

# Reaction Mechanism for Nitrating Paraffin Hydrocarbons

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A thorough study was made of the variables which affect the nitration mechanism. A mechanism is formulated that will account for the products of the reaction.

The following postulates are offered: The reaction appears to involve a free radical mechanism. Oxidation of the paraffin by the nitric acid, or some induced dissociation, may give free radicals which may in turn undergo any or all of the typical free radical reactions. The oxidation products may be accounted for by assuming either direct oxidation of the parent hydrocarbon or the oxidation of olefins or other intermediates that are formed.

THE purpose of this research was to study certain variables which affect the nitration reaction and to postulate a mechanism that will logically account for the products obtained.

The aliphatic nitro compounds were first prepared by Meyer (7) by metathesis of an alkyl halide and silver nitrite. The production of nitro compounds by direct nitration of paraffins has been studied extensively. Konowaloff (5), Markownikoff (6), and Worstall (14) are outstanding among the early investigators of this field.

Konowaloff (5) studied the liquid-phase nitration of a wide variety of compounds, and the following conclusions appear in his articles: (a) Tertiary hydrogen atoms are easily replaced by a nitro group by direct nitration; (b) primary hydrogen atoms are the most difficult to replace by direct nitration; (c) nitration takes place before oxidation; (d) oxidation occurs on the carbon atom to which the nitro group is attached; and (e) the rate of nitration increases with the concentration of the nitric acid used, but an increase in the concentration of the nitric acid is attended by an increase in the rate of oxidation.

Hass, Hodge, and Vanderbilt (4) recently made an extensive study of the vapor-phase nitration of the lower paraffins. Upon nitrating isobutane at 150° C. in sealed tubes, almost pure *tert*-nitrobutane was obtained. They found that oxidation of the parent hydrocarbon took place at temperatures too low for nitration, and that oxidation is a competing reaction even at the optimum conditions for nitration. They suggested the following mechanisms to account for the formation of the homologous nitroparaffins: (a) Nitration results from the action of nitric acid upon the paraffin, and the production of the lower homologs may be accounted for by oxidation to a fatty acid at the point of nitration and then nitration on the alpha-carbon atom of the fatty acid with subsequent loss of carbon dioxide to yield a nitroparaffin with one less car-

bon atom than the parent acid; or (b) the nitration mechanism involves free radicals.

According to the literature, nitric acid is completely decomposed at 250° C. into nitric oxide, nitrogen dioxide, water, and oxygen. Since nitrogen dioxide (NO<sub>2</sub>) is not present in the reaction tube to any appreciable extent, it must follow that (a) it is never formed, (b) it is immediately reduced to nitric oxide (NO), (c) it is rapidly converted to a stable compound by uniting with a reactive fragment such as a free radical, or (d) it forms nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>) and nitrates a paraffin by metathesis.

Since nitrogen dioxide can act as a nitrating agent, as shown by Hodge, the first postulate is invalidated; since at the temperatures used for vapor-phase nitration the concentration of nitrogen tetroxide would be minute, postulate d is improbable. Thus b and/or c must represent the fate of nitrogen dioxide in the reaction chamber. Postulate b undoubtedly accounts for a large part of the loss of nitrogen dioxide since most of the nitrogen passing out with the exit gas is present as nitric oxide.

An examination of the electronic structure of the nitrogen dioxide molecule reveals an odd electron. Thus if a molecule of nitrogen dioxide should collide with a fragment such as a free radical, under suitable conditions, a stable bond should be formed.

## Apparatus

The nitration apparatus described by Hodge (4) was revised and adapted for use with either liquid or gaseous hydrocarbons. The nitric acid was not preheated. It was forced, in a fine stream, directly into the reaction tube where it was mixed with the paraffin. The reaction products were separated by careful rectification in a modified Podbielniak column.

## Nitroparaffins from $\alpha$ -Nitro Fatty Acids

Nitromethane, nitroethane, and 1-nitropropane were prepared by heating nitroacetic,  $\alpha$ -nitropropionic, and  $\alpha$ -nitrobutyric acids, respectively. These nitro acids were prepared by the reaction of the sodium salt of the halogen acids with potassium nitrite. These experiments show that the  $\alpha$ -nitro fatty acids do yield the expected nitroparaffins upon decarboxylation. If they are involved as intermediates in the nitration reaction, their origin must be established. The two possible sources of these  $\alpha$ -nitro acids are the direct nitration of fatty acids, and the oxidation of nitro compounds.

Acetic, propionic, butyric, and isobutyric acids were each mixed with concentrated nitric acid (mole ratio, 1.5 to 1), and passed through a reaction tube, similar to that used for the nitration of paraffins, at 400–410° C. (4). Much carbon dioxide was evolved in each case which indicated that quite a portion of the acid was oxidized. The remainder came through unchanged. In the cases of acetic and isobutyric acids, no nitroparaffins were obtained. In the case of propionic and butyric acids, only traces of nitro compounds were

formed. It must be concluded, therefore, that fatty acids are not intermediate products in the nitration of paraffins.

Nitroethane, 1-nitropropane, 2-nitropropane, and 2-nitrobutane were each mixed with concentrated nitric acid (mole ratio, 1.5 to 1), and passed through the nitrator tube at 400–410° C. In no case was it shown that any lower homologs were formed. In each case there was a copious evolution of carbon dioxide and a loss of nitroparaffin. In view of these results it must be concluded that oxidation of the primary reaction products is not a step towards the formation of the lower homologs. The data show, furthermore, that  $\alpha$ -nitro fatty acids are not intermediate products, since the reactions by which they could be produced do not take place under the conditions used for vapor-phase nitration.

### Tetraethyllead Plus Nitric Acid

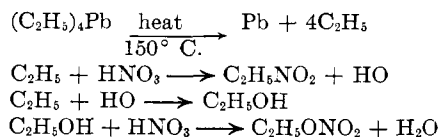
Since all the mononitroparaffins are obtained which are possible without a skeleton rearrangement (4), it was suspected that their presence might be due to the decomposition of the parent paraffin into free radicals which in turn might react with the nitrating agent to yield nitroparaffins.

Calingaert (1) gives for the temperature of decomposition of the tetraalkyllead compounds, the range of 100–150° C. The reaction between tetraethyllead and nitric acid at these temperatures is vigorous; in order to avoid explosions and complete oxidation, the reactants were diluted with carbon dioxide. The reaction tube, which consisted of a Pyrex glass tube 25 mm. in diameter and 100 cm. long, was heated to 150° C. at the zone of contact of the reacting vapors. The remainder of the tube was kept relatively cool by the application of a wet towel. The tetraethyllead (supplied through the courtesy of the Ethyl Gasoline Corporation) was admitted dropwise from a dispensing buret and fell directly into the hot zone. The nitric acid was carried into the reaction chamber by passing a stream of carbon dioxide through a flask containing hot nitric acid. The carbon dioxide stream was kept constant and was arranged with a by-pass so that the fraction of the gas passing through the hot acid could be regulated.

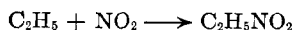
Thirty milliliters of nitroethane were prepared in this manner from approximately 150 ml. of tetraethyllead. The nitroethane was identified by its boiling point (111–112° C. at 745 mm. mercury) and refractive index ( $n_D^{25} = 1.3902$ ).

The rectification of the oily layer obtained from these experiments showed the presence of another compound boiling at 87–90° C. Upon re-rectification of this portion of the product a good sample was obtained which boiled at 87–88° C. and had a refractive index of 1.3847 at 21.5° C. Ethyl nitrate boils at 88.7° C. and has a refractive index of 1.3848 at 21.5° C.

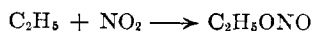
The equations for the reactions involved may be:



It is probable that some of the nitroethane was formed by a collision of an ethyl radical with a nitrogen dioxide molecule since nitrogen dioxide was present in the reaction zone to a considerable extent:



Since similar experiments, in which nitrogen dioxide was used instead of nitric acid, usually resulted in an explosion, there is no direct experimental evidence that this union occurs. It is probable that the following reaction occurs:



### Free Radicals and Chain Reactions

Calculations, using the reaction-rate constant for the decomposition of *n*-butane at 425° C. (3), show a decomposition of about 0.0002 per cent for the exposure time used in the nitration reaction. If this is correct, it seems that some factor besides ordinary pyrolysis must be responsible for the formation of the free radicals.

Considerable proof has been given of the effect of free radicals, both in initiating chain reactions in the decomposition of organic compounds and in inducing decomposition at temperatures far below that at which the pure compound decomposes (2, 11, 13).

In the system we are considering in the nitration reaction, the thermal decomposition of nitric acid and/or the thermal decomposition of unstable oxidation products should readily produce active fragments which would induce the evident decomposition of the butane. If decomposition of the paraffin does occur as postulated, analysis of the exit gas should reveal the presence of the particular olefins predicted by the theory of thermal decomposition advanced by Rice (10).

### Olefins in Exit Gas

The exit gas from the nitration of propane, butane, pentane, and isopentane was examined for olefin content by allowing it to pass through an absorption tube containing a solution of bromine in carbon tetrachloride.

The individual dibromides were identified by their boiling point, refractive index, and density. The following table gives a summary of the olefins that should be formed according to the theory of chain reactions involving free radicals (10, 11) and a list of those found to be present by the analyses:

Paraffin	Olefins That Should Be Formed	Olefins Found
Ethane	Ethylene	Not studied
Propane	Ethylene Propylene	Ethylene Propylene
<i>n</i> -Butane	Ethylene Propylene 1-Butene <sup>a</sup> 2-Butene <sup>a</sup>	Ethylene Propylene 1-Butene 2-Butene
Isobutane	Propylene Isobutylene	Not studied
<i>n</i> -Pentane	Ethylene Propylene 1-Butene	Ethylene Propylene 1-Butene
Isopentane	Ethylene Propylene Isobutylene 1-Butene 2-Butene	Ethylene Propylene Isobutylene 1-Butene 1-Butene

<sup>a</sup> In the case of butane, Neuhaus and Marek (8) found appreciable quantities of 1-butene and 2-butene, which indicated that the reaction involving direct separation of molecular hydrogen was occurring as well as the chain reaction. Five pentenes might also be formed by the separation of molecular hydrogen but not, according to theory, by free radical formation.

It is significant that, in every case studied, all of the olefins were found that would be predicted if we assumed that free radicals are the active intermediates. This fact establishes the conjecture that the olefins were formed by decomposition of the paraffin and furnishes the needed evidence that free alkyl radicals are actually existent in the reaction tube. In each case the hydrocarbon used was found to be free from olefins.

### Nitration of Butane

In order to study the effect of certain variables upon the nitration reaction, a series of runs was made using butane as

the starting material. The data are given in Tables I, II, and III.

### Effect of Temperature upon Ratio of Nitro Products

Konowaloff (5) found that at higher temperatures the ratio of primary nitro compound to secondary nitro compound became larger. These results were verified in this laboratory, using butane. The data obtained are given in Table III.

The change in the ratio of 1-nitrobutane to 2-nitrobutane is probably due primarily to a change of the relative reaction rates of the primary and secondary hydrogen atoms with the change in temperature.

### Factors Influencing Olefin Formation

It seems probable that an increase in the relative amount of nitric acid used should foster the formation of butenes due to its dehydrogenation effect on the butane. An examination of the data from runs B-1, 2, 3, 4, 7, and 8 (Table II) confirms this postulate.

Further examination of Table II reveals a higher relative yield of ethylene and propylene per unit of nitro compounds formed when a relatively smaller amount of nitric acid is used. This is good evidence that the free radicals (the immediate precursors of ethylene and propylene) are present in the reaction tube and that they are involved in the nitration reaction, since a change in the relative concentration of the nitrating agent causes the expected fluctuation in the yields of olefins and nitro compounds. In other words, if the probability of a collision or a free radical with a molecule of nitrating agent is decreased, the probability of its decomposition into an olefin and a smaller free radical is increased.

Experiments B-5, 6, 10, 11, and 12 give a good indication of the effect of temperature upon the amount of decomposition taking place. Tables I and II show that there is a marked increase in the amount of decomposition at the higher temperatures as evidenced by olefin formation. It is not surprising, then, that the ratio of the lower homologous nitro compounds to the nitrobutanes is greater at the higher temperature (Table III) since there is a greater concentration of the lower free radicals due to increased pyrolysis.

TABLE I. EFFECT OF VARIABLES ON NITRATION REACTIONS

Run No.	C <sub>4</sub> H <sub>10</sub> Liters/ hr.	HNO <sub>3</sub> Ml./hr.	Temp. ° C.	Time Hr.	Crude Nitro Compounds Ml.	Water Layer Ml.	C <sub>4</sub> H <sub>10</sub> / Mole HNO <sub>3</sub>
B-1	60	43	422	8	150	270	3.92
B-2	60	66	420	8	270	415	2.54
B-3	60	32	422	8	130	209	5.25
B-4	60	71	418	8	295	435	2.38
B-5	60	60	445	8	120	575	2.82
B-6	60	55	395	8	148	415	3.00
B-7	60	73	420	7	265	425	2.30
B-8	60	38	420	9	153	235	4.45
B-10	40	46.6	393	9	230	340	2.41
B-11	60	66	393	6.5	205	310	2.56
B-12	60	62.5	450	6.5	151	345	2.68

### Oxidation Products

During the nitration of isopentane and pentane in this laboratory, flashes of fire could be seen in the reaction tube when a mole ratio of isopentane to nitric acid of about 2.0 or lower was used.

The principal products of the oxidation reaction identified were carbon dioxide, acetic acid, acetone, and aldehydes. Acetone was found only in the cases of isobutane (4) and isopentane (12).

Formaldehyde and propionaldehyde resulted from the nitration of propane; although no data are available on alde-

hyde formation concurrently with the nitration of other lower paraffins, the odor of the water layer indicated their presence.

A survey of the literature on air oxidation of paraffins indicates that any or all of the probable oxidation products can be obtained if the proper conditions are maintained.

TABLE II. EFFECT OF VARIABLES ON NITRATION REACTIONS

Run No.	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> + C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub> Ml.	(C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> + C <sub>3</sub> H <sub>6</sub> Br <sub>2</sub> )/100 Ml. RNO <sub>2</sub>	C <sub>4</sub> H <sub>8</sub> Br <sub>2</sub> Ml.
B-1, B-3	70.5	25.1	41.0
B-2, B-4	53.0	9.4	60.0
B-5	44.0	36.7	80.0
B-6	13.0	8.8	11.0
B-7	28.0	10.5	65.0
B-8	25.0	16.4	35.0
B-10	8.0	3.5	24.0
B-11	7.0	3.4	18.0
B-12	48.0	31.8	72.0

Pope, Dykstra, and Edgar (9) concluded from their work on vapor-phase oxidation of the octanes that octanal was the first product of the oxidation. Octanal was then oxidized to heptanal and carbon monoxide or dioxide, and then by similar steps through the lower aldehydes. When branched-chain octanes were used, the oxidation and degradation proceeded until a branch in the chain was reached. At this point the reaction was distinctly retarded. Reasoning by analogy, it is easy to account for the acetone produced during the nitration of isobutane and isopentane.

TABLE III. EFFECT OF TEMPERATURE ON RATIO OF NITRO PRODUCTS

Run No.	Temp. ° C.	Nitro- methane %	Nitro- ethane %	1-Nitro- propane %	2-Nitro- butane %	1-Nitro- butane %
B-5	445	5.9	18.2	6.5	37.0	31.8
B-6	395	2.1	12.7	4.9	49.0	30.5
B-10	393	6.0	19.0	7.0	41.0	27.0
B-11	393	5.0	11.0	5.0	46.0	32.0
B-12	450	9.0	25.0	7.0	28.0	31.0

Another possible source of the oxidation products is through the oxidation of the olefins shown to be present. Vigorous oxidizing agents bring about a cleavage of the carbon chain at the position of the double bond with the subsequent conversion of the fragments to acids, ketones, and aldehydes. The oxidation of an olefin containing a branched chain should yield, among other things, the ketone corresponding to the branched chain. For example, trimethylethylene should yield acetone, acetic acid, and possibly formic acid, formaldehyde, and acetaldehyde.

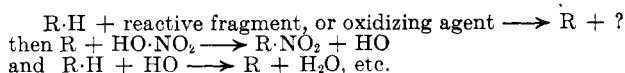
Some trimethylethylene was prepared by dehydration of *tert*-amyl alcohol, purified by rectification, and passed through the nitration apparatus with concentrated nitric acid at 410° C. Acetone and acetic acid were identified as products of the reaction.

In view of the fact that the partial pressure of the olefins is quite small in comparison to the partial pressure of the parent paraffin, it is logical to predict that most of the oxidation products are derived directly from the paraffin.

### Summary

The following mechanism is suggested to account for all the products of vapor-phase nitration:

A. The reaction appears to involve a free radical mechanism. In nitrating with nitric acid the cycle may be:

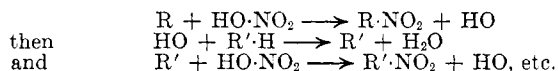


B. Oxidation of the paraffin by nitric acid, or the thermal decomposition of some unstable intermediate, gives free radicals which may react as follows:

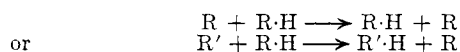
1. Decompose to form an olefin and a free radical of lower molecular weight which, in turn, could undergo any or all of the possible reactions of its predecessor, as



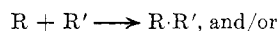
2. Unite with a molecule of the nitrating agent to yield a nitroparaffin and an active fragment, as



3. Collide with a molecule of the parent paraffin and instigate a chain reaction, as



4. Unite with another free radical to form an alkane, as



5. Become oxidized to carbon dioxide and water, or to some oxidized intermediates.

C. The oxidation products may be accounted for by assuming:

1. Direct oxidation of the parent hydrocarbon, and/or
2. Oxidation of the nitroparaffins, and/or
3. Oxidation of free radicals, cleavage products, and olefins.

### Literature Cited

- (1) Calingaert, G., *Chem. Rev.*, **2**, 43-83 (1935).
- (2) Frey, F. E., *IND. ENG. CHEM.*, **26**, 200 (1934).
- (3) Frey, F. E., and Hepp, H. J., *Ibid.*, **25**, 441 (1933).
- (4) Hass, Hodge, and Vanderbilt, *Ibid.*, **28**, 339-44 (1936).
- (5) Konowaloff, M., *Ber.*, **26**, 878 (1893); **28**, 1852 (1895), **29**, 2199 (1896); *Chem. Zentr.*, **76**, (2), 818 (1905), **77** (2), 312 (1906).
- (6) Markownikoff, W., *Ber.*, **32**, 1441, 1445 (1899), **35**, 1584 (1902); *Chem. Zentr.*, **70** (2), 472-3 (1899).
- (7) Meyer, Victor, *Ber.*, **5**, 203, 399, 514, 1029, 1034 (1872), **9**, 529 (1876); *Ann.*, **175**, 88 (1875), **180**, 134 (1876).
- (8) Neuhaus and Marek, *IND. ENG. CHEM.*, **24**, 400 (1932).
- (9) Pope, Dykstra, and Edgar, *J. Am. Chem. Soc.*, **51**, 1875, 2203 (1929).
- (10) Rice, F. O., *Ibid.*, **53**, 1959 (1931).
- (11) Rice, F. O., and Rice, K. K., "Aliphatic Free Radicals," Baltimore, Johns Hopkins Press, 1936.
- (12) Seigle, L. W., unpublished work.
- (13) Sickman and Allen, *J. Am. Chem. Soc.*, **56**, 1251 (1934).
- (14) Worstall, R. A., *Am. Chem. J.*, **20**, 202 (1898).

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## Nitration of *n*-Pentane<sup>1</sup>

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The vapor-phase technic for the nitration of saturated hydrocarbons has been extended to *n*-pentane. The nitroparaffins thus formed are 1-nitropentane, 2-nitropentane, 3-nitropentane, 1-nitrobutane, 1-nitropropane, nitroethane, and nitromethane. These include all of the compounds theoretically derivable by adding a nitro group to the free radicals obtainable from pentane by loss of a hydrogen atom or by fission of a carbon-to-carbon linkage.

THE vapor-phase technic for the nitration of volatile saturated hydrocarbons was previously described by Hass, Hodge, and Vanderbilt, and results obtained with ethane, propane, and the two butanes were reported (1). The present paper deals with an extension of this process to *n*-pentane which is one of the hydrocarbons readily available in pure form from natural gas gasoline.

This study may be regarded as a critical test of the free-radical theory of nitration discussed in the paper in this symposium by McCleary and Degering (page 64). Since

<sup>1</sup> This paper, which contains material abstracted from the M.S. thesis of J. A. Patterson, is the seventh in a series on the subject of syntheses from natural gas hydrocarbons. The others appeared in *IND. ENG. CHEM.*, **23**, 352 (1931); **27**, 1190 (1935); **28**, 333, 339, 1178 (1936); **29**, 1335 (1937).

excellent evidence is at hand for the presence of each of the expected products, and there is no reason for believing that any other nitro compounds were formed, the theory must be regarded as having been confirmed at least to some extent.

Every nitroparaffin has been obtained which is theoretically derivable by adding a nitro group to the free radicals obtainable from a given hydrocarbon by loss of hydrogen or by fission of a carbon-to-carbon linkage. Thus, loss of an appropriate hydrogen atom from *n*-pentane can yield the radicals 1-pentyl, 2-pentyl, or 3-pentyl. Fission between carbon atoms 1 and 2 can yield the radicals butyl and methyl while a break between carbon atoms 2 and 3 can give ethyl and propyl. These radicals correspond to the nitroparaffins actually found, which were 1-nitropentane (boiling at 172° C.), 2-nitropentane (boiling at 152° ± 1° C., estimated), 3-nitropentane (boiling at 152° C.), 1-nitrobutane (boiling at 151° C.), 1-nitropropane (boiling at 131° C.), nitroethane (boiling at 114° C.), and nitromethane (boiling at 101.7° C.). The literature does not record a boiling point for 2-nitropentane, but a comparison of the boiling points of any known nonassociated derivative of pentane substituted in the 2-position with the corresponding 3-isomer shows that the boiling point of the one is never more than 1° from that of the other.

Rectification of the reaction mixture can thus be relied upon for the isolation of nitromethane, nitroethane, 1-nitropropane, and 1-nitropentane, while the other three components—i. e., 1-nitrobutane, 2-nitropentane, and 3-nitropentane—appear as a composite fraction. The analysis of this ternary mixture involved reduction to amines, removal by rectification of 1-aminobutane (boiling at 76° C.) from 2-