

[CONTRIBUTION FROM THE ESSO RESEARCH &amp; ENGINEERING Co.]

## The Radiation-Induced Chain Alkylation of Propylene with Isobutane

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RECEIVED FEBRUARY 27, 1959

A study has been made of the gas phase alkylation of propylene with isobutane initiated by nuclear radiation at 55 atm. pressure and 350–400°. At these conditions, Co-60 radiation initiates a chain reaction and the purely thermal reaction is negligibly slow. Detailed product composition data are given as a function of conversion level. Although the radioalkylation chain reaction gives a complex mixture of products, the major products above butane are dimethylpentanes, isopentane and olefins. The chain length for this reaction is of the order 20–100. It increases with temperature and total pressure, increases directly with increasing olefin concentration and inversely with the half power of radiation dose rate. In addition, the chain radioalkylation has an induction period. It is not possible to decide unequivocally whether this new reaction is an accelerated thermal (*i.e.*, free radical) chain alkylation or a chain reaction propagated by species (ions) peculiar to the radiation method of initiation. However, the data are discussed from the viewpoint of ordinary free radical chemistry and it is shown that the major results can be reconciled with well established radical reactions.

### Introduction

The thermal or free radical alkylation of olefins with paraffins has been of theoretical importance and of practical interest since 1936.<sup>1</sup> This reaction has been discussed both experimentally and theoretically,<sup>2,3</sup> although few systematic studies have been published. For example, we are not aware of any detailed product composition data in the free radical alkylation of propylene with isobutane. From the viewpoint of mechanism, although the general free radical chain mechanism advanced is undoubtedly valid, no experimental measurement has been made of the chain length of these reactions and no direct study of the chain nature of the reaction has been reported.

On the other hand, the radiation chemistry of hydrocarbons has been studied so far predominantly in the region of low temperatures.<sup>4–7</sup> Recently, it has been pointed out that nuclear radiation is a convenient initiator for such chain reactions as the gas phase decomposition of paraffins at high temperatures.<sup>8</sup> Since these radiation-induced chain reactions are carried out at conditions where the thermal background reaction is negligible, a knowledge of energy absorption gives directly the rate of initiation. This information, coupled with measured conversions, gives an experimental chain length which is difficult to obtain directly in purely thermal chemistry. In the event that the radiation merely initiates the reaction and does not give new reactions or affect the propagation steps, as obtained in radioalkylation,<sup>8</sup> radiation serves as a powerful tool for probing the details of ordinary (thermal) radical chain processes at carefully controlled conditions. Of course, in the special cases where the radiation-induced chain processes are due to intermediates peculiar to radiation initiation, the chain reactions are of special interest in themselves. In any event, the study of radiation-induced chain reactions of hydrocarbons represents

an important new area of research in hydrocarbon chemistry.

In this work, Co-60  $\gamma$ -radiation was used to initiate the alkylation of propylene with isobutane at conditions where the thermal reaction is negligible. This purely radiation-induced chain reaction has not been reported previously. In this paper, the detailed product composition data are presented at varying extent of reaction. In addition, the effects of experimental conditions on the chain nature of the radioalkylation are discussed. Finally, the data are discussed from the viewpoint of a free radical chain mechanism.

### Experimental

The batch experiments reported in this study were made in electrically heated stainless steel vessels. The radiation source was a 3200 curie Co-60 facility. Both the batch reactors and the radiation facilities have been described elsewhere.<sup>9</sup> The  $\gamma$ -energy absorption was measured by  $\text{Fe}^{++}$ - $\text{Fe}^{+++}$  dosimetry<sup>9</sup> and also by the method of Henley<sup>10</sup> which uses dyed cellophane dosimeters for  $\gamma$ -radiation. In this method, a dye-containing cellophane is exposed to  $\gamma$ -radiation and the increase in transparency is taken as a measure of the dosage. This increase in transparency is measured at 6550 Å. In addition to these experimental methods of dosimetry, the dosage existing inside the reactor was calculated using a standard technique<sup>11</sup> and accounting for the shielding due to the reactor material and insulation.<sup>12</sup> These different techniques gave energy absorption values which agreed within 15–20%. This uncertainty in the dosimetry is not considered serious since the radiation yields measured in this work were high. All energies reported in this work refer to energy absorbed and are given in energy absorption units, Rads (100 ergs/g. by definition). The isobutane and propylene reagents were Phillips pure grade (>99.5%) and were used without further purification. Products were carefully analyzed by gas-liquid partition chromatography and mass spectrometry which analyzed all components with an uncertainty  $\pm 4\%$  of the amount present. The reactants were dried and charged to the reactor as liquid. All data reported in this work refer only to radiation-induced reactions. In purely thermal experiments at the same conditions as those used for the radiation experiments essentially no reaction between isobutane and propylene was observed. Therefore, there is no thermal background to separate from the radiation-induced conversion, and the measured conversions and energy absorption give directly the radiation yield or chain length of the radioalkylation.

Typical experimental conditions used were 55 atmospheres total pressure, 350–400°, 8/1 mole ratio of paraffin to olefin, and  $1.2 \times 10^5$  Rad/hour absorbed by the reagents.

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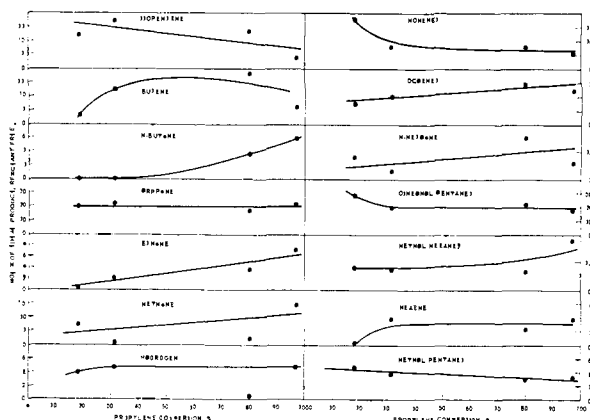


Fig. 1.—Product composition as a function of degree of conversion in the radioalkylation of propylene with isobutane at 370° and 55 atm. pressure.

### Results

**Product Distribution.**—At the relatively mild conditions of 370° and 55 atm. total pressure, the thermal reaction between isobutane and propylene (8/1 mole ratio) is so slow that only negligible conversion is obtained after 4–5 days. However, in the presence of  $1.2 \times 10^5$  Rad/hr. of Co-60 radiation (absorbed) an alkylation chain reaction is initiated. At these conditions, the purely radiation-induced conversion of the propylene is, for example, about 31% in 6 hours and 80% in 24 hours in a batch system. The product distribution is given in Fig. 1 as a function of propylene conversion. Although there are not enough data to establish firmly the product-conversion curves, the data provide an interesting insight into the nature of the reaction.

The major product is a dimethylpentane fraction. Although a mixture of dimethylpentanes is made and these are difficult to separate by gas chromatography, 2,2-dimethylpentane is the predominant isomer. This is the expected addition product on either a radical or ionic mechanism. However, the reaction gives a one-tenth as large but nevertheless definite yield of methylhexanes and *n*-heptane. With regard to the paraffinic products having a molecular weight greater than butane, isopentane is a major product although no *n*-pentane is formed. Therefore, the major paraffinic products above butane are dimethylpentane and isopentane. The paraffinic products below butane are predominantly propane with a much smaller contribution due to ethane and methane. Olefinic products are abundant and include, in decreasing order of importance, propylene trimer, dimer and butenes. In short, although the major products are dimethylpentanes, isopentane and olefins, virtually all paraffinic products up to the octanes are present with the exception of *n*-pentane, *n*-hexane and dimethylbutanes. As is frequently observed in the radiation chemistry of hydrocarbons, hydrogen also was found in the products.

**Chain Nature of Alkylation.**—The chain nature of the alkylation reaction is illustrated by the high radiation yields, or *G*-values, expressed as product molecules containing five carbon atoms and heavier

(“C<sub>5</sub>+”) made per 100 e.v. absorbed. Assuming about 7 free radicals made per 100 e.v.,<sup>7</sup> the observed *G*-values (in the range 100–600 at  $1.2 \times 10^5$  Rad/hr. intensity) indicate a chain length of the order 20–100 at these conditions. This establishes the chain nature of radioalkylation.

**Factors Affecting the Chain Length.**—In Fig. 2, the *G*-value of C<sub>5</sub>+ product is given as a function of dose rate at the same conditions as described above and a constant total energy absorption of  $4 \times 10^5$  Rad. The *G*-values increase to well over 1000 at lower dose rate and, in fact, the *G*-values vary with dose rate according to the familiar inverse square root relation.

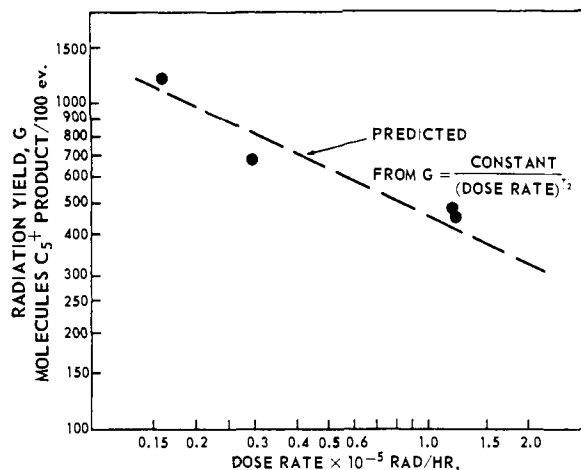


Fig. 2.—Chain length as a function of dose rate in the radioalkylation of propylene with isobutane at 55 atm. and 370°.

The experiments at 370° and 55 atm. pressure gave evidence of an induction period. For example, in Fig. 3 the *G*-value is given as a function of dosage (energy absorbed) at the constant dose rate of  $1.2 \times 10^5$  Rad/hr. There is at first a rapid increase in *G*-value with exposure, followed by decrease in *G* at longer residence times. The portion of the curve in which the *G*-value decreases with exposure is expected in batch experiments in which the olefin concentration is decreasing with time. However, the initial increase is not expected and indicates the presence of an induction period. The most plausible explanation for this induction period is the presence of trace impurities which are well known to prevent the propagation of chain reactions.

With regard to the dependence of chain length on external variables such as olefin concentration, the data in Fig. 4 show that the *G*-values increase linearly with olefin concentration in the range 4–16 mole % propylene concentration. Although only qualitative data were obtained on the effect of temperature and pressure, the *G*-value-dosage curve presented in Fig. 3 for the reaction at 260 and 370° shows that the chain length increases with temperature. The pressure effect is also quite pronounced. For example, at 370° and  $1.2 \times 10^5$  Rad/hr., the irradiation of isobutane/propylene at 8/1 mole ratio was compared at two pressure levels: 55 and 25 atm. At the same

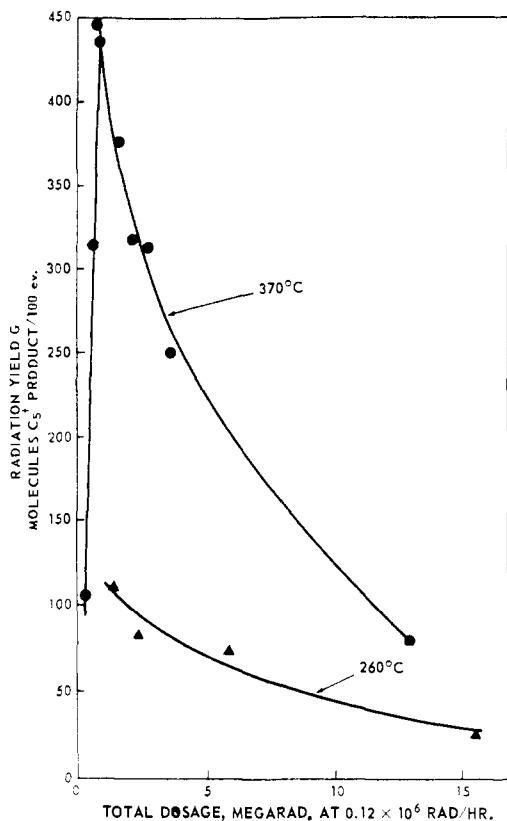


Fig. 3.—Chain length as a function of total energy absorbed (contact time) in batch radioalkylation of propylene with isobutane at  $1.2 \times 10^6$  Rad/hr., 55 atm., 370 and 260°.

conversion of propylene (14%), the  $G$ -value of products having five or more carbon atoms and of the products having four or less carbons were 60 and 100, respectively, at the higher pressure. These values were 20 and 600 at the lower pressure of 25 atm. Therefore, the effect of increasing pressure is to increase the chain length of the addition reactions, as expected and to decrease the chain length of the decomposition side reactions.

### Discussion

The radiation-induced chain condensation of paraffins and olefins is a new reaction of intrinsic interest. From the viewpoint of mechanism, however, the radiation chemistry of hydrocarbons is in a highly speculative state of development because of the complex nature of the initiation process.

There are two aspects of radiation-induced alkylation reactions involving paraffins and olefins. The first involves consideration of the radiation chemistry of the process, and the second involves the purely thermal alkylation reaction. For example, it is well known that nuclear radiation produces ions, excited species and free radicals. We must therefore consider that a mixture of isobutane and propylene exposed to nuclear radiation is quite different from the corresponding system exposed to purely thermal energy. In the latter case, we need to consider only ordinary or "thermal" free radicals, but in the radiation case we must contend with radicals and ions and, in addition, with excited states. The basic question, there-

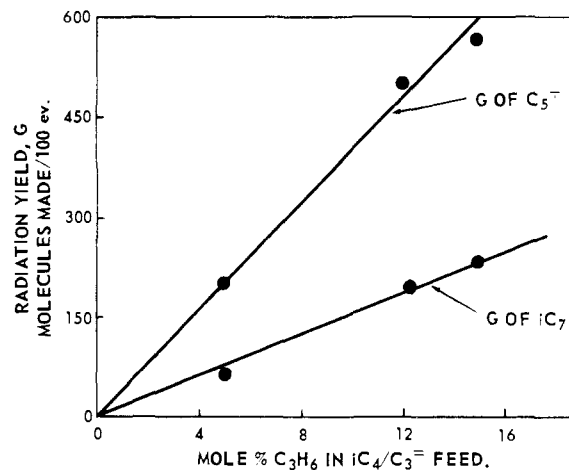
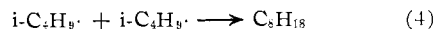
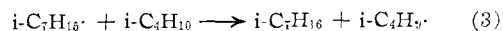
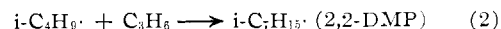
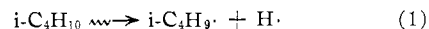


Fig. 4.—Chain length as a function of olefin concentration in the radioalkylation of propylene with isobutane at 55 atm. and 370°. At a Co-60 dose rate of  $1.2 \times 10^6$  Rad/hr. and a total dosage of  $7.2 \times 10^6$  Rad.

fore, is whether or not the chemistry observed in the radiation-induced chain reaction is due predominantly to thermal free radicals. This involves the assumption that ions and excited states, though formed initially, cannot take part in the chain propagation. Such an assumption seems reasonable with regard to the excited states. However, the assumption is less certain in the case of ions, because ion-molecule reactions in the gas phase are extremely rapid.<sup>13</sup>

At present, it is not possible to discuss radiation-induced chain reactions from the viewpoint of the basic chemistry of molecule ions since very little is known about their reactions. However, in a previous study of radiation-induced decomposition of paraffins,<sup>8</sup> it was shown that this chain process fits reasonably well the assumption that the major reactions are due to ordinary free radical processes. Therefore, it seems worthwhile to examine whether the radiation-induced alkylation of propylene with isobutane at "moderate" temperatures and pressures can be interpreted on the basis of an ordinary free radical mechanism.

Considering the formation of heptanes, which is the major alkylation reaction, a simple chain mechanism can be written which neglects the primary radiation steps and considers the gross effects of radiation as producing isobutyl radicals.



The usual steady-state treatment leads to equation 5 which relates the  $G$ -values (chain length) to the olefin concentration, ( $\text{C}_3\text{H}_6$ ), the paraffin concentration, ( $i\text{-C}_4\text{H}_{10}$ ), and the dose rate,  $I$ . The

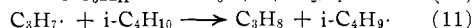
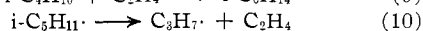
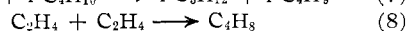
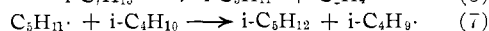
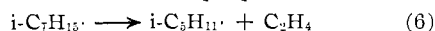
$$G = \frac{k_2}{(k_4)^{1/2}} \times \frac{(\text{C}_3\text{H}_6)}{I^{1/2}} \quad (5)$$

constants  $k_2$  and  $k_4$  are the rate constants for steps 2 and 4, respectively.

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This equation predicts that alkylation  $G$ -values should vary directly with propylene concentration and inversely with the square root of dose rate. The experimental data fit this prediction well. Equation 5 also predicts that the alkylation  $G$ -values should vary directly with total pressure. The experimental pressure effect is much larger than this, but the discrepancy could result from the neglect of cracking side reactions in the mechanism. The  $G$ -value should have a positive temperature coefficient and should, in fact, increase with temperature with the same activation energy as that of the addition step 2. The reason for this is that the initiation step is temperature independent, being radiation-induced, and the termination step has zero or only slight activation energy.

As pointed out, the addition reaction accounts for less than half of the total reaction. Of the many side reactions observed, many can be reconciled with free radical theory by considering that the net reaction is made up of chain decomposition reactions of paraffins, chain alkylation between paraffins and olefins, and chain self-condensation of olefins. The formation of propylene dimer and trimer is clearly a self-condensation side reaction and these are rather well established in free radical chemistry. With regard to other side reactions, the decomposition of heptyl radicals can lead to a variety of products—for example, to pentane, butene, hexane and propane.



The unexpectedly high selectivity of propane may be partly the result of reaction between propylene and hydrogen and partly from the side reactions discussed above.

In the case of radioalkylation of propylene with isobutane, it can be said that the bulk of the available data can be explained on the basis of what is known of ordinary free radical processes. There does not seem to be a need for attributing to the radiation-induced reaction a mechanism that goes through intermediates, such as ions, peculiar to radiation. However, ionic chain processes could also be postulated and can be made to fit the experimental data. Therefore, the best that can be said is that the available data can be reconciled with rather well established free radical reactions and no new reactions need to be postulated. Unfortunately, the question could not be answered unequivocally because the very slow thermal reaction made it difficult to compare the products made with radiation and by the purely thermal reaction at the same conversion of olefin. However, work in this Laboratory on the more reactive propane-ethylene system, which will be published shortly, has shown the products are quite similar when compared at the same conversion of olefin.

The technique of nuclear radiation initiation has made available a new reaction—the chain alkylation of olefins with paraffins. The initial data are not in conflict with ordinary free radical chemistry. However, it remains to be seen whether radiation provides a new and specific chain alkylation reaction or, equally important, a new probe for getting insight into the ordinary thermal chemistry of hydrocarbons.

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## Effect of Temperature and Br<sub>2</sub>/Ar Ratio on the Rates of Recombination of Br Atoms Produced by Flash Photolysis of Gaseous Br<sub>2</sub>

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RECEIVED APRIL 1, 1959

The rate constants  $k_{Ar}$  and  $k_{Br_2}$  for the reactions  $2\text{Br} + \text{Ar} \rightarrow \text{Br}_2 + \text{Ar}$  ( $d[\text{Br}_2]/dt = k_{Ar}[\text{Br}]^2[\text{Ar}]$ ) and  $2\text{Br} + \text{Br}_2 \rightarrow 2\text{Br}_2$  ( $d[\text{Br}_2]/dt = k_{Br_2}[\text{Br}]^2[\text{Br}_2]$ ) have been determined from atom recombination measurements over a range of Br<sub>2</sub>/Ar ratios from  $4 \times 10^{-3}$  to  $6 \times 10^{-2}$  and at cell temperatures from 273 to 418°K. The ratio of the efficiency of Br<sub>2</sub> as the "third body" for the recombination to that for Ar is approximately 100 at these temperatures. CO<sub>2</sub> is about 4 times as efficient as Ar. The apparent activation energy for recombination in Ar, Br<sub>2</sub> or CO<sub>2</sub> over the temperature range studied is in all cases between -1.4 and -2.9 kcal./mole. For all Br<sub>2</sub>/Ar ratios above  $10^{-2}$  it was necessary to apply a correction for thermal inhomogeneities which were produced in the cell contents by the flash and which affected the transmission of the analyzing beam.

### Introduction

Studies of the recombination of iodine atoms produced by flash photolysis of gaseous I<sub>2</sub> have been reported from four laboratories.<sup>2-5</sup> There is agree-

ment that recombination follows the rate law  $d[\text{I}_2]/dt = k[\text{I}]^2\text{M}$ , that the rate constant is dependent on the nature of M, the "third body" and that the reaction has a negative temperature coefficient. For the most part the values obtained in different laboratories for the rate constants are in good quantitative agreement. Correlations

(1) More complete details of this work are available in the Ph.D. thesis of W. G. Givens, Jr., filed with the University of Wisconsin Library in 1959. It may be obtained from University Microfilms, Ann Arbor, Michigan.

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