clude the likelihood of reversal to the random coil form; otherwise its formation will be of no consequence.[29] Without resort to a detailed analysis, it is apparent in light of the considerations presented above that the minimum size of the embryo which offers reasonable assurance of subsequent growth to stable size will increase as T_m is approached (*i.e.*, as $\Delta T \rightarrow 0$). Moreover, the form of the dependence of this minimum size on ΔT may be expected to duplicate eq. 6, and this leads directly to (8).

In order to apply the foregoing scheme to the transformation process (which occurs at temperatures $T > T_m$), we assume that I remains in equilibrium with H. Then

$$I = K_2 H^{1/3} \tag{9}$$

where $K_2 = k_2/k_2'$ and H and I are concentrations of H and I, respectively. Since the rate R of transformation must be governed by step 1

$$R = R_1 = k_1 I = k_1 K_2 H^{1/3} \tag{10}$$

The equilibrium constant K for reaction 1 is related to the constants for the scheme (3) as

$$K^{1/3} = K_1 K_2 = k_1 K_2 / k_1'$$

Hence

$$R = K^{1/3} k_1' H^{1/3} \tag{11}$$

The temperature coefficient of the equilibrium constant K is positive and very large as previously noted. The observed temperature coefficient for k_1' is negative but smaller than that of $K^{1/3}$. Hence, the temperature coefficient of the latter dominates that of the former, with the result that the temperature coefficient of R is predicted to be positive and large in accordance with observation. The transformation should be one-third order according to eq. 11. Experimental results of this investigation are indecisive on this point (see above).

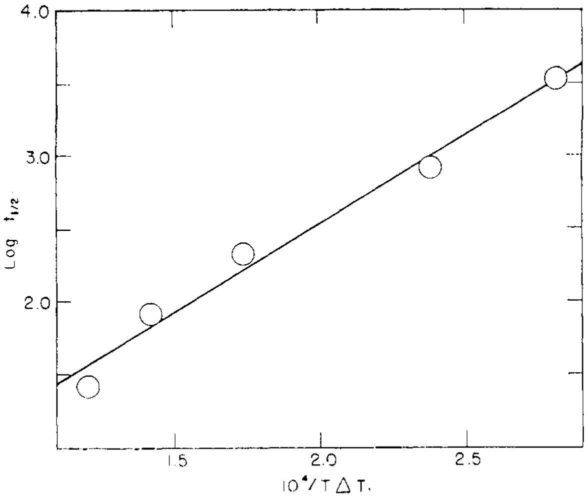

Fig. 8.—Logarithm of the half-time for reversion *versus* $1/T\Delta T$, where $\Delta T = T_m - T = 308 - T$ in °K.

Thus, the main features of the kinetics of the reversion and transformation processes can be satisfactorily explained by the foregoing scheme involving an intermediate, the formation of which is considered to be rate determining. The interpretation given is compatible with a model for the collagen protofibril consisting of a plurality of polypeptide chains which separate on transformation.

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[29] Regeneration of native structures by first joining three random coil polypeptide chains in suitable juxtaposition followed by stepwise helical coiling of successive units of the member chains has been considered. The kinetics become third order; although the temperature coefficient is negative, the rate is linear in ΔT rather than exponential in $-(T\Delta T)^{-1}$ as prescribed by eq. 8.

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

The Radiation-induced Chain Alkylation of Ethylene with Propane

BY W. BARTOK AND P. J. LUCCHESI

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The gas phase reaction of propane with ethylene has been studied in static experiments. Experiments performed using the mixed neutron-gamma radiation available from a nuclear reactor were also done thermally, without radiation. Propane-rich systems containing 4.5–10 mole % ethylene were investigated in the range of temperatures of 240–454°, at initial total pressures of 9 to 20 atm. Irradiations were done at two levels of intensity corresponding to energy absorption rates of 17×10^6 and 48×10^6 rad./hr. G values exceeding 100 molecules of ethylene reacted per 100 ev. establish the chain nature of the reaction. At the conditions of this work, radiation only accelerates the thermal process, since the products of both the thermal and the radiation-induced reactions were very similar at the same conversions of ethylene. Changing the surface/volume ratio by packing the reactor with stainless steel wire has practically no effect. The equivalence between the radiation-promoted and thermal reactions suggests that ions and other species peculiar to radiation-initiation are not an important factor at the conditions of this work. This also means that the radiation technique can be used to gain valuable insight concerning the mechanism of the ordinary thermal reaction and indicates the chain nature of alkylation.

Introduction

The question whether the chain reactions of hydrocarbons induced by ionizing radiation occur *via* free radical or other mechanisms remains unanswered to date. In the case of vapor phase alkylation reactions, the experimental evidence reported previously is overwhelming in favor of a chain mechanism[1–4] for the alkylation reactions of al-

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

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

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[4] W. Bartok and P. J. Lucchesi, THIS JOURNAL, **81**, 5918 (1959).

kenes or alkynes with paraffins. The chain nature of these processes is borne out by the high *G* values or 100 ev. yields obtained. Although, generally speaking, the results of the earlier work are in good accord with free radical type chain mechanisms, a more positive conclusion as to the mechanism is needed. Since in the initiation step radiation produces excited species, ions and free radicals, the radiation-promoted reaction could be an accelerated thermal (radical) process or a chain reaction propagated by species peculiar to radiation.

This question as to the mechanism of radiation-induced chain processes is important not only from the viewpoint of radiation chemistry but also in considering the ordinary chemistry of hydrocarbons. For example, if the radiation behaves essentially as an accelerator for thermal processes, then a convenient tool is available for initiating hydrocarbon chain reactions over a wide range of experimental conditions. This makes available a probe for establishing directly the chain nature of these reactions (data not available for alkylation reactions) and for elucidating the effect of experimental conditions on the chain length. However, at the present state of development, the free radical nature of radiation-induced hydrocarbon chain reactions such as alkylation is by no means generally established.

A good way to shed more light on the mechanism is to study the effect of radiation on the reaction products and to compare these products with those obtained thermally in the absence of radiation, but at the same conditions and degree of conversion. Under certain conditions, however, the radiation-induced chain reaction is so rapid that it has no thermal counterpart and the comparison cannot be made. Thus, for the relatively slow acetylene–propane reaction,[4] the products could be compared only at such high temperature levels that nuclear radiation had no measurable accelerating effect since the acetylene decomposed and polymerized too rapidly, while at lower temperatures the alkylation reaction could not be initiated without radiation.

In the present communication, the effects of nuclear radiation on the ethylene–propane reaction are reported. This system lends itself ideally to a systematic investigation of the products obtained thermally and with radiation at different temperature levels, because the purely thermal alkylation reaction also takes place at reasonable rates. As a source of radiation, the mixed neutron-gamma radiation available from a swimming pool reactor used previously[4] was applied to the ethylene–propane system. This paper compares the thermal and radiation-induced reactions and discusses the influence of temperature, radiation intensity and surface/volume ratio of the reactor.

Experimental

The ethylene–propane reaction was studied in the temperature range of 240–454°, at initial total pressures of 9 to 20 atm. Both the irradiation and the thermal experiments were conducted in static systems, using cylindrical reactors of identical construction. These stainless steel reactors, having a volume of 1.01 l., have been described in detail previously, and the experimental procedures were also the same as those employed for the propane–acetylene system.[4] Mixtures of Matheson instrument grade propane and ethylene were prepared without further purification and admitted into the reactor as in the previous work. After irradiation in the swimming pool nuclear reactor, the products were analyzed by gas chromatography which was also used for analyzing the products of the thermal experiments. A silica gel column at 91° was used for the determination of methane, ethane and unreacted ethylene and propane in the product. Propylene and higher molecular weight components were analyzed by means of a hexanedione column at 0°. The surface/volume ratio of the reactor was increased from 0.59 to 394 cm.$^{-1}$ by packing it with 200 mesh stainless steel wire cloth.

Dose rates were measured by means of the radiolysis of methane, using as standard a *G* value of 5.7 molecules of hydrogen per 100 ev. determined by the polymerization of acetylene as a dosimeter.[5,6] Two positions were used in the swimming pool reactor, corresponding to energy absorption rates of 48×10^6 and 17×10^6 rad./hr. with the methane dosimeter. The accuracy of this method is estimated to be ± 20%. The dose rate values were unaffected by changing the surface/volume ratio for the methane decomposition. The radiation yields, or *G* values, reported in this work are integral values obtained from the 100 ev. yields comparing radiation experiments with thermal experiments at otherwise identical conditions.

Results and Discussion

Radiation Yields and Reaction Rates.—The chain nature of the radiation-induced propane–ethylene reaction is clearly established by the high radiation yields obtained in the range of temperatures studied. Since, as pointed out later, the radioalkylation reaction is, at the conditions of this work, probably radical in nature, these high *G* values also establish the chain nature of the thermal reaction at these conditions. Using a value of about five to seven primary initiation acts per 100 ev. of energy absorbed, *G* values as high as 800 are obtained at an intensity of 48×10^6 rad./hr., and at a total pressure of 15–18 atm. The high values are indicative of chain processes in the reaction of ethylene with propane. Since no attempt was made to determine absolute G values of chain lengths, these results are minimum estimates and are given solely to illustrate the chain nature of the reaction.

The integral *G* values for ethylene disappearance generally decrease with dosage, or time, increase with temperature, and are insensitive to surface/volume ratio. These trends are also evident from the ethylene conversion data presented in Fig. 1. The rate of the ethylene–propane reaction is influenced strongly by irradiating the system. In fact, the thermal reaction was negligible at the conditions of the experiments which provided the data of Fig. 1. Due to the analytical difficulties in determining small changes in the concentration of propane, the rate of propane disappearance could not be measured in a reliable fashion. Within the limits of the analytical errors, the rate of ethylene disappearance seems to be affected very little by increasing the pressure from about 15 to 30 atm., or increasing the surface/volume ratio by packing the reactor. However, increasing the temperature shows a very strong influence on the rate of the radiation-induced reaction over the entire range studied. Since the results of Fig. 1 were all obtained at the constant rate of initiation corresponding to an intensity of 48×10^6 rad./hr., the chain propagating processes must be accelerated by raising the reaction temperature.

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(5) F. W. Lampe, This Journal, **79**, 1055 (1957).

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The Reaction Products.—In Table I, the products of the thermal ethylene–propane reaction are compared with those obtained at the same conditions using radiation. These results represent the composition of the total reaction product. Since the reaction rates were much faster in the irradiation experiments, the product compositions were compared for reaction times which were longer thermally than with radiation, but at the same ethylene conversion levels. In the temperature range of 400 to 454° and at 18 atm. initial pressure, the products were virtually the same, both thermally and at a dose rate of 48 × 10^6 rad./hr. At temperatures below about 400°, the reaction rate was too low thermally for making a similar comparison of the data at significant conversion levels. At the conditions of the comparison, the data suggest a free radical type mechanism in the chain reaction of ethylene with propane. This is based on the similarity between thermal and radiation reactions.

TABLE I

PRODUCTS OF THERMAL AND OF RADIATION-INDUCED REACTION BETWEEN ETHYLENE AND PROPANE

Total initial pressure = 18 atm. Initial ethylene concentration = 10 mole %. Surface/volume ratio = 0.59 cm.$^{-1}$

Radiation intensity, rad./hr.	48 × 10^6	0	48 × 10^6	0
Temperature, °C.	400	400	454	454
Reaction time, min.	1	60	1	30
Conversion of ethylene, %	24	22	36	30
Composition of product, wt. %				
$CH_4 + C_2H_6$	18	20	36	34
C_3H_6	27	31	29	35
n-C_4H_{10}	10	11	10	5
iso-C_4H_{10}	0	0	0	0
C_4H_8	17	4	4	8
n-C_5H_{12}	8	7	8	5
iso-C_5H_{12}	20	27	13	13

The complexity of the reaction products suggests that ethylene reacts with propane according to a number of competing reaction paths. The yield of isopentane also exceeds that of n-pentane, as would be expected in a free radical alkylation reaction involving the addition of n-propyl and *sec*-propyl radicals to ethylene, because of the greater ease of formation of *sec*-propyl radicals. This is a consequence of the lower C–H bond strength in the secondary position of propane as compared with the primary, which leads to favored exchange reactions of the type $n\text{-}C_3H_7\cdot + C_3H_8 \rightarrow C_3H_8 + \text{sec-}C_3H_7\cdot$. As the temperature is raised, the yield of the alkylation products, isopentane and n-pentane, decrease and decomposition reactions tend to predominate.

The Effect of Surface.—It is, of course, necessary to establish as far as possible whether gas phase reactions are truly homogeneous. Table III presents typical results of irradiation experiments in which the surface/volume ratio of the reactor was increased to 394 cm.$^{-1}$ by packing it with stainless steel. The intensity was constant at 48 × 10^6 rad./hr. in these experiments, and the irradiated mixture contained 10 mole % ethylene.

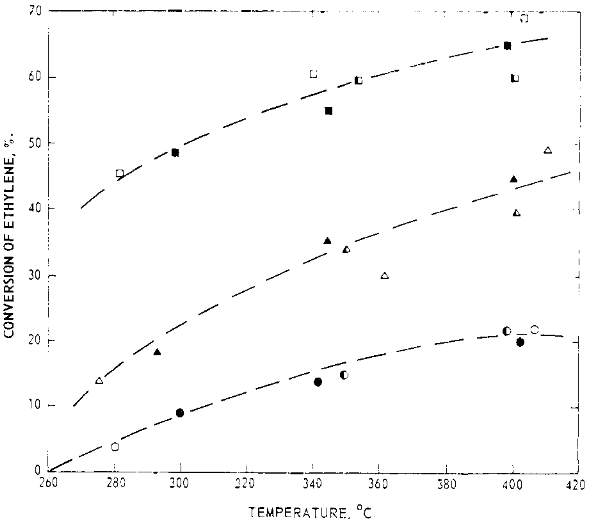

Fig. 1.—Radiation-induced conversion of ethylene in the alkylation of propane with ethylene. Dose rate of pile irradiation = 40 × 10^6 rad./hr. Initial ethylene concentration = 10 mole %.

S/V = 394 cm.$^{-1}$ 15–16 atm.	S/V = 0.59 cm.$^{-1}$ 15–18 atm.	S/V = 0.59 cm.$^{-1}$ 27–31 atm.
◐, 1 min.	○, 1 min.	●, 1 min.
◭, 5 min.	△, 5 min.	▲, 5 min.
◧, 15 min.	□, 15 min.	■, 15 min.

As shown in Table II, the product compositions at the same degree of conversion are very similar for both the high and the low surface/volume ratios used. It appears that at lower temperatures, in the range of about 250 to 350°, the yield of isopentane is somewhat higher in the packed reactor. The high yields of isopentane at 240 to 250° are in line with the mechanism of competing free radical processes: addition of radicals to ethylene at lower temperatures and decomposition of radicals at higher temperatures. The alkylation reaction should be relatively more important at low temperatures, provided the reaction can be initiated

TABLE II

EFFECT OF SURFACE ON THE ETHYLENE–PROPANE REACTION AT 48 × 10^6 RAD./HR.

Total initial pressure = 18 atm. Initial ethylene concentration = 10 mole %.

Surface/volume ratio, cm.$^{-1}$	0.59	394	0.59	394	0.59	394
Temperature, °C.	354	354	404	404	241	252
Reaction time, min.	5	5	5	5	120	120
Conversion of ethylene, wt. %	30	35	42	38	75	73
Composition of product, wt. %						
$CH_4 + C_2H_6$	17	13	24	23	20	21
C_3H_6	16	17	25	28	5	6
n-C_4H_{10}	6	9	8	10	8	9
iso-C_4H_{10}	0	0	0	0	0	0
C_4H_8	16	20	12	12	26	12
n-C_5H_{12}	17	14	10	8	7	11
iso-C_5H_{12}	18	27	21	20	33	41

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

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