initial iodide:		
1st sample	0.398	0.418
2nd sample	0.385	0.389
S for final iodide	0.384	0.404
S for C_2 fraction	0.378	0.410
S for C_4 fraction		0.395

vities are given in terms of the quantity S, defined previously. It is clear from the table that the variations in S are within the probable error of its determination and that the decomposition of ethyl iodide does not involve an appreciable isotope effect.

TABLE IV

			5	250°C.				27.	5°C.
Experiment No. Initial ethyl iodide, mm. Initial ethylene, mm. Time, hr. Ethane formed, mm. Ethylene formed, mm.* Total alkanes formed, mm. Butyl iodide formed, mm.	1130.469.4151.20.4521.4	1377.969.5164.71.0861.5	$ \begin{array}{c} 14 \\ 4.0 \\ 141.2 \\ 16.5 \\ \hline 2.3 \end{array} $	$ \begin{array}{r} 12 \\ 10.7 \\ 137.8 \\ 16 \\ 0.4 \\ 1.1 \\ \overline{5.3} \end{array} $	$ \begin{array}{r} 17 \\ 24.5 \\ 136.8 \\ 38 \\ 1.9 \\ 0.8 \\ 9 \\ \end{array} $	$27 \\ 33.2 \\ 154.3 \\ 24 \\ 2.0 \\ 0.5 \\ 12 \\ 5.0$	$ \begin{array}{r} 15 \\ 34.0 \\ 134.5 \\ 17 \\ 1.8 \\ 0.4 \\ 10 \\ - \\ \end{array} $	$\begin{array}{c} 21 \\ 11.2 \\ 143.5 \\ 19 \\ 0.5 \\ 0.9 \\ 5 \\ 0.6 \end{array}$	$\begin{array}{c} 29 \\ 34.2 \\ 151.3 \\ 6.8 \\ 2.5 \\ -15 \\ 15 \\ -15 $
Ethane Propylene Butane Butene-1)†	$1.0 \\ 0.92$	$\begin{array}{c}1.0\\-1.1\end{array}$	 0.56	$0.89 \\ \\ 0.8$	$0.83 \\ 0.30 \\ 0.94 \\ 0.1$	$\frac{1.0}{0.92}$	$\begin{array}{c} 0.89 \\ \hline 0.88 \\ 0.88 \end{array}$	0.8 0.3 0.7	$\begin{array}{cccc} 3 & 1.05 \\ 5 & 0.36 \\ 4 & 1.04 \end{array}$
trans Butene-2 2-Methyl butene-1 Hexane Hexene-1 \†	0.4	0.94	0.72	$\frac{-}{0.72}$	0.1	0.4 0.4 0.96	0.3	0.5	0.4
<i>trans</i> Hexene-2) C7 and higher‡ Butyl iodide	1.7	1.7		 1.04 	$\frac{1.2}{-}$	0.9	1.08	1.1	9 <u>-</u> 0.6

*Amount present with molar activity of unity.

†Calculated from composition of fraction and activities before and after removing olefin.

‡Based on an average carbon number of nine.

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Activity of the Products

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The results of a series of experiments using active ethyl iodide are shown in Table IV.

The use of a tracer does not make it possible to determine the amount of ethylene *formed* in the reaction since it might not have originated from ethyl iodide. However, the minimum amount formed can be estimated on the assumption that it would have a molar activity of unity. The values given in Table IV for ethylene formed were obtained in this way. About all that can be said with certainty is that some ethylene is formed and that its amount is probably of the same order as that of the ethane.

Experiments 11 and 13 are of particular interest because of the very large amounts of n-butyl iodide formed when the concentration of ethyl iodide approaches that of the ethylene.

DISCUSSION

One would infer from previous work that the initial process involves the decomposition of ethyl iodide into an ethyl radical and an iodine atom. However, a comparison of the results of experiment 31 (Table III) and experiment 27 (Table II) shows that the presence of ethylene greatly accelerates the rate of decomposition of ethyl iodide, which suggests that equilibria of the following type may be involved.

$$C_2H_5I + Hg \rightleftharpoons C_2H_5 + HgI$$
[3]

$$C_2H_5I + HgI \rightleftharpoons C_2H_5 + HgI_2$$
[4]

The addition of ethylene would lower the ethyl radical concentration and accelerate the decomposition of ethyl iodide.

Although the initial stages of the polymerization of ethylene undoubtedly consist in the successive addition of ethylene to ethyl radicals, a number of possible steps can be suggested for the formation of the ultimate products from the linear 1-alkyl radicals produced in this way.

(i) Reaction with Ethyl Iodide to Form a Linear Alkane (Reaction [1])

It has been suggested by a number of workers that reactions of this type play an important role in the photolysis of ethyl iodide (5, 11). However, their evidence is by no means convincing. West and Schlessinger (11) found that methylene iodide was formed in the photolysis of methyl iodide provided no "getter" was used to trap the iodine; in the presence of silver none was formed. In the case of ethyl iodide they found no ethylene iodide under either circumstance. Jungers and Yeddenapalli (5) did not subject their products to chemical analysis, but simply quoted the results of West *et al.* as showing that [1] would occur at high concentrations of ethyl iodide. We were unable to find ethylene iodide under any conditions.

If it were formed, the radical C_2H_4I could conceivably disappear in a number of ways. If it decomposed to form ethylene and an iodine atom, or if it reacted with mercury to form ethylene and mercurous iodide, then 1 mole of active

ethylene would have to be formed for every mole of alkane formed by [1] or every mole of ethyl iodide decomposed by [1]. However, it is evident from Table IV that the amount of ethylene formed with a molar activity of unity did not exceed one-eighth of the total alkanes even at high concentrations of ethyl iodide. The possibility that the C_2H_4I radical could react with ethyl iodide to form ethylene iodide can be eliminated since the latter was not formed. If it reacted with alkyl radicals to form higher alkyl iodides, then these, in particular butyl iodide, would be expected to have a molar activity of two, which was not the case. Furthermore, in experiments 11 and 13 (Table IV) the amount of butyl iodide formed far exceeded the amount of alkanes produced, which could not be the case if reaction [1] had occurred. A suggested mechanism for the formation of butyl iodide will be given later.

(ii) Combination of Radicals to Form Linear Alkanes

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It is evident from the olefin/paraffin ratios given in Table II that this process does not play a leading role. It can also be shown that only a small proportion of the paraffin could be formed in this way. The molar activity of the butane is much less than two. If it were formed by the combination of ethyl radicals a considerable proportion of the latter would have to be inert, i.e. arise from processes other than the decomposition of ethyl iodide. Since it is reasonable to assume that ethane is formed from ethyl radicals, it would follow that the molar activity of the ethane would have to be of the order of 0.5 or less, in disagreement with the data of Table IV. The same argument applies to the formation of hexane and higher paraffins.

(iii) Disproportionation of Radicals to Form Alkanes and Either Cycloparaffins or Olefins

This process would lead to olefin/paraffin ratios of unity or, if any combination took place as well, less than unity. While disproportionation cannot account for the major part of the olefin (and cycloparaffin) it can account for the alkanes and the corresponding amount of olefin.

(iv) Hydrogen Abstraction from Olefins

Reactions of this type can be discounted since the radicals of the vinyl type formed in this way would be certain to yield, ultimately, some diolefin, and no evidence for this could be obtained.

(v) Decomposition of Radicals to Yield Olefins or Cycloparaffins, and an Alkyl Radical

Reactions of this type must account not only for the compounds having an odd number of carbon atoms but also for the major portion of the olefin produced. It is readily seen, however, that a simple C—C bond rupture followed by the isomerization of the biradical is not the most probable process, as only inert olefins would be formed in this way.

If the observed olefin activities were due to disproportionation reactions, which involve two radicals, then the ratio of active to inactive butene would be expected to increase markedly with the radical, i.e. the ethyl iodide, concentration. Evidence for this is not conclusive. The results of experiments 17, 27, and 15 given in Table IV indicate an increase in the activity of the butene when

the ethyl iodide pressure is increased, but similar experiments at 275° C. show a decrease in the molar activity of the butene from 0.5 to 0.4 when the ethyl iodide pressure is increased from 11.2 to 34.2 mm.

In their experiments on tetramethylene biradicals Bawn and Milsted reported "butylene" as one of their products but did not identify the particular isomer (2). Benson and Kistiakowsky (3), on the other hand, found cyclobutane to be the only C_4 product from the photolysis of cyclopentanone and questioned the previous conclusions of Norrish *et al.* (1). It seems likely, therefore, that if tetramethylene biradicals were formed by the decomposition of a linear alkyl radical some evidence of cyclobutane would be found. This was not the case.

Kossiakoff and Rice (6) have pointed out that in many cases the activation energy for the isomerization of a long-chain free radical is much less than the activation energy for its decomposition and that as a result there should be an equilibrium process involving isomeric forms of the free radical. In particular, they suggest that 1-hexyl radicals should isomerize readily by a 1–5 shift of the free valence to form 2-hexyl radicals. Furthermore, the latter should decompose more readily than the 1-hexyl isomer since propylene and a propyl radical would be formed in a single step. The propylene formed in this way would be active.

It is evident that 1-hexyl-5-C¹⁴ radicals can give rise to 2-hexyl-2-C¹⁴ radicals by a 1–5 shift of the free valence, or to 1-hexyl-2-C¹⁴ radicals by a 1–6 shift. The latter could isomerize to 2-hexyl-5-C¹⁴ by a 1–5 shift. Similar considerations may be applied to other large radicals. Their disproportionation will yield paraffins and olefins with molar activities of unity; their decomposition will yield olefins with molar activities less than unity.

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Isomerization of 1-alkyl radicals is undoubtedly involved in the formation of olefins containing the group $CH_2 = C - R$. If the 2-methyl butene-1 were pro-| R'

duced by the addition of (active) ethyl radicals to propylene, followed by the disproportionation of the resulting 2-methyl butyl-1 radical with another radical, then its molar activity would be at least as great as unity. The observed activity of less than 0.5 suggests that it arises through the addition of ethylene to 2-hexyl-2-C¹⁴ or 2-hexyl-5-C¹⁴ radicals, followed by a 1–7 and then a 1–5 shift of the free valence. Subsequent decomposition of the radical could yield either 2-methyl butene-1 and a propyl radical, or 2-methyl hexene-1 and a methyl radical. The molar activity of the pentene would be less than that of the heptene. As mentioned previously, evidence for compounds of the latter type was found in the "C₇ and higher" fraction.

The postulate that radical decomposition is usually preceded by isomerization of the original 1-alkyl radicals also affords an explanation for the fact that the activities of the ethane and butane are slightly less than unity. The decomposition of large radicals into olefins will give rise to some radicals having molar activities less than unity. The ethane and butane formed by the disproportionation of ethyl or butyl radicals with larger radicals will then have activities somewhat less than unity. This is supported by the fact that in any

particular experiment the molar activities of the ethane and butane were closely related, as shown in Table V. It is also seen that the activities of these

TABLE V

COMPARISON OF MOLAR ACTIVITIES OF ETHANE AND BUTANE										
Expt. No.	Temp., °C.	Molar activity of ethane	Molar activity of butane	Olefin/paraffin calc.						
 $\begin{array}{c} 27\\21\\28\end{array}$	$250 \\ 275 \\ 300$	1.0 0.83 0.71	$0.92 \\ 0.74 \\ 0.68$	1.3 2.7 3.3						

products are lower in the experiments in which the olefin/paraffin ratio was high, i.e. in the experiments in which radical decomposition was more important.

(vi) Formation of Butyl Iodide

It is significant that no butyl iodide was formed in the absence of ethylene. Also, its molar activity is less than unity, whereas it would be greater than unity if it were formed by the reaction

$$C_{2}H_{5} + C_{2}H_{4}I = C_{4}H_{9}I.$$
[5]

In experiments performed at 250°, 275°, and 300°C. with ethyl iodide and ethylene but in the absence of mercury there was no butyl iodide formed, which shows that its method of production is not through the reaction

$$C_{2}H_{5}I + C_{2}H_{4} = C_{4}H_{9}I.$$
 [6]

Evidence has already been given to show that the decomposition of ethyl iodide in the presence of mercury and the mercury iodides involves equilibrium processes. If so, butyl radicals could take part in similar equilibria, viz.,

$$C_4H_9 + HgI = C_4H_9I + Hg$$
[7]

$$C_4H_9 + HgI_2 = C_4H_9I + HgI.$$
 [8]

Reactions of this type appear to afford the most satisfactory explanation for the formation of butyl iodide. The fact that its molar activity is somewhat less than that of the butane suggests that a small amount of the latter is probably formed by the combination of ethyl radicals.

SUMMARY

The use of C^{14} -labelled ethyl iodide together with extensive chemical analysis of the products has revealed a number of features of the ethyl iodide sensitized polymerization of ethylene not previously established. Some of these features apply specifically to the use of alkyl iodides as sources of free radicals while others would be expected to apply quite generally to the free radical sensitized polymerization of olefins.

The primary process in the presence of mercury has long been considered to be a C—I bond rupture, followed by the reaction of the iodine atom with mercury,

$$RI = R + I$$
 [9]

$$I + Hg = HgI.$$
 [10]

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However, the fact that butyl iodide was only formed in the presence of mercury (and ethylene), and the fact that ethylene accelerates the rate of decomposition of ethyl iodide suggest that [11] is the primary process in the decomposition of alkyl iodides.

$$RI + Hg \rightleftharpoons R + HgI$$
 [11]

It is evident that if [10], as well as [9], is considered to be a reversible process then in the absence of reactions other than those indicated it is immaterial whether [9] or [11] is considered to be the primary process, since $K_{11} = K_9 \cdot K_{10}$.

The present experiments confirm previous evidence that larger 1-alkyl radicals are built up by the successive addition of ethylene to ethyl radicals,

$$C_{2}H_{5} + C_{2}H_{4} = C_{4}H_{9}$$
[12]

$$C_4H_9 + C_2H_4 = C_6H_{13}, [13]$$

etc.

The concentrations of the radicals would be expected to decrease in the order ethyl, butyl, hexyl, etc., since radical growth can be terminated at any stage. This is in keeping with the fact that butyl iodide was formed (by the reverse of [11]), but not hexyl or higher iodides.

The large olefin/paraffin ratios and the formation of products containing an odd number of carbon atoms show that the decomposition of large radicals into olefins and smaller alkyl radicals plays a major role under the experimental conditions used. Furthermore, the structures and molar activities of these olefins indicate that in many cases the large 1-alkyl radicals isomerize by 1-5and 1-6 (and presumably other) shifts of the free valence before they decompose. As would be expected, the radical decomposition reactions are more important at low than at high radical concentrations.

Chain termination occurs by both combination and disproportionation of radicals, but the latter appeared to be the more important.

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