sufficiently fast. The generally small effect of the S/V ratio established the reaction as essentially a homogeneous gas phase process.

Effect of Intensity.—The effect of intensity was studied in the range of 17×10^6 to 48×10^6 rad./hr. As expected from the similar product distributions obtained at thermal conditions and at 48×10^6 rad./hr., no effect of intensity was observed on the product distribution at comparable degrees of ethylene conversion. Generally, $G(-C_2H_4)$ decreased at higher intensities in the work using pile radiation. Some experiments were made with the Esso 3200 curie Co^{60} source of gamma radiation (*1*) at the same conditions of temperature, pressure and concentration. At these low intensities (0.1×10^6 rad./hr.) the G values were generally 8–10-fold higher than those obtained in the pile work. Comparison of these data with those reported by Lampe[3] for electron irradiation at even higher intensities than those of the present pile work shows that over approximately a 1000-fold intensity range the G values decrease with increasing intensity. The effect can be represented, at least approximately, with an inverse square root effect within the limits of the rather large errors involved in comparing such widely different irradiation conditions. The results are in a semi-quantitative way consistent with well-known intensity effects for the case of chain termination by bimolecular gas phase recombinations.

In the light of the results of this study, it seems reasonable to conclude that the effect of nuclear radiation is to accelerate a thermal free radical chain reaction for the ethylene–propane system. This conclusion can, of course, be made only for the experimental conditions at which strict comparison between thermal and radiation products was possible. The good agreement between the products obtained using either thermal or radiation initiation is in favor of the argument that the same processes of chain propagation must be operative in either case. Therefore, at the conditions of this work and for hydrocarbon chain reactions of this type, the hydrocarbon ions or excited species made in the initial interaction of radiation with hydrocarbons are apparently incapable of chain propagation. Therefore, in addition to their intrinsic interest in the area of hydrocarbon radiation chemistry, these results would point to the important role radiation-initiation could play as a convenient technique for elucidating the mechanism of ordinary hydrocarbon chain reactions.

The known reactivity of hydrocarbon ions and the very complex dependence of radical and ion lifetimes on experimental conditions make it difficult to generalize the free radical nature of radiation-induced hydrocarbon chain reactions to all mixtures and all experimental conditions. However, it appears likely that at least over the conditions of this work the radio-alkylation is a free radical chain process and no contributions from ionic species need to be invoked.

[CONTRIBUTION FROM THE ESSO RESEARCH & ENGINEERING COMPANY, LINDEN, NEW JERSEY]

The Controlled Chain Oxidation of *n*-Hexane Induced by Co-60 Radiation

BY P. J. LUCCHESI AND W. BARTOK

RECEIVED MARCH 2, 1960

The reaction between *n*-hexane and oxygen has been studied at 3.4 atm. total initial pressure and at 2/1 mole ratio of hydrocarbon to oxygen. This system was studied thermally and in the presence of 10^5 and 10^6 rad./hr. intensity Co-60 radiation in static experiments. In the temperature range of 150–235°, nuclear radiation initiates a controlled oxidation chain reaction with integral G values of 10^3 to 2×10^4 molecules of *n*-hexane converted per 100 ev. The products are mainly oxygenated hydrocarbons—epoxides, acetone, methanol. Above 235°, the reaction gives mainly degradation products, CO and CO_2, and the thermal reaction is so rapid that the acceleration due to radiation is not noticeable in static experiments. This controlled chain oxidation made possible by radiation initiation is affected by temperature, pressure and radiation intensity. Although little can be said about its mechanism, it is of intrinsic interest because it offers a technique for exploring hydrocarbon chain oxidations at conditions where the reaction is not initiated thermally.

Introduction

In the development of radiation chemistry with regard to hydrocarbons, most of the literature published to date has emphasized low temperature reactions characterized by the low 100 ev. yields ($G<10$) typical of nonchain radiation chemistry.[1–3] Recently, more attention has been given to the use of nuclear radiation to accelerate chain catalytic[1] and noncatalytic reactions of hydrocarbons[4–7] and thereby gaining some insight into ordinary hydrocarbon chain processes. One important chain reaction of hydrocarbons, vapor phase oxidation, has not been studied with radiation initiation, although some reports are available on the nonchain radiooxidation of hydrocarbons at quite low temperatures.[8–10] The study of oxidational chain processes presents both experimental and interpretive difficulties. The problems become even more complex when nuclear radiation is used as initiator, because the detailed mechanism is still obscure and

---

(1) E. Collinson and A. J. Swallow, *Chem. Revs.*, **56**, 471 (1956).

(2) *Discussions Faraday Soc.*, No. 12 (1952).

(3) B. M. Tolbert and R. M. Lemmon, *Radiation Research*, **3**, 52 (1955).

(4) P. J. Lucchesi, B. L. Tarmy, R. B. Long, D. L. Baeder and J. P. Longwell, *Ind. Eng. Chem.*, **50**, 879 (1958).

(5) P. J. Lucchesi, D. L. Baeder and J. P. Longwell, *Proc. Fifth World Petroleum Congress*, N. Y., June (1959).

(6) P. J. Lucchesi and C. E. Heath, THIS JOURNAL, **81**, 4770 (1959).

(7) W. Bartok and P. J. Lucchesi, *ibid.*, **81**, 5918 (1959).

(8) N. A. Bakh and V. V. Saraeva, *Zhur. Fiz. Khim.*, **32**, 209 (1958).

(9) V. V. Saraeva, N. A. Bakh, *et al.*, Paper presented at All-Union Conf. Appl. Radioactive and Stable Isotopes and Radiation, Moscow, April 1957.

(10) B. M. Mikhaeilov, *et al.*, paper presented at All-Union Conf. Appl. Radioactive and Stable Isotopes and Radiation, Moscow, April 1957.

one must deal with all the species made initially by radiation—with radicals, ions and excited species.[11]

However, despite these difficulties, it is of interest to study the radiation chemistry of hydrocarbon–oxygen systems at moderately low temperatures sufficient to sustain controlled chain oxidation. Hydrocarbon oxidation is a chain reaction in which the reaction temperature plays a crucial role. For example, the temperature must be sufficiently high to allow efficient chain initiation. However, it must not be high enough to support the branching chain reactions which lead to final degradation products, carbon oxides and water. For every system, there is a delicate balance of conditions which allows a controlled chain reaction to intermediate oxidation products. Since nuclear radiation is ideal as an initiator of chain reactions at virtually any condition of pressure and temperature, it can be used for initiating hydrocarbon oxidations at controlled conditions with respect to external variables.

This paper presents results of initial studies on the Co^{60} gamma-radiation induced reaction between *n*-hexane and oxygen.

Experimental

All studies reported in this work were made in static systems with electrically heated stainless steel reactors having a surface/volume ratio of about 1 $cm.^{-1}$. The experiments were done at a 2/1 mole ratio of *n*-hexane (Phillips 99% pure grade) to oxygen. Co^{60} gamma radiation sources of 2000 and 16,000 curies were used, corresponding to intensity levels of 10^5 and 10^6 rad./hr., respectively, in the oxidation experiments. The values of energy absorption rates were based on ferrous–ferric dosimetry[12] and on methane radiolysis using as standard the *G* value of 5.7 molecules of hydrogen per 100 ev. at low temperatures. The dosimetry was considered reliable within ± 15%.

The static experiments reported in this work were performed both as thermal and as radiation-induced oxidations at otherwise identical conditions. The *G* values reported are integral radiation yields of molecules of *n*-hexane reacted per 100 ev., measured by comparing thermal and radiation experiments. In the range of 150–205° the thermal reaction was generally negligible and no correction was required. To obtain consistent results, it was necessary to compare radiation and thermal experiments using the same reactor to eliminate spurious surface effects. In fact, aged reactors were used throughout, since occasional experiments in freshly cleaned reactors gave complete degradation to carbon oxides and water even at low temperatures where the degradative oxidation was normally slight after aging the reactor. The reaction product generally consisted of an organic layer and of an aqueous layer. The organic layer was analyzed by gas-liquid partition chromatography, by infrared spectroscopy and by a fluorescent indicator adsorption method.[13] The solubility of the organic layers in phosphoric acid was used to determine their content of partially oxygenated products. The carbon contents of the small aqueous layers were determined by combustion.

Results and Discussion

Effects of Radiation.—The results of *n*-hexane conversion are shown in Fig. 1 for one-hour static experiments at 3.4 atm. total initial pressure. The results were obtained in purely thermal experiments and in radiation-induced oxidations at 10^5 and 10^6 rad./hr. intensities. The integral *G* values are given in Table I as molecules of *n*-hexane reacted per 100 ev. Below about 200°, there is no measurable thermal conversion at the conditions of these experiments. Radiation initiates a long-chain reaction with *G* values in the range of 1000–20,000. The radiation yields are higher at the lower of the two intensities studied. The amount converted increases with temperature, but the thermal reaction itself becomes appreciable already at 235°. Below about 235°, the reaction is one of controlled oxidation—*i.e.*, formation of *n*-hexane oxidation products, with only slight amounts of degradation products. Above this temperature the reaction gives mainly carbon oxides and water, whether it is induced thermally or by radiation. In fact, the thermal reaction is so rapid that no radiation effects could be discerned in the static experiments.

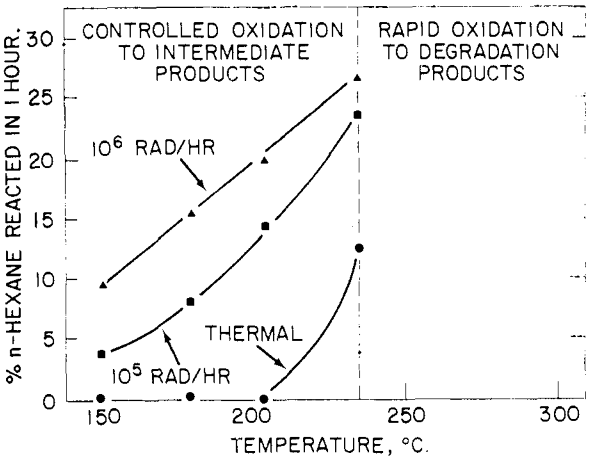

Fig. 1.—Effect of Co^{60} γ-radiation on oxidation of *n*-hexane; initial *n*-hexane/oxygen mole ratio = 2.0; total initial pressure = 3.4 atm.

TABLE I

INTEGRAL *G* VALUES FOR RADIATION-INDUCED OXIDATION OF *n*-HEXANE

Total pressure = 3.4 atm.; *n*-hexane/oxygen mole ratio = 2/1

Intensity, rad./hr.	Temp., °C.	*G*, Molecules of *n*-hexane reacted/100 ev.[a]
10^5	150	3,000 (2.7)
10^6	150	950 (8.4)
10^5	178	7,300 (6.5)
10^6	178	1,700 (12.0)
10^5	205	14,600 (13.1)
10^6	205	2,000 (17.7)
10^5	235	16,800 (24.0)
10^6	235	1,800 (25.1)

[a] Values of the per cent. conversion of *n*-hexane are given in parentheses. The *G* values at higher conversions are listed only to illustrate the long-chain nature of the oxidation process.

Effect of Absorbed Dose on Conversion.—Table II summarizes the results of *n*-hexane conversion as a function of the absorbed dose at an intensity of 10^6 rad./hr. and in the temperature range where the controlled oxidation predominates. The decreasing rate at increasing dosage is typical for static experiments and reflects the depletion of the reactants with time. However, the cause of the complete inhibition of the reaction at the higher

---

(11) M. Burton, "Radiation Chemistry," in Annual Reviews of Physical Chemistry, Annual Reviews, Inc. (Calif.) **1**, 113 (1950).

(12) N. Miller, *J. Chem. Phys.*, **18**, 79 (1950).

(13) B. T. Witham in "Vapour Phase Chromatography," D. H. Destry ed., Butterworth Scientific Publications, London, 1957, p. 395.

conversion levels remains unexplained. In view of the large decrease of free energy for oxidation reactions, there cannot be any question of the extent of reaction being limited by equilibrium. A likely possibility is that the oxidation is inhibited by one of the intermediate products, however, too little is known of the process for an attempt to identify such an intermediate.

Table II

n-Hexane Conversion as a Function of Radiation Dose at 10^6 Rad./Hr. Intensity

Radiation dose abs., megarads	*n*-Hexane conversion, % 178°	205°
0.5	5.5	7.0
1.0	..	17.0
2.0	9.5	..
3.0	13.0	16.0
4.7	..	15.5

Effect of Pressure.—At 205° and at a 2/1 mole ratio of *n*-hexane to oxygen, static experiments at 10^6 rad./hr. showed a considerable pressure effect. Increasing the total initial pressure from 3.4 to 10 atm. increased the *n*-hexane conversion from 17 to 40% with *G* values of about 6000 hexane molecules converted per 100 ev. The oxidation at 10 atm. remained a controlled reaction giving a low yield of carbon oxides corresponding to about 2% of the initial *n*-hexane concentration.

Composition of Products.—At temperatures higher than about 235°, large amounts of CO, CO_2 and water are formed. At 150–235°, the major products are oxygenated hydrocarbons obtained in a highly complex mixture. The four major products were unidentified epoxides of *n*-hexane containing 3- and 4-membered cyclic structures, 2,5-dimethyl tetrahydrofuran, acetone and methanol, in decreasing order of abundance. The presence of the cyclic ethers as major products agrees with the thermal oxidation results of Norrish and Bailey.[14]

The detailed mechanism of *n*-hexane oxidation in the presence of nuclear radiation is obviously very complex. However, it is of interest that radiation initiation can be used for achieving the controlled chain oxidation of hydrocarbons. This chain reaction is sensitive to radiation intensity, temperature and pressure. At some conditions it is very sensitive to the state of the reactor walls. Whether this radiation-induced reaction is a free radical chain process due to the radiation initiation or an entirely new kind of chain reaction propagated by ions, for example, is a question that cannot be answered on the basis of this work. In either case, it is important, since even if the reaction is only an accelerated thermal chain, controlled hydrocarbon oxidation chain processes are so difficult to achieve thermally that the radiation technique provides a useful initiation device for this area of hydrocarbon chemistry.

(14) H. C. Bailey and R. G. W. Norrish, *Proc. Royal Soc.* (*London*), **A212**, 311 (1952).

[Contribution from the Esso Research and Engineering Company, Linden, New Jersey]

Radiation-induced Carbonium Ion Reactions and the Chain Nature of Acid Catalyzed Isomerization

By P. J. Lucchesi, C. E. Heath and D. L. Baeder

Received March 2, 1960

Co-60 gamma rays and X-rays have been found to accelerate the rate of isomerization of *n*-hexane and methyl cyclopentane catalyzed by $AlCl_3$. This acceleration at 30–50° indicates a fairly long chain reaction, as evident from the high radiation yields observed with Co-60 radiation and the very high values (5×10^3) obtained with low intensity X-rays. The reaction is a chain reaction for both *n*-hexane and MCP even at conditions where little or no decomposition or disproportionation side reaction occurs. The results offer directly measured values of the chain length for these chain reactions and tend to support the chain carbonium ion mechanism for acid catalyzed isomerization.

Introduction

The skeletal isomerization of alkanes over acid catalysts such as activated aluminum chloride has been a commercially important chemical reaction for the past decade. It has also received considerable attention from the theoretical viewpoint. In this connection, there has been some controversy concerning the mechanism of isomerization. For example, in the case of *n*-butane one view[1,2] suggests essentially a molecular mechanism in which the activated complex is formed between catalyst and paraffin. In the field of the catalyst molecule (AlX_4^-, $HAlX_4$, etc.) there is a concerted, molecular rearrangement of the alkane without formation of a charged carbonium ion intermediate. However, Pines[3] has criticized this mechanism on the ground that pure HX/AlX_3 systems do not catalyze the isomerization of *n*-butane but require the presence of trace promoters such as olefins.[4]

The mechanism proposed to explain these effects, now widely applied to the isomerization of alkanes other than *n*-butane, considers the isomerization as a chain mechanism involving carbonium ions. These are normally written as free ions but they are, of course, associated with the catalyst.

$$RH + AlX_3 + \text{Initiator} \longrightarrow R^{\oplus}$$

$$CH_3CH_2CH_2CH_3 + R^+ \longrightarrow CH_3\,CH\overset{\oplus}{C}H_2CH_3 + RH$$

$$CH_3\overset{\oplus}{C}HCH_2CH_3 \longrightarrow (CH_3)_3C^{\oplus}$$

$$(CH_3)_3C^{\oplus} + CH_3CH_2CH_2CH_3 \longrightarrow$$

$$\text{Isobutane} + CH_3\,\overset{\oplus}{C}HCH_2CH_3\text{, etc.}$$

---

(1) J. D. Heldman, This Journal, **66**, 1789 (1944).

(2) T. M. Powell and E. G. Reid, *ibid.*, **67**, 1020 (1945).

(3) H. Pines, "Advances in Catalysis," Vol. I, Academic Press, Inc., New York, N. Y., 1948, pp. 201–255.

(4) H. Pines and J. D. Wackher, This Journal, **68**, 595 (1946).