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The Chain Alkylation of Acetylene with Propane Induced by Nuclear Radiation

BY W. BARTOK AND P. J. LUCCHESI

RECEIVED MAY 14, 1959

A new reaction is reported—the chain alkylation of acetylene with propane to yield predominantly 3-methyl-1-butene. This reaction is initiated by mixed pile nuclear radiation at 10–15 atm. pressure and 250–400°. At these conditions, it has a chain length which varies between 7 and 12 and increases inversely with the square root of intensity. The rate is roughly first order in acetylene. At the same conditions, no alkylation is observed thermally and indeed the thermal alkylation cannot be studied because at temperatures required for its initiation, acetylene side reactions predominate. The reaction is discussed from the viewpoint of a free radical chain mechanism. From the data and the assumed mechanism, a value of 4.5 kcal. can be estimated as the activation energy for the addition of *sec*-propyl radicals to acetylene.

Introduction

The radiation chemistry of acetylene–propane at high temperatures and pressures is important from several points of view. In ordinary chemistry, the condensation reaction between light paraffins and olefins ("olefin alkylation") has been studied in some detail, but there are no reported systematic studies of the corresponding alkylation reaction between light paraffins and alkynes. This lack of data applies at any temperature and pressure. Therefore, the chemistry of alkyne alkylation reactions is essentially unknown with regard to the products of addition, kinetics and chain mechanism. Indeed, no experimental basis exists for assuming the reaction to be a chain process.

The reason for the lack of data on alkyne alkylation, particularly with regard to acetylene, is undoubtedly related to the hazards involved in acetylene chemistry. But a much more important reason is that at temperatures and pressures required to initiate the thermal reaction between propane, for example, and acetylene, the decomposition and polymerization of acetylene are so rapid that no paraffin–alkyne reaction is observed. However, in the presence of nuclear radiation a condensation reaction can be initiated at very mild conditions. This new reaction can be studied very conveniently since there is no thermal contribution to consider. Therefore, the purely radiation-induced degree of conversion and the rate of initiation are *directly* measured, and it is possible to observe directly the chain nature of the reaction and the effect of experimental conditions for systems that could not be studied with conventional techniques.

This direct alkylation of acetylene with light paraffins is of intrinsic interest. At present, no firm decision can be made whether it is an accelerated thermal (radical) reaction or a chain process that is peculiar to the radiation initiation technique. It is well known that radiation makes ions as well as free radicals, in the ground state and in excited states. Since ions are extremely reactive,¹ it is by no means certain that the chain reactions observed in hydrocarbon radiation chemistry at ordinary conditions are solely free radical chain processes. Therefore, the radiation-induced reaction between light paraffins and acetylene may be a chain process peculiar to radiation with no thermal counterpart. On the other hand, it has been shown^{2,3} recently that at superatmos-

pheric pressures and 200–500°, the radiation-induced chain decomposition of paraffins and paraffin–olefin alkylation reactions can be explained adequately by an ordinary free radical chain mechanism. Therefore, it seems worthwhile to discuss the data on the basis of well established free radical reactions without introducing new reactions unless it is necessary to do so. In this paper, we present direct experimental data pertaining to the alkylation of acetylene with propane in propane-rich mixtures at 250–400° and 10–15 atm. total pressure. The reaction was radiation-induced using the highly intense mixed radiation from a "swimming pool" atomic reactor. At these conditions, the thermal alkylation reaction is negligibly slow and the purely radiation-induced reaction can be studied directly.

The reaction is discussed from the viewpoint of an ordinary free radical chain process. Assuming this mechanism, it is possible to derive the activation energy for the addition of *sec*-propyl radicals to acetylene.

Equipment.—Irradiations were performed in a static system using a cylindrical reactor vessel made from stainless steel. The nine inch long reaction vessel, which had a volume of 1.01 l., was enclosed in an aluminum jacket. The reactor was heated electrically, with the electrical and thermocouple leads housed in a long aluminum pipe which was welded to the top of the jacket. This reactor assembly was immersed in a "swimming pool" nuclear reactor at distances of 10 cm. and 20 cm. from the core face. The bottom of the reactor was resting in the holder on an irradiation table specially designed for positioning the equipment inside the reactor.

Mixtures of propane and acetylene were admitted into the reactor through a long feed line which reached down to the bottom of the reactor along its vertical axis. The same line served for product withdrawal at the conclusion of each irradiation. The feed-product line was heated to prevent condensation. Feed mixtures were prepared by admitting the required amounts of Matheson instrument grade propane and acetylene (without further purification) into an evacuated, 34-liter stainless steel tank. Care was taken to ensure an excess of propane during the preparation, in order to avoid creating hazardous conditions. The mixtures were charged from the feed tank to the reactor vessel to the specified pressure, which was always below the dew point of the mixture. A reactor system of the same construction was employed in the study of surface effects. The surface/volume ratio was increased from 0.59 cm.⁻¹ for the empty reactor to 394 cm.⁻¹ by packing it with 200-mesh stainless steel wire cloth.

Analysis of Products.—The product gas was collected at room temperature in an evacuated stainless steel tank, 1.3 l. in volume, by opening a valve to the reactor vessel until the

(1) D. P. Stevenson, *J. Phys. Chem.*, **61**, 1453 (1959).

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

(3) P. J. Lucchesi, D. L. Baeder and J. P. Longwell, paper presented at World Petroleum Congress, June, 1959, New York, N. Y.

pressures equalized. Before sample collection, about 10% of the gas was bled from the reactor to purge the lines. A gas meter was used for measuring the product remaining in the system after sample collection.

The products were analyzed by gas chromatography. Silica gel, 2,5-hexanedione on firebrick, and Octoil-5 on firebrick were employed for column packing. The Octoil-5 column was the most satisfactory. A few samples were analyzed by mass spectrometry and infrared absorption. These tests showed good agreement with the chromatographic analyses. The chromatographic technique was adequate for hydrocarbons containing six carbon atoms or less. However, evidence was obtained that the products from the experiments which were conducted at 360° or above also contained small amounts of heavier products. These components could not be analyzed by gas chromatography due to their long retention times in the column. In addition to this loss in the chromatographic column, other losses occurred by deposition of heavy products in the reaction vessel itself. These products could not be recovered completely by evacuating the reactor, as evidenced by a burn-out of the unpacked reactor with air at 1000°F. and atmospheric pressure. The amount of CO₂ formed by the burn-out indicated that 3.5% of the carbon feed was deposited in the reactor after 22 experimental runs. Therefore, the amounts of propane and acetylene reacted were calculated as minimum estimates for experiments at higher temperatures. The low value of the carbon feed which was recovered by the burn-out provided evidence for the lack of appreciable polymerization of the hydrocarbons. Because of the large excess of propane used in both the irradiation and the thermal experiments the conversion of propane could be estimated only as the difference between two large quantities. Since this would have introduced relatively large errors, only the conversion of acetylene was calculated accurately in this study.

Dosimetry.—The highest flux available from the reactor was of the order of 3×10^{12} thermal neutrons/cm.² and 10^{12} fast neutrons/cm.²/sec. The rate of radiation energy absorption at the two pool positions was determined by the use of methane as a chemical dosimeter. The principle of this technique consists of irradiating samples of pure methane for fixed time intervals, followed by the measurement of the hydrogen yield due to irradiation. For calculating the rate of energy absorption, a *G*-value of 5.7 molecules of hydrogen per 100 e.v. was used.⁴ This *G_H* has been shown to be independent of temperature and pressure. At the two positions which were studied in the swimming pool reactor, energy absorption rates of 48×10^6 rad./hr. and 17×10^6 rad./hr. were measured, with an estimated accuracy of $\pm 20\%$.

Results

Conversions.—In the range 200–400° and 10–13 atm. total pressure, the thermal alkylation reaction between propane and acetylene was negligible. In the case of the radiation-induced reaction, at temperatures up to 320°, 20–30% of the acetylene reacts with propane to give addition product. At temperatures above 320° (Fig. 1) the thermal reaction of acetylene is so rapid that it masks the radiation effect. At these temperatures, the direct alkylation reaction is negligible. As shown in Fig. 1, the low temperature radiation-induced alkylation rate increases with temperature. Also, as will be discussed later, radiation yields or chain lengths are increased at lower radiation intensity.

The experiments were repeated at the same conditions except that stainless steel packed reactors were used which allowed a 670-fold increase in surface area. In the low temperature region (200–320°) the effect of added surface was to increase slightly the conversion of acetylene. Therefore, the reaction can be partially heterogeneous at certain conditions. As pointed out in the following discussion, although the added surface

(4) F. W. Lampe, *THIS JOURNAL*, **79**, 1055 (1957).

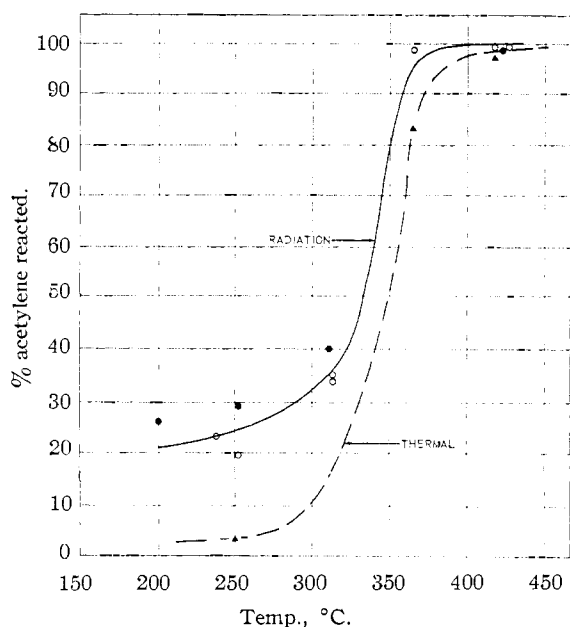


Fig. 1.—Effect of temperature on acetylene conversion in the radiation-induced alkylation of acetylene with propane. Total pressure 10–13 atm., initial C₂H₂ concentration 9.0 mole %: ●, 40 min. at 17×10^6 rad./hr.; ○, 15 min. at 48×10^6 rad./hr.; ▲, 60 min., thermal.

causes an increase in acetylene conversion, the selectivity to alkylation *decreases*. Therefore, it is probable that the polymerization and decomposition of acetylene is favored by the higher *S/V* ratio and the alkylation reaction is only slightly affected.

Selectivity.—The selectivity data are given in Fig. 2 as a function of temperature, surface to volume (*S/V*) ratio, and radiation intensity. In the low temperature region, the selectivity of the reaction (wt. % of total reaction product) is about 50% to the propane-acetylene alkylation product. This product, isopentene, analyzed exclusively as 3-methyl-1-butene. Although the chain addition of propane to acetylene would be expected to give this pentene isomer, the complete absence of other pentene isomers in the product is unexpected. It is possible that very small amounts of pentenes other than 3-methyl-1-butene are formed and are not separated in the column. However, the important point is the very high selectivity of the alkylation to 3-methyl-1-butene. In this low temperature region, no products above C₅ were found. The only products found other than pentene were methane, ethane, ethylene and propylene. These latter products are typical of the non-chain radiolysis of propane. Therefore, in the low temperature region essentially all the acetylene is reacting through alkylation with propane. Material balance considerations also justify this conclusion.

As shown in Table I, the composition of the low molecular weight products seems unaffected by the added surface in the low temperature region. However, at the higher temperatures when the lighter products predominate, the additional surface promotes the formation of methane, while the yield

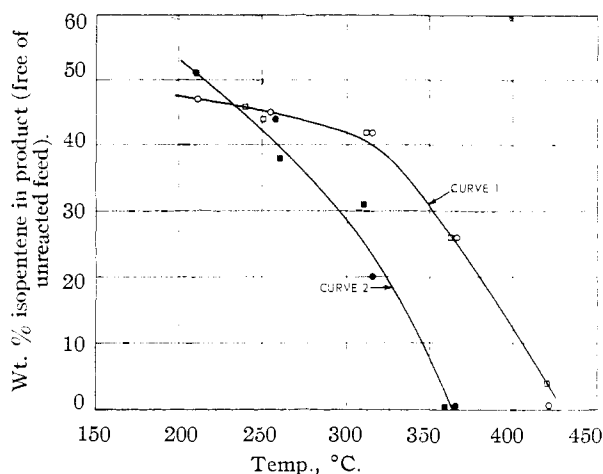


Fig. 2.—Effect of temperature on selectivity to propane-acetylene addition product in the radioalkylation of acetylene: curve 1, $S/V = 0.59 \text{ cm.}^{-1}$; curve 2, $S/V = 394 \text{ cm.}^{-1}$; circles, 40 min. at $17 \times 10^6 \text{ rad./hr.}$; squares, 15 min. at $48 \times 10^6 \text{ rad./hr.}$

of ethylene decreases. Although it is more pronounced in irradiation experiments, this change also occurs thermally.

TABLE I
COMPOSITION OF THE LOW MOLECULAR WEIGHT PRODUCTS
(FREE OF UNREACTED FEED)

Temp., °C.	254	257	420	425	420	420
Dose rate $\times 10^{-6}$ rad./hr.	17	17	17	17	0	0
Time, min.	40	40	40	40	60	60
$S/V, \text{ cm.}^{-1}$	0.59	394	0.59	394	0.59	394
% C_2H_2 reacted	28	42	98	94	97	91
Compn. of product, wt. %						
CH_4	7	7	30	61	42	50
C_2H_6	10	8	27	28	27	24
C_2H_4	26	27	18	3	13	6
C_3H_6	12	14	17	9	18	20

Radiation Yields.—The G -values for acetylene disappearance (molecules of acetylene reacted per 100 e.v.) are presented in Table II for the unpacked reactor. In the temperature range where the alkylation reaction predominates and the thermal reaction is negligible, the G -values vary from 36 to 59 molecules per 100 e.v. This magnitude of the G -values indicates that the propane-acetylene alkylation reaction is a short chain process. The chain length can be estimated by assuming that on the average the absorption of each 100 e.v. of energy gives rise to five primary acts of initiation. Therefore, the chain length varies from about 7 to 12 at the radiation intensity levels used in this study.

As shown in Table II, the G -values increased with decreasing radiation intensity. Since the range of intensities used for irradiations was not sufficiently wide, only a semi-quantitative estimate can be made of the dependence of the G -values on the intensity. Applying the usual assumption that the radiation yield is a function of some power of the intensity, G is found to be proportional to the intensity raised to the -0.48 power. Taking into account that the measurement of the intensity

can be in error by as much as $\pm 20\%$, it may be assumed that G is inversely proportional to the square root of the intensity. This suggests that the alkylation chain reaction is terminated by binary radical recombinations in the vapor phase, a common termination step in thermal chemistry which gives rise to the well-known "inverse square root" law.

TABLE II
EFFECT OF RADIATION INTENSITY ON THE RADIATION YIELDS
IN THE RADIOALKYLATION OF ACETYLENE

Dose rate, rad./hr.	G , molecules of C_2H_2 reacted per 100 e.v. ^a
17×10^6	59
48×10^6	36

^a Average values based on results obtained below 260° .

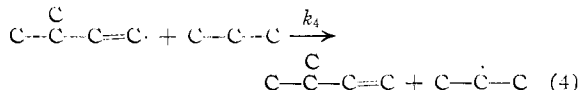
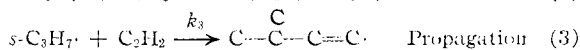
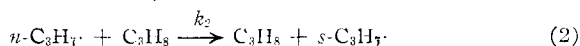
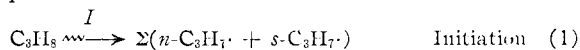
Rate of Reaction.—A plot of the logarithm of the fraction of acetylene remaining vs. time for three irradiations in the absence of packing yielded a straight line. The intensity of radiation was maintained constant at $48 \times 10^6 \text{ rad./hr.}$, the initial acetylene concentration was 9.0 mole %, and the temperature was kept low and was allowed to vary over only a small range (238 to 243°) so that thermal effects could be considered negligible. The straight line plot having a slope of $2.51 \times 10^{-4} \text{ sec.}^{-1}$ indicates that the rate of disappearance of acetylene in the radioalkylation reaction is first order with respect to the concentration of acetylene.

Discussion

As pointed out previously, the direct alkylation of acetylene with propane is a new reaction with no thermal counterpart. Therefore, it is not possible to compare the reaction products made with radiation and thermally at the same conversion level. This means one cannot decide on an experimental basis whether the radioalkylation is a new chain process peculiar to radiation initiation (ionic chain) or a reaction typical of thermal chemistry (free radical chain).

Nevertheless, previous studies on radiation-induced cracking and olefin-alkylation reactions showed that the data could be explained by assuming an ordinary free radical chain mechanism. In that work, it was not found necessary to postulate a new type of chain reaction such as an ionic chain process. It is of interest to apply this approach to the radioalkylation of acetylene with propane.

Based on the observations that the rate of consumption of acetylene is apparently first order and that the reaction chains are terminated by binary collisions, simple elementary steps may be postulated for the reaction



where I is the rate of initiation, and k_2 , k_3 , k_4 and k_5 are the rate constants for reactions 2, 3, 4 and 5. The above reaction scheme was made to fit the experimental observations, so that only 3-methyl-1-butene is formed as a product of the chain reaction. As pointed out before, a distribution between this isomer and 1-pentene should be expected, but this would not affect the general form of the reaction scheme.

Applying the usual steady-state treatment to the above mechanism, the rate of consumption of acetylene is given by

$$-\frac{d(\text{C}_2\text{H}_2)}{dt} = k_3(I/k_5)^{1/2}(\text{C}_2\text{H}_2) \quad (1)$$

This rate equation, which also yields the rate of product formation, predicts that the reaction rate should be first order in the acetylene concentration. Since the chain length L is equal to the rate of propagation divided by the rate of initiation, it follows that

$$L = \frac{k_3}{(k_5 I)^{1/2}}(\text{C}_2\text{H}_2) \quad (2)$$

Equation 2 shows that the chain length is inversely proportional to the intensity of radiation. Therefore, the simple chain mechanism accounts for the observed reaction order and intensity dependence. It is also interesting that the assumed mechanism and the experimental data can be used for estimating the activation energy of the addition of the isopropyl radical to acetylene. The value of the activation energy based on the above reaction mechanism is really an average for a mixture of propyl and isopropyl radicals in which isopropyl radicals are more abundant. However, the error introduced in this portion should be negligible since no significant difference is expected between the acti-

vation energies for addition of propyl and isopropyl radicals to acetylene.

The rate of initiation at a dose rate of 48×10^6 rad./hr. is 4.05×10^{14} radicals cc.⁻¹ sec.⁻¹, at 240° and 10.0 atm. total pressure. Therefore, from the experimentally measured rate of disappearance of acetylene, $k_3/k_5^{1/2} = 1.25 \times 10^{-11}$ molec.^{-1/2} cc.^{1/2} sec.^{-1/2}.

Since the activation energy for reaction 3 is calculated from the measured rate and not from the temperature dependence of the rate constant, the value of the steric factor must be assumed. Mandelcorn and Steacie⁵ found the value of the steric factor to be of the order of 10^{-4} for the addition of methyl radicals to acetylene. This rather low value seems to be characteristic of radical additions to multiple bonds.⁶

Using the value of $P_3 = 10^{-4}$ for the addition of isopropyl radicals to acetylene and assuming the pre-exponential factor for k_5 is the normal collision number, it follows that $E_3 - E_5/2 = 4.5$ kcal. Since the activation energy E_5 for the recombination of radicals is estimated to be about 1 kcal., the agreement with the value of 5.5 kcal. found by Mandelcorn and Steacie for the addition of methyl radicals to acetylene⁵ is remarkably good. This agreement also tends to favor a free radical chain mechanism for the radiation-induced alkylation of acetylene with propane. If this mechanism is correct, radiation offers a powerful new tool for exploring a free radical hydrocarbon reaction that is exceptionally difficult to study thermally.

(5) L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 474 (1954).

(6) N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Vol. I, Princeton University Press, Princeton, N. J. 1958.

LINDEN, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL & REFINING COMPANY]

High Energy Electron Irradiation of *n*-Hexane

BY JEAN H. FUTRELL*

RECEIVED JUNE 1, 1959

A study of the radiation chemistry of normal hexane in gas and liquid phase as the pure compound and in admixture with radical scavengers in the gas phase is reported. The radiolysis products which were determined are hydrogen, propane, ethylene, *n*-butane, ethane, methane, propane, acetylene, hexane isomers, isobutane, butene, isopentane and *n*-pentane, listed in order of decreasing "G"-values. The nature and yields of these products and the effect of radical scavengers are rationalized with satisfactory precision from the assumption that initial ionization processes, followed by very fast ion-molecule reactions of the hydride ion transfer type, dominate the reaction process. It is therefore tentatively suggested that such a partial mechanism has considerable validity for normal hexane and related compounds.

Introduction

It is well known that hydrocarbons yield a great variety of products on radiolysis and little attempt has been made to establish detailed quantitative yields for a representative system. The early work by Lind¹ and co-workers established for the first members of the paraffin series that the gaseous products consist chiefly of hydrogen and of smaller amounts of saturated compounds. A number of subsequent papers have added very little to this

generalization, with many investigations reporting only such data as total gas yields, or yields of "polymer" remaining after distillation of reactant. Until very recently experimental difficulties in detecting and measuring these products have discouraged a detailed repetition of the pioneering work.

The development of modern analytical techniques, particularly of gas-liquid partition chromatography, has rendered a detailed study feasible.² Hexane appeared attractive for this purpose as a representative paraffin hydrocarbon. The radiol-

* Headquarters, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

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