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High Temperature Reactions of Iodine with Hydrocarbons. I. Dehydrogenation

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The stoichiometric, reversible reaction of elemental iodine with C_2 to C_5 paraffins, cyclopentane, and methylcyclopentane at $\geq 500^\circ$ produces monoolefinic, diolefinic, or acetylenic hydrocarbons with the same carbon skeleton as the reactant. Hydrogen iodide is formed in amounts equivalent to the reacted iodine. Oxygen added to the reaction mixture reacts primarily with hydrogen iodide and the resulting iodine reacts with additional hydrocarbon. A free radical mechanism is proposed.

Introduction

Although the reaction of elemental iodine with terpene or hydroaromatic hydrocarbons to produce HI has long been known,¹ iodine generally has been regarded as otherwise unreactive toward saturated hydrocarbons. We have found, however, that at high temperatures ($\geq 350^\circ$), iodine reacts essentially stoichiometrically with hydrocarbons, including the lower paraffins, to form hydrogen iodide and a variety of unsaturated hydrocarbons.² These reactions are described in a series of three papers. In part I the dehydrogenation of C_2 - C_5 paraffins, cyclopentane, and methylcyclopentane is discussed. Aromatization and rearrangement reactions are described in parts II^{3a} and III.^{3b}

Experimental

Apparatus and Procedure.—A schematic diagram of the apparatus is shown in Fig. 1. Vapor from molten iodine, held at about 250° ($p_{I_2} \sim 4$ atm.) in a specially designed, Hastelloy C pressure vessel, was passed through a metering valve, rotameter, and connecting tubing (all constructed of Hastelloy C and heated electrically to 250 - 300°) to the reaction tube. A white heat lamp mounted near the rotameter permitted visual observation of the platinum float. Connection to the reaction tube was made by a spherical joint, the Hastelloy C ball being ground slightly under size to allow for expansion.

The hydrocarbon was also passed through a rotameter or, if liquid, alternatively delivered by a suitable pump.

sorption of radiant energy from the furnace elements by the thermocouples. The reaction times listed are those calculated from the volume of the tube, average temperature, and total moles of reactants and diluents introduced per unit time but neglecting volume changes due to reaction or nonideal behavior of the gases.

For reactions incorporating oxygen, tubes with two or three reaction sections separated by mixing zones were used. Oxygen could then be introduced either with the other reactants or after some dehydrogenation had occurred.

In order to isolate the unsaturated hydrocarbon products and prevent their reacting with HI or residual I_2 after emergence from the reaction tube, the hot, gaseous effluent was quenched with a solution which preferentially absorbed and reacted with HI and I_2 . In some experiments the gases, after passage through a small-volume, heated (400°) Vycor tube, were bubbled through a solution of sodium acetate in ethylene glycol (weight ratio, 0.5:1) held at 150° . In others, as shown in Fig. 2, the gases were mixed rapidly, first with a large quantity (e.g., 10 volumes) of steam and then with a spray of aq. NaOH or aq. HI solution. Temperature reduction and neutralization were thus accomplished within a few milliseconds. The latter procedure was necessary for satisfactory recovery of diolefinic products. A series of condensers, separatory receivers, and traps then served to separate the quench solution from the organic reaction products.

Gaseous and liquid products were analyzed by mass spectrometric (m.s.) and gas-liquid chromatographic (g.l.c.) methods. Occasionally the liquids were distilled and the fractions analyzed by infrared. The g.l.c. analyses were normally carried out using a 50 ft. by 0.25 in. column packed with 20% dimethylsulfolane on 40-60 mesh firebrick operated with a helium flow of 50 cc.

TABLE I
REACTION OF IODINE WITH ETHANE, PROPANE, AND ISOBUTANE
Flow Experiments at One Atmosphere

| Temperature, $^\circ\text{C}$. | C_2H_6 | | C_3H_8 | | | $i\text{-C}_4\text{H}_{10}$ |
|--|------------|------------------|-------------------|------------------|-------------------|-----------------------------|
| | 600 | 685 | 525 | 550 | 685 | 495 |
| I_2/C_nH_{2n+2} | 0.64 | 4.6 | 0.66 | 0.86 | 1.73 ^a | 0.4 |
| Reaction time, sec. | 18 | 1.3 | 40 | 36 | 0.28 | 25 |
| Quench | | | | | | |
| I_2 reacted, % | ... | 24 | ~80 | ~60 | 68 | ~90 |
| Moles/100 moles C_nH_{2n+2} introduced | | | | | | |
| C_nH_{2n+2} | 59.0 | 1.9 | 56.0 | 50.1 | 2.9 | 66.5 ^e |
| C_nH_{2n} | 37.7 | 72.0 | 12.8 | 48.4 | 87.0 | 28.8 ^e |
| C_nH_{2n-2} | <0.1 | 10.0 | 0.3 | 1.1 | 8.6 ^f | ... |
| $C_{<n}$ hydrocarbons | 0.2 | 0.1 | 2.7 | 3.8 | 5.4 | 0.5 |
| C_{2n} hydrocarbons | ≥ 1.2 | 1.3 ^g | 0.04 ^h | 0.2 ^h | ... | .5 ⁱ |
| H_2 | 3.7 | 6.6 | 1.2 | 2.5 | ... | .4 |
| Organic iodides | ... | 4.9 | 29.2 ^d | 1.3 | ... | ... |

^a Diluted with 0.52 atm. He. ^b NaOAc-glycol. ^c Steam-NaOH. ^d Effluent vapors cooled to 200° and bubbled through ethylene glycol in pyridine at 70 - 90° ; organic iodides converted to pyridinium iodides but expressed as C_3H_7I . ^e No $n\text{-C}_4\text{H}_{10}$ or $n\text{-C}_3\text{H}_8$ detected. ^f $\text{CH}_2=\text{C}=\text{CH}_2$, 2.6; $\text{CH}_3-\text{C}\equiv\text{CH}$, 6.0. ^g C_4H_8 , 0.5; C_4H_6 , 0.8. ^h Benzene. ⁱ C_8H_{10} (>90% *p*-xylene) + C_8H_{18} .

The quartz (Vycor) reaction tube (1.2-4.0 cm. diameter, 40-180 cc. reaction volume; Fig. 2) provided for separate pre-heating, followed by rapid and thorough mixing of the reactant vapors and inert diluent (N_2 or He), if present. The reported reaction temperature is an average of temperatures over the length of the reaction zone. The latter values varied considerably because of the endothermicity of the reactions and the ab-

per minute at 30 or 0° . The HI and I_2 contents of the gaseous product were inferred from analysis of the quench solution. With the glycol solution this determination was approximate because of side reactions. The reactant iodine was also determined from the rotameter setting or occasionally from the loss of weight from the pressure vessel.

Materials.—Reagent grade (resublimed, Baker and Adamson) iodine was used without further purification. Most of the hydrocarbons were commercially available "pure" grade materials of 99.5+ % purity. In general, these were analyzed by the same procedures used for the reaction products. Cylinder oxygen, 99.9+ %, was used as received.

Results

Typical data for the reaction of elemental iodine with ethane, propane or isobutane in a flow system are given

(1) (a) A. Etard and H. Moissan, *Bull. soc. chim.*, [2] **34**, 69 (1880); *Ber.*, **13**, 1862 (1880); (b) F. J. Nellensteyn, *Chem. Weekblad*, **21**, 102 (1924); *Chem. Abstr.*, **18**, 1976 (1924); (c) K. Shishido and H. Nozaki, *J. Soc. Chem. Ind. Japan*, **47**, 819 (1944); *Chem. Abstr.*, **42**, 6351h (1948).

(2) J. H. Raley, U. S. Patent 2,901,518 (1959); J. H. Raley and R. D. Mullineaux, U. S. Patent 2,880,252 (1959).

(3) (a) R. D. Mullineaux and J. H. Raley, *J. Am. Chem. Soc.*, **85**, 3178 (1963); (b) L. H. Slauch, R. D. Mullineaux, and J. H. Raley, *ibid.*, **85**, 3180 (1963).

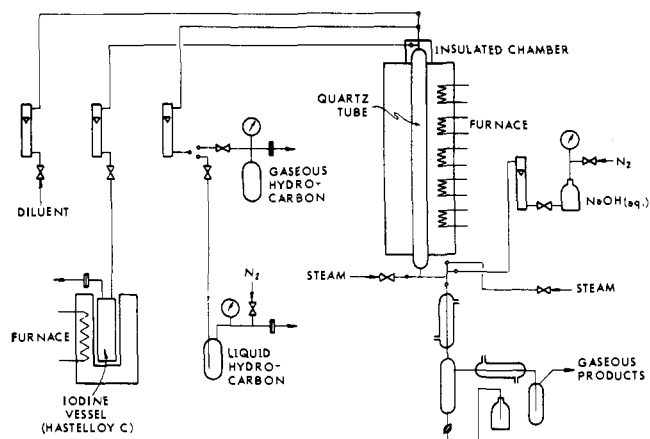


Fig. 1.—Apparatus.

in Table I. If the reaction is suddenly halted by "quenching" the effluent vapors (see Experimental) the predominant organic product is the corresponding monoolefin. Under these conditions hydrogen iodide accounts for 90% or more of the abstracted hydrogen and nearly all of the reacted iodine. If the vapors are allowed to cool before neutralization, however, substantial amounts of organic iodides are formed.

At very high conversion, ethane produces acetylene and propane gives methylacetylene and allene in significant quantities.

Small amounts of dimeric products were also observed. The principal dimer from propane was benzene. From isobutane an aromatic fraction (>90% *p*-xylene) and one or more octenes were found. Dimer yields were essentially independent of temperature, iodine mole fraction, or reaction time. Reaction of iodine with propylene or isobutylene, or pyrolysis of a 2:1 mixture of isobutylene and isobutyl iodide, gave only slightly larger amounts of the corresponding dimers.

With *n*-butane and *n*- or isopentane, the monoolefinic products are accompanied by substantial amounts of the corresponding conjugated dienes (Table II). At

TABLE II
REACTION OF IODINE WITH *n*-BUTANE, *n*-PENTANE, AND ISOPENTANE

| | <i>n</i> -C ₄ H ₁₀ | <i>n</i> -C ₅ H ₁₂ | <i>i</i> -C ₅ H ₁₂ |
|--|--|--|--|
| Temperature, °C. | 575 | 525 | 548 |
| I ₂ /C _n H _{2n+2} | 1.87 | 1.0 | 1.5 |
| Reaction time, sec. | 1.5 | 4.0 | 2.6 |
| I ₂ reacted, % | 52 | 77 | 75 |
| Moles/100 moles C _n H _{2n+2} introduced ^a | | | |
| C _n H _{2n+2} ^b | 12.8 | 35.5 | 9.8 |
| C _n H _{2n} ^b | 53.8 | 33.9 | 63.2 |
| C _n H _{2n-2} ^b | 25.4 | 15.3 | 17.5 |
| Skeletal isomers | Not detected. | 2.5 ^c | 1.0 ^d |
| C< _n hydrocarbons ^e | 3.6 | 3.4 | 2.7 |
| C> _n hydrocarbons ^e | 3.7 ^f | 1.2 | 3.2 ^g |
| Organic iodides | Trace | 0.4 | 0.6 |
| H ₂ | ≤ 0.5 | < 1 | < 1 |

^a Steam-NaOH quench. ^b Same carbon skeleton as reactant. ^c 2-Methyl-2-butene, 1.3; isopentane, 0.8; 2-methyl-1,3-butadiene, 0.4; may include traces of cyclopentene and 1,4-pentadiene. ^d 1,3-Pentadienes. ^e Expressed as equivalents of reactant hydrocarbon. ^f Largely *o*-xylene. ^g C₁₀ aromatics, 0.5; C₈-C₉ aromatics, 0.7.

475° to 575, with a variety of initial iodine concentrations and reaction times, these products account for over 90% of the reacted paraffin. No skeletal isomerization was observed with *n*-butane (or with isobutane; Table I). The limited isomerization of C₅ structures is discussed in a later paper.^{3b}

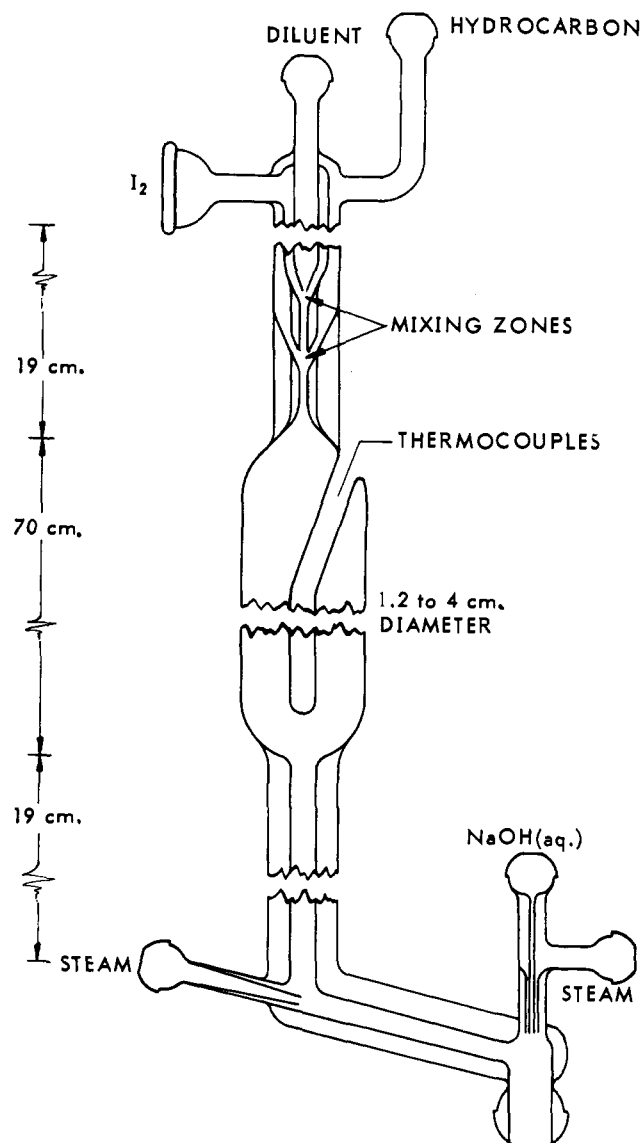
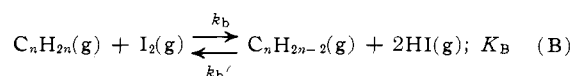


Fig. 2.—Quartz reaction tube.

From cyclopentane and methylcyclopentane, even at relatively low temperature and initial iodine concentration, the corresponding dehydrogenation products were accompanied by solid, carbonaceous deposits in the reaction tube. No isomerization of methylcyclopentane (or products therefrom) to form benzene was detected.

Methane undergoes but little net reaction. At 750–815° (I₂/CH₄ = 1) only 13–18% conversion was obtained in 1 sec. The organic products included (in moles/100 moles of reacted methane at 750°): CH₃I (21), C₂H₂ (4.4), and 1,3-butadiene (1.3).

Comparison with Calculated Equilibria.—The distribution of hydrocarbons of unchanged carbon skeleton from the experiments reported in Tables I⁴ and II is compared in Table III with the distribution calculated from the simultaneous equilibria⁵



(4) Omitted are experiments in which the reacted I₂ was not determined.

(5) When more than one unsaturated isomer is present, these equilibria are, of course, composites of the equilibria for each isomer.

TABLE III
 EXPERIMENTAL AND CALCULATED^a PRODUCT DISTRIBUTIONS^b

| | C ₂ H ₆ , 685 | | C ₃ H ₈ , 685 | | Reactant C _n H _{2n-2} , temp., °C. | | | | i-C ₄ H ₁₀ , 548 | |
|--|-------------------------------------|---------|-------------------------------------|--------|--|-------|--|-------|--|--------|
| | Exptl. | Calcd. | Exptl. | Calcd. | n-C ₄ H ₁₀ , 575 | | n-C ₅ H ₁₂ , 525 | | Exptl. | Calcd. |
| K _A | | 5.289 | | 51.65 | | 18.18 | | 13.00 | | 34.84 |
| K _B | | 0.02476 | | 0.0836 | | 1.234 | | 4.182 | | 0.9246 |
| Moles/100 moles C _n hydrocarbon | | | | | | | | | | |
| C _n H _{2n+2} | 2.3 | 3.2 | 2.9 | 1.8 | 13.9 | 7.8 | 41.9 | 32.6 | 10.8 | 7.4 |
| 1-C _n H _{2n} | .. | .. | .. | .. | 19.7 | 15.8 | 7.3 | 7.7 | .. | .. |
| trans-2-C _n H _{2n} | .. | .. | .. | .. | 22.0 | 26.6 | 21.5 | 19.1 | .. | .. |
| cis-2-C _n H _{2n} | .. | .. | .. | .. | 16.8 | 18.1 | 11.2 | 19.5 | .. | .. |
| 2-Methyl-1-butene | .. | .. | .. | .. | .. | .. | .. | .. | 22.9 | 31.4 |
| 2-Methyl-2-butene | .. | .. | .. | .. | .. | .. | .. | .. | 42.4 | 36.9 |
| 3-Methyl-1-butene | .. | .. | .. | .. | .. | .. | .. | .. | 4.5 | 5.0 |
| Total C _n H _{2n} | 85.8 | 86.0 | 88.4 | 90.6 | 58.5 | 60.5 | 40.0 | 46.3 | 69.8 | 73.3 |
| 1,3-C _n H _{2n-2} | .. | .. | .. | .. | 27.6 | 31.7 | 14.5 (trans) | 9.7 | 19.4 | 19.3 |
| | | | | | | | 3.6 (cis) | 11.4 | | |
| CH ₂ =C=CH ₂ | .. | .. | 2.6 | 1.6 | .. | .. | .. | .. | .. | .. |
| CH ₃ -C≡CH | .. | .. | 6.1 | 6.0 | .. | .. | .. | .. | .. | .. |
| HC≡CH | 11.9 | 10.8 | .. | .. | .. | .. | .. | .. | .. | .. |
| I ₂ reacted, % | 24 | 23.4 | 68 | 61 | 52 | 66 | 77 | 88 | 75 | 75 |

^a Equilibrium constants were calculated from data compiled by the American Petroleum Institute⁶ (for the hydrocarbons) and the National Bureau of Standards⁷ (for HI). Values at the experimental temperatures were obtained by interpolation using the expression: $\log K = (A/T) + B$. Only the reactant paraffin and those products with the same carbon skeletal structure were considered in the equilibrium system. Experimental yields of these products were normalized to 100 for comparison with the calculated values. The assumption made in this normalization is that the H/C ratio of the composite of all other products is the same as that of the composite of the normalized species. Data from a large number of experiments support this assumption. ^b See Tables I and II for reaction conditions.

It is clear that, disregarding isomer distribution, the systems approach the compositions defined by these equilibria except for small contributions from irreversible decomposition, condensation, and iodide-forming reactions.

In contrast, the observed distributions of the isomeric monoolefins from *n*-butane and the pentanes, as well as of the conjugated diolefins from *n*-pentane, differ significantly from the calculated values. The same monoolefin isomer distribution was observed at a given temperature regardless of total monoolefin yield or the conditions used to obtain that yield. Furthermore, data from the iodine-catalyzed isomerization of 1- or 2-butene are in agreement with those in Table III and a similar distribution has been reported from the isomerization of *n*-butenes over bauxite.⁸

When the reaction of *n*-butane or isopentane is limited by decreasing the reaction time, the ratio C_nH_{2n-2}/C_nH_{2n} is increased substantially, but the diolefin yield is little affected (Table IV). Under some conditions the latter even exceeds the equilibrium value.

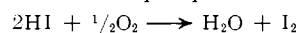
 TABLE IV
 EFFECT OF REACTION TIME AT 550°

| Reaction time, sec. | <i>n</i> -Butane (I ₂ /C ₄ H ₁₀ , 1.3) | | | Isopentane (I ₂ /C ₅ H ₁₂ , 1.5) | | |
|--|--|------|---------------------|--|------|---------------------|
| | 0.7 | 1.3 | Equil. ^a | 1.3 ^b | 2.6 | Equil. ^a |
| C _n H _{2n-2} converted, % | 51 | 76 | 82 | 69 | 90 | 92 |
| C _n H _{2n-2} /C _n H _{2n} | 0.38 | 0.28 | 0.24 | 0.42 | 0.28 | 0.27 |
| C _n H _{2n-2} yield, % | 14 | 16 | 16 | 19 | 18 | 20 |

^a Calculated. ^b I₂/C₅H₁₂, 1.7.

Effect of Oxygen.—The effect of adding oxygen to an iodine-hydrocarbon system has also been determined. Typical results are given in Table V for a mixture of *n*-butane and 1-butene. The oxygen reacts rapidly, and additional butane and *n*-butenes are consumed, principally to form butadiene. The major effect is that expected from (1) a selective oxidation of

HI to form I₂, and (2) reaction of the latter with the hydrocarbons toward establishment of a new equilibrium position. This view is supported by the agreement between the observed oxygen consumptions and those calculated for the examples of Table V from the measured⁹ rate of the vapor phase reaction



Carbon monoxide was the only organic, oxygen-containing product found which could be attributed to hydrocarbon oxidation. Decomposition products, various C₁–C₃ hydrocarbons, increased slightly. The ratio of this increased decomposition to the CO formed suggests that, for each C₄ species which reacts with oxygen, one carbon atom appears as CO and three as C₁–C₃ hydrocarbons.

 TABLE V
 EFFECT OF OXYGEN AT 550 ± 5°

| Reactants | 0.75 | 1.0 | 1.0 | 1.0 |
|---|------|------|------|------------------|
| <i>n</i> -C ₄ H ₁₀ /1-C ₄ H ₈ | 0.75 | 1.0 | 1.0 | 1.0 |
| I ₂ /hydrocarbons | 0.65 | 0.76 | 1.3 | 1.5 |
| O ₂ /hydrocarbons | 0 | 0.23 | 0 | 0.12 |
| Reaction time, sec. | 1.1 | 0.9 | 1.4 | 1.0 ^d |
| O ₂ reacted, % | .. | 91.0 | .. | 86.4 |
| Moles/100 moles hydrocarbon introduced ^b | | | | |
| <i>n</i> -C ₄ H ₁₀ ^c | 21.0 | 12.6 | 16.7 | 9.9 |
| <i>n</i> -C ₄ H ₈ ^c | 55.0 | 42.6 | 51.2 | 41.1 |
| 1,3-C ₄ H ₆ | 20.2 | 34.3 | 22.4 | 36.7 |
| C ₁ –C ₃ hydrocarbons ^d | 1.6 | 5.8 | 1.2 | 3.2 |
| CO | 0 | 5.5 | 0 | 1.2 |
| Condensation and oxidn. prod. ^d | 2.2 | 1.0 | 1.9 | 1.2 |

^a O₂ admitted after 0.3 sec. ^b Steam–NaOH quench. ^c No skeletal isomers detected. ^d Expressed as equivalents of reactant hydrocarbons.

With decreasing iodine or increasing oxygen initial concentrations, the iodine-catalyzed oxidation of the hydrocarbons increases continuously, culminating in excessively high reaction temperature.

With *n*-butane the equilibria A and B were shifted in the expected manner also by the introduction of

(6) "Selected Values of Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Institute of Technology, Pittsburgh, Penna., December 31, 1952.

(7) "Selected Values of Chemical Thermodynamic Properties," Series III, U. S. Natl. Bur. Standards, Washington, D. C., June 30, 1948.

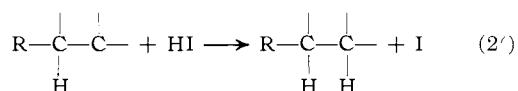
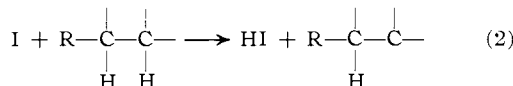
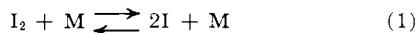
(8) H. H. Vogt and N. C. May, *J. Am. Chem. Soc.*, **68**, 550 (1946).

(9) G. G. Baylé and C. R. Gum, private communication.

ethylene. Ethane was produced and a corresponding additional amount of *n*-butane and *n*-butenes were dehydrogenated. The $\text{HI}-\text{C}_2\text{H}_4$ reaction was sufficiently slower than the $\text{I}_2-\text{C}_4\text{H}_{10}$ reaction, however, that reversible decomposition reactions became important before over-all equilibrium was established.

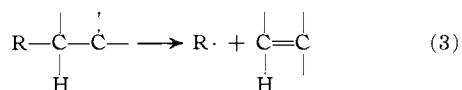
Discussion

A free radical mechanism consisting of successive hydrogen abstraction reactions involving both atomic and molecular iodine encompasses all of the experimental observations. The formation of free radicals from the hydrocarbon is attributed, as in iodine-catalyzed pyrolyses,¹⁰ to attack by iodine atoms produced by the equilibrium dissociation of I_2 . At 800°K . and $p_{\text{I}_2} = 0.5$ atm., the equilibrium pressure of iodine atoms is 3 mm.¹¹ Reaction 2 is endothermic by 27 ± 3 kcal./

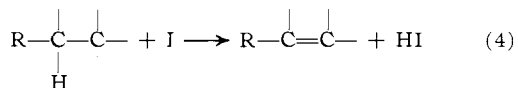


mole for ethane and for attack at the primary positions of higher alkanes.¹² For secondary and tertiary positions in alkanes the corresponding values are estimated as 23 and 18 kcal./mole,¹³ respectively, while for allylic positions the endothermicity should be ~ 10 kcal./mole. One should expect, therefore, a substantial selectivity for attack by atomic iodine on the various carbon-hydrogen bonds and a reflection of this selectivity in temperature requirement.

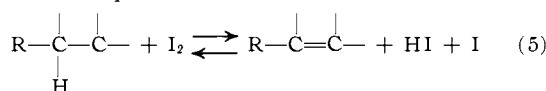
At very low initial I_2 concentrations, radical decomposition by cleavage of β -carbon-carbon bonds predominates^{3a, 10b, 10d}



With the high initial iodine concentrations in this study, however, another reaction leading to dehydrogenation supersedes 3. There are two paths which might be suggested



and the over-all process



ΔH for reaction 5 for isopropyl and *sec*-butyl radicals $\sim +5$ kcal./mole. Although 4 should have a high specific rate in view of its exothermicity (~ 30 kcal./mole for the isopropyl or *sec*-butyl radical), 5 must also be considered in view of the known rapidity of reactions between alkyl radicals and I_2 ¹⁵ and the high ratio of molecular to atomic iodine.

(10) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 204; (b) H. J. Schumacher, "Chemische Gasreaktionen," Theodor Steinkopff, Leipzig, 1938, pp. 388-395; (c) G. K. Rollefson and R. F. Faull, *J. Am. Chem. Soc.*, **59**, 625 (1937); (d) S. Bairstow and C. N. Hinshelwood, *J. Chem. Soc.*, 1155 (1933).

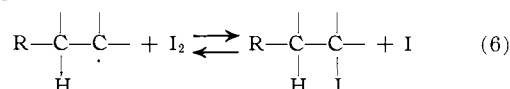
(11) Calculated from data in ref. 7.

(12) Using $D_{\text{HI}} = 71$ kcal./mole¹⁴ and $D_{\text{R-H}} = 98 \pm 3$ kcal./mole for $\text{R} = \text{C}_2\text{H}_5$, *n*- C_3H_7 , *n*- C_4H_9 .^{13, 14}

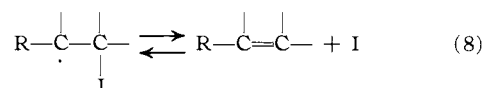
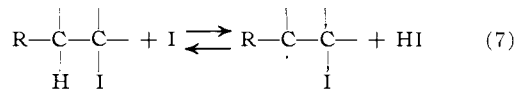
(13) T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954, p. 272.

(14) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 95-98.

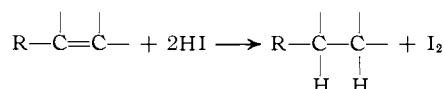
At lower temperatures, alkyl iodides would be the expected products from 6



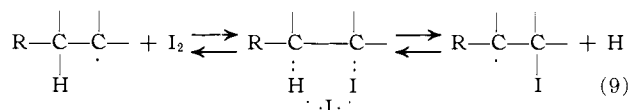
but, since these, at $\geq 300^\circ$, are known^{15, 16} to decompose rapidly, especially in the presence of iodine, or to react with HI, their role under the present conditions can be at most that of an intermediate. The most plausible steps for 5, including 6, are those suggested by Benson,¹⁶ who has analyzed the original data of Jones and Ogg¹⁷ for the I_2 -catalyzed pyrolysis of *n*- $\text{C}_3\text{H}_7\text{I}$. They are 7 and 8



The sum of 6, 7, and 8 is 5. Furthermore, combination of the reverse reactions for 8, 7, 6, and 2 provides a route for the reverse of the over-all dehydrogenation reaction



Benson¹⁶ has pointed out that 8 may participate in lowering the activation energy of 7. An additional possibility is that 6 and 7 are combined in a single reaction (9)



A path for the reverse of the over-all reaction is also provided by the formation of alkyl iodide from HI and olefin,¹⁸ followed by the reverse of 6 and of 2.^{15b} Alternatively, formation of an alkyl radical may occur directly from reaction of HI and an olefin by the reverse of 4, as suggested by Bose and Benson.¹⁸

The sequence of 2 and 4 or 5 also may be applied to the conversion of monoolefins to the corresponding $\text{C}_n\text{H}_{2n-2}$ products. Step 2 is faster for attack at an allylic position and, where conjugated diolefins can be formed, hydrogen atom abstraction from the allylic radical also is rapid. Therefore, $k_b/k_a \gg 1$. Since both calculated and experimental results have established that K_B/K_A for *n*-butane and *n*- and isopentane is in the range of 0.025 to 0.5 at 475 - 575° , $k_b/k_a \gg K_B/K_A$. Consequently, the diolefin/monoolefin ratio must increase continuously as the system is moved from an equilibrium- toward a rate-controlled composition. Also, since $k_b' \gg k_a'$, the partial equilibrium B is maintained at much shorter reaction times than are required for establishment of A. Under such circumstances, the diolefin yield can equal or exceed (and the monoolefin yield will be less than) that corresponding to over-all equilibrium. With *n*-butane at 500° and $\text{I}_2/\text{C}_4\text{H}_{10} = 1.3$, the observed compositions of the system at 2-7 sec. reaction time are in good agreement with those calculated from the measured I_2 conversions assuming attainment of the partial equilibrium B.

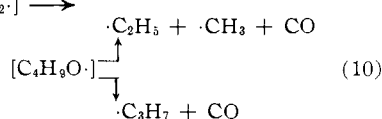
(15) (a) See ref. 14, pp. 263-274, 733-747, for discussion of $\text{R}\cdot + \text{I}_2 \rightarrow \text{RI} + \text{I}$ and thermal reactions of RI; (b) S. W. Benson and E. O'Neal, *J. Chem. Phys.*, **34**, 514 (1961).

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The proposed mechanism also is qualitatively consistent with the results given in Table V. At high initial I_2 concentration, the oxidation of hydrocarbon radicals *via* a sequence such as 10 should be minimized



by 5 or 4 and by 2' and the oxygen principally consumed by reaction with HI. With I_2 (and, hence, HI) in smaller amounts, or at higher oxygen concentrations, 10 becomes more important.

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High Temperature Reactions of Iodine with Hydrocarbons. II. Aromatization

BY RICHARD D. MULLINEAUX AND JOHN H. RALEY

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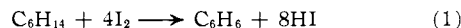
Aromatic hydrocarbons and hydrogen iodide are the predominant products from the reaction of elemental iodine with hydrocarbons containing a chain of six or more adjoining, nonquaternary carbon atoms. The structures of the aromatic products are defined by the structure of the reactant hydrocarbon and a specific mode of decomposition of a cyclic free radical intermediate. Ring closure is attributed to cyclization of a triene to a cyclohexadiene. If the hydrogen iodide decomposes *in situ*, further reaction of the resultant iodine ensues.

Introduction

In part I of this series,¹ the reversible, free radical reactions of elemental iodine with C_2 – C_5 paraffins at high temperatures were discussed. This paper describes the reactions of iodine with straight and branched chain, higher members of the aliphatic series.

Results

The type of product obtained from the reaction of a higher alkane with elemental iodine at *ca.* 500° is markedly influenced by the mole fraction of reactant iodine. Typical results are illustrated in Fig. 1 for *n*-hexane. At the conditions used, *n*-hexane in the absence of iodine undergoes negligible reaction. The addition of ~1% iodine brings about an iodine-sensitized decomposition similar to that observed with many organic compounds,^{2,3} characterized by carbon-carbon scission reactions yielding methane and C_2 – C_5 hydrocarbons, mainly olefins, and interpretable by a Rice-Herzfeld⁴ type of mechanism. With further additions of iodine, degradation reactions become less important and C_6 compounds account for more than 80% of the products at the highest I_2/C_6H_{14} value shown. Benzene becomes the major product, accounting for 75% of the reacted hexane and corresponding to a 96% yield on iodine from reaction 1



Coincident with these increases is a rise in the saturate:olefin ratio of the C_2 – C_5 products to a value of ~6.

The products from the reaction of several C_6 – C_{10} aliphatic hydrocarbons with one or more moles of iodine are given in Table I. Except in the case of 2,2,5-trimethylhexane, the products formed in highest yield are aromatic hydrocarbons containing the same number of carbon atoms as the reactant. With *n*-hydrocarbons containing seven or more carbon atoms, however, aromatic products of lower carbon number are also observed, their relative importance increasing with increasing chain length of the original compound. Significantly, each lower (C_{n-x}) aromatic is accompanied by a nearly equivalent yield of a C_x paraffin. These C_x paraffins constitute the other major group of de-

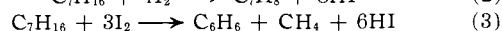
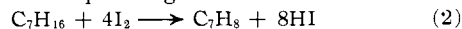
composition products. These data indicate a specific cleavage path rather than random or successive decomposition reactions. A single, specific cleavage process is also inferred from the structures of the aromatic products from *n*-decane. The infrared spectra showed that the C_{10} fraction contained both monosubstituted and *o*-disubstituted benzenes, whereas the C_8 and C_9 aromatics consisted of only monosubstituted compounds. A very small yield of naphthalene, but no methylindanes nor methylindenes, was found.

The results for 2,5-dimethylhexane are in distinct contrast. Although the yield of total aromatics is comparable to that from *n*-octane and 1-octene, benzene and toluene account for less than 2% (instead of 40–50%) of the aromatic material.

Other pertinent observations are: (a) the high ($\geq 95\%$) *o*-content of the xylenes from the straight-chain compounds and the high *p*-content of the xylenes from 2,5-dimethylhexane, (b) the formation of *n*-octane from 1-octene, and (c) the greater reactivity of an olefin compared to the corresponding paraffin. These observations demonstrate the absence of methyl migration and confirm other conclusions drawn in the preceding paper.¹

Cyclohexane is converted almost exclusively to benzene. With a 30-fold excess of cyclohexane at 350°, however, a product containing a cyclohexene/benzene ratio of 2 was obtained. Cyclohexadiene or five-membered ring structures were not detected under any reaction conditions investigated.

The small amount of H_2 formed in these reactions in Vycor tubes is consistent with the well known rate of the homogeneous, vapor-phase decomposition of HI.^{5,6} Since this decomposition is subject to surface catalysis, especially by noble metals,^{7,8} the reaction tube in some experiments was partially filled with platinum-containing solids. As illustrated in Table II, both H_2 formation and the combined yield of toluene and benzene increased markedly, the latter exceeding that corresponding to reactions 2 and 3



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