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NITRATION STUDIES. VI. FACTORS INFLUENCING PRODUCT RATIOS IN VAPOR PHASE PROCESSES[1, 2]

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Despite the fact that studies in vapor phase nitration have been pursued for about twenty years, accurate determinations of the ratios of nitroparaffins produced in the process have been available only since 1949 when the mass spectrographic analytical method was introduced in place of the fractional distillation method formerly used. The new method is more convenient and less time consuming as well as more accurate.

The reliable analytical data which have been accumulated have now been analyzed and a number of valuable new relationships have been discovered. They have made it possible to correlate the effects of changes in reaction conditions with the distributions of nitroparaffins formed and to account in part for the variations in yields and conversions by considering the effects of conditions on the various reaction mechanisms believed to apply.

The present paper is written largely in terms of the nitration of propane since this hydrocarbon is typical of the series and has received more attention than any other. Four nitroparaffins are produced in considerable quantities by the vapor phase nitration of propane. These are nitromethane (NM), nitroethane (NE), 2-nitropropane (2NP), and 1-nitropropane (1NP). They are produced in varying ratios depending on the reaction conditions.

There is little doubt that vapor phase nitration proceeds by free radical processes. It is believed that nitroparaffin formation results from the reaction of an alkyl radical with an $\cdot NO_2$ radical:

$$R\cdot + \cdot NO_2 \rightarrow RNO_2$$

Thus, the precursor of NM is a methyl radical, that of NE is an ethyl radical, and those of 2NP and 1NP are respectively an isopropyl radical and an *n*-propyl radical. Therefore, it is reasonable to assume that any set of reaction conditions which will favor the formation of a particular alkyl radical in the reacting vapors will also favor the formation of the corresponding nitroparaffin in the product mixture.

Alkyl radicals may be produced in various ways (6, 10). These include: attack on the hydrocarbon by $HO\cdot$ radicals (from HNO_3), by $Cl\cdot$ atoms (from added chlorine), by $NO_2\cdot$ radicals (from the nitrating agent), by O_2 or peroxides (from added oxygen). Alkyl radicals smaller than those obtained directly from

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the original hydrocarbon by loss of a hydrogen atom arise primarily from degradation of propyl or propoxy radicals. Direct dissociation of propane to alkyl radicals must be excluded since it is negligible at the temperatures and reaction times studied (12). By proper combinations of these various radical-creating processes it is possible to account for observed variations in the distribution of the nitroparaffins formed in the vapor phase nitration of propane.

EXPERIMENTAL

APPARATUS

The *apparatus* used was identical with that described in the previous papers in this series (2–4).

Chlorine was introduced as a solution in the nitric acid or as a gas metered into the propane stream through an orifice-type flowmeter.

PRODUCT ANALYSIS

Unusual connotations are employed with regard to the terms conversion and yield. Throughout this paper the term *conversion* implies the molar ratio RNO_2 obtained/NO_2 charged as such or as HNO_3. The yields based on HNO_3 were not obtained since some of the nitric acid "lost" consists of nitric oxide and nitrous acid, readily recoverable as nitric acid in recycling operations. Also, throughout this paper the term *yield* implies the molar ratio RNO_2 obtained/RH consumed. The conversions based on hydrocarbons were not obtained since a large excess of the hydrocarbon was used.

The distribution of the nitroparaffin product mixture was determined by mass spectrographic analysis. The authors are indebted to Dr. James Neerman, formerly of the Commercial Solvents Corporation, for all the mass spectrographic analyses reported in this paper. Dr. Neerman employed the Consolidated Engineering Corporation Mass Spectrometer model 21-103, which had been converted from the original model 21-101.

MASS SPECTRAL ANALYSIS OF NITROPARAFFINS

Ionizing current values ranged from 7 to 15 μa. The chosen value, selected to give optimum peak heights on the records, is influenced by gradual changes in instrument sensitivity and occasionally by presence of various sample impurities, *e.g.*, chloroform. The ionizing voltage was fixed at 70 v. With a magnet current of 0.560 a., the range of accelerating voltages enabled scanning of the m/e range 12 to 126; an additional 100 mass units was sometimes scanned. The primary data are photographic records of peak heights *versus* m/e values, in which four simultaneously recorded galvanometer traces offer an expanded sensitivity range such that peak heights can be read to 1 division in 30,000.

The liquid samples were introduced into the evacuated mass spectrometer inlet system through a mercury orifice by using a constant-volume self-flushing micropipette, or "capillary dipper", of 1 μ-liter capacity. If desired, the pressure of the vaporized sample could be measured on a micromanometer.

Sample and reference runs were made according to a definite time schedule and under identical operating conditions on any particular day. Individual runs were made on pure "calibration" nitroparaffins to provide data for: (a) "pattern factors", which express all peak heights relative to that of a selected "principal" peak (of unity), and (b) "sensitivity", calibration of the principal peak in μ-grams per division. In addition, runs were made on one or more accurate synthetic blends for a validity check on the over-all method.

The basis of the analysis is the existence of highly selective mass peaks (called "principal" peaks) at masses 61, 29, 43, and 57 for nitro-methane, -ethane, -propane, and -butane, respectively. This is illustrated by the typical calibrating patterns in Table A. The poorest differentiation, or "leverage", is between the 1- and 2-nitropropane isomers. This 1-NP/2-

TABLE A

CALIBRATING PATTERNS AND SENSITIVITIES

m/e	NM	NE	2-NP	1-NP	2-NB	$CHCl_3$
29	0.1556	1.0000	0.0107	0.0545	1.3316	0.0034
42	.0296	0.0052	.0866	.1444	0.0656	.0044
43	.0612	.0069	1.0000	1.0000	.0203	.0020
57	.0000	.0002	.0008	.0021	1.0000	.0000
61	1.0000	.0001	.0000	.0074	.0000	.0005
85	0	0	0	0	0	1.0000
Sensitivity[a]	.6885	.2447	.3839	.4299	.5827	.7377

[a] in μ-grams per division of the principal peak (underlined).

NP split is based largely on the mass 42 peak, for which the mathematical leverage is poor. Table A further includes the pattern for chloroform, which was present in a number of samples, and also the sensitivity calibrations of the principal peaks.

An analysis requires measurement of the mass 29, 42, 43, 57, 61 and 85 peak heights, the last one for chloroform. Since the spectra are strictly additive, these six observables afford six simultaneous linear equations in the six component contributions, namely,

$$h_m = \Sigma_n a_{mn} c_n,$$

where the *h*'s are the observed mixture peak heights, the *a*'s are pattern factors, and the *c*'s are the desired individual component peak contributions; *m* and *n* are mass and component indices respectively.

In actual calculation, the mass 85 peak height determines the amount of chloroform present, if any. The relative chloroform contribution at the other masses follows from its calibration pattern, and these contributions can simply be eliminated by subtraction. Similarly, the nitrobutane content is determined from the total 57 peak height, and its relative contributions to lower masses are subtracted. The remaining four-component matrix equation is then solved simultaneously. We have employed the matrix reduction to diagonal form introduced by Crout (13), which is conveniently adapted to a Monroe calculator. The individual peak contributions thus found (in divisions) readily give analyses in weight per cent from the known sensitivity calibration (in μ-grams per division) for each pure component.

A typical replicate analysis on a known synthetic mixture is given in Table B. The mean

TABLE B

ANALYSIS OF SYNTHETIC BLEND

	NM	NE	2NP	1NP	2NB
Made Up Value[a]........	24.37	15.26	29.73	29.63	1.01
Run No. 1..............	24.12	15.47	29.56	29.67	1.19
Run No. 2..............	24.26	15.98	29.17	29.42	1.17
Run No. 3..............	24.05	15.05	29.78	29.93	1.18
Mean of runs...........	24.14	15.50	29.50	29.67	1.19
Av. deviation of runs....	±0.08	±0.32	±0.22	±0.17	±0.01

[a] All values are given in wt.-%.

values of the runs showing the degree of accuracy and the average deviations of the runs showing the degree of precision are also shown.

For nitroparaffin samples which contain no impurities in perceptible amounts the accuracy of the mass spectral results is equal to, or better than, the maximum deviations tabulated in Table B. Impurities like chloroform or benzene, which can be identified and estimated, will probably not affect the accuracy much, if at all. No general statement of accuracy can be made in case of appreciable *unidentified* impurities, although careful scrutiny of the complete mass spectral record for anomalous and unexplained peaks minimizes the chance that serious interference by an unknown material and the attendant errors will go unsuspected. Our experience has shown that in such a case the total nitropropane determination may still be valid, although the breakdown into the isomers may be much in error, due to an impurity contribution at the 42 mass peak.

EFFECT OF CHANGES IN TEMPERATURE ON THE NITROPARAFFIN DISTRIBUTION

There are two places in the reaction system for vapor phase nitration at which changes in temperature could conceivably affect the distribution of the nitroparaffins in the product. The first of these is in the reactor, and the second is in the preheater.

Hass, Hodge, and Vanderbilt (8) have shown that an increase in reactor temperature results in an increased yield of primary nitroparaffins. They found that, in the vapor phase nitration of isobutane at 150°, the sole product was tertiary nitrobutane while at 420° this product comprised only 7% of the product mixture.

Kohn's (10) runs (Nos. 5, 6, 26, and 27) and Millikan's (11) runs (Nos. 2, 3, 4, and 5) seem to indicate that the effect of increased reactor temperature in the vapor phase nitration of propane is to lower the product mole ratio of 2NP and to increase that of NE. No appreciable change is noted in the product mole ratios of 1NP and NM (10, 11). Mole-% of carbonyl compounds and of nitric oxide produced are higher at higher temperatures.

A series of runs was undertaken by the authors in order to study more critically the effect of increased reactor temperature on the nitroparaffin distribution from the vapor phase nitration of propane. The results are shown in Figures 1 and 2. They indicate that higher reactor temperatures favor the formation of NE, hinder the formation of 2NP, and leave essentially unchanged the formations of NM and 1NP. These trends may be explained as follows. Higher temperatures decrease the selectivity of attack on propane and hence increase the ratio of 1-propyl/2-propyl radicals produced. Higher temperatures also increase the degree of degradation of the propyl radicals to lower alkyl radicals in such a way that 1-propyl radicals degrade primarily to ethyl radicals while 2-propyl radicals degrade primarily to methyl radicals (14).

As the temperature is raised a greater relative formation of 1-propyl radicals occurs but also a greater degree of degradation of these radicals to ethyl radicals occurs. This results in a nearly constant rate of production of 1NP but a greatly increased production of NE as indicated in the figures. Similarly the lower rate of formation of 2-propyl radicals and the greater degree of degradation of these radicals to methyl radicals results in a decrease in production of 2NP but a constant rate of production of NM.

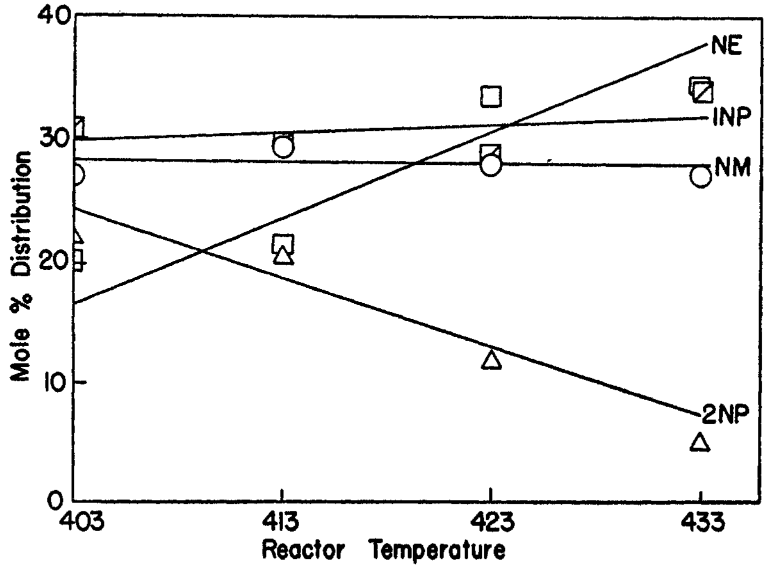

Figure 1. Effect of Reactor Temperature on Mole-Percent Distribution of the Product Nitroparaffins.

Degradation of propyl radicals probably proceeds principally through propoxy radicals produced through oxidation by the nitrating agent or oxygen itself.

$$CH_3CH_2CH_2\cdot \rightarrow CH_3CH_2CH_2O\cdot \rightarrow CH_3CH_2\cdot + CH_2O$$
$$(CH_3)_2CH\cdot \rightarrow (CH_3)_2CHO\cdot \rightarrow CH_3\cdot + CH_3CHO$$

In agreement with this postulate the amounts of aldehydes and of nitric oxide produced both increase with temperature (10, 11, 14).

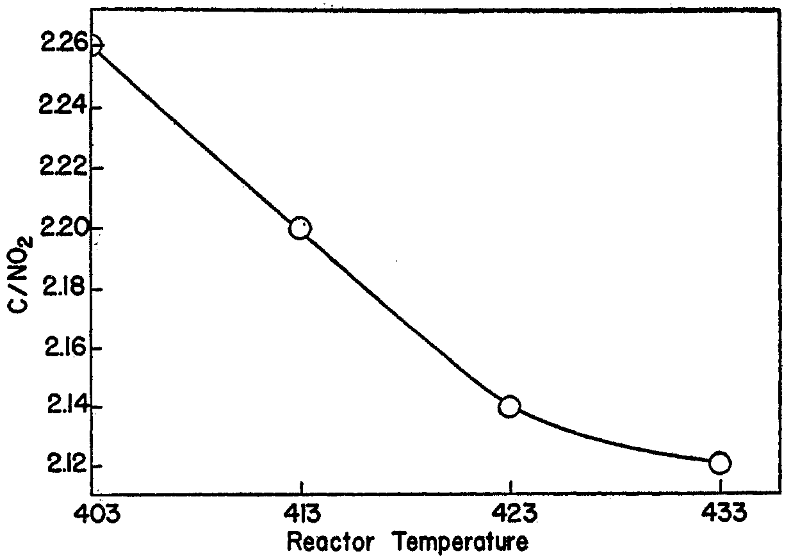

Figure 2. Effect of Reactor Temperature on the C/NO$_2$ Ratio of the Product Nitroparaffins. Data from Table 1.

TABLE I

EFFECT OF C_3/HNO_3 RATIO

RUN NO.	$\frac{C}{NO_2}$	$\frac{S}{V}$	CONV, %	$\frac{C_3}{HNO_3}$	$\frac{O_2}{HNO_3}$	$\frac{Cl_2}{HNO_3}$	NM	NE	2NP	1NP
K-48	2.23	300	39.2	10.5	0.9	0.42	27	23	15	35
P-10	2.34	300	43.6	25.6	1.0	.39	23	21	27	30
K-61	2.14	300	44.8	10.5	1.01	.05	31	23	17	29
P-9	2.28	300	49.1	30.8	1.29	.07	26	21	27	26
K-51	2.08	300	43.3	10.5	0.99	.1	35	24	16	26
P-12	2.25	300	42.6	46.7	1.34	.1	28	20	21	31
K-27	2.16	28	47.6	11.7	1.17	.01[a]	29	26	19	25
K-29	2.24	28	52.8	18.4	1.06	.01[a]	27	22	26	25

In each run: H_2O/HNO_3 input = 1.55; preheater temperature = 300° ± 10°; reactor temperature = 423°; contact time = *ca.* 1.7 sec.

[a] Refers to Br_2/HNO_3 instead of Cl_2/HNO_3.

Variations in preheater temperatures from 270° to 430° produced negligible changes in nitroparaffin distributions, C/NO_2 ratios, and in mole ratios of aldehydes and nitric oxide produced.

EFFECT OF INCREASED PROPANE/NITRIC ACID RATIO ON THE DISTRIBUTION OF THE NITROPARAFFINS

The data from a series of runs have been assembled in Table I to show the effect of increased propane/nitric acid ratio on the product distribution in the presence of oxygen and halogen. They indicate that, as the C_3/HNO_3 ratio is increased, the following changes occur in the nitroparaffin distribution: NM—decreases; NE—decreases; 2NP—increases; 1NP—erratic or little change; C/NO_2 ratio—increases.

These trends indicate that higher C_3/HNO_3 ratios, contrary to the effect of higher temperatures, decrease both the ratio of 1-propyl/2-propyl radicals produced as well as the degree of degradation of these radicals to lower alkyl radicals.

As the C_3/HNO_3 ratio increases the relative amounts of 2-propyl radicals formed increase. Since less oxygen is present the degradation of these radicals to methyl radicals *via* 2-propoxy radicals decreases. Hence there is more 2NP and less NM produced. Similarly the 1NP produced remains about constant since fewer 1-propyl radicals are produced but also fewer are degraded to ethyl radicals *via* 1-propoxy radicals. This results in a constant amount of 1NP and a decreasing amount of NE.

EFFECT OF CHANGES IN SURFACE TO VOLUME RATIO (S/V) ON THE NITROPARAFFIN DISTRIBUTION

In recent years four different reactor surface/volume ratios have been used (3, 10) in vapor phase nitrations: 4 cm.$^{-1}$, 28 cm.$^{-1}$, 150 cm.$^{-1}$, and 300 cm.$^{-1}$. The s/v ratio of the reactor is determined by the packing and by the size tubes making up the reactor.

A series of runs with propane was made by the present authors in which all reaction conditions, with the exception of s/v ratios, were kept nearly the same. Comparison of these results shows that changes in s/v ratio cause no definite trends in the nitroparaffin distribution or in the C/NO_2 ratio of the product nitroparaffins.

EFFECT OF OXYGEN ON THE DISTRIBUTION OF THE NITROPARAFFINS

It has been demonstrated (2) that the effect of increased oxygen in the nitration of butane is to increase the mole distribution ratios of the lower nitroparaffins at the expense of the two nitrobutanes. It was further shown that the decrease in the yield of secondary nitrobutane exceeds that of the primary isomer.

Addison and Bachman (1, 2) did considerable work on the effect of increased oxygen on the by-product distribution from the vapor phase nitration of butane. They showed that the effect of an increased oxygen/butane ratio is to increase the yields of carbonyl compounds, olefins, and carbon monoxide.

A series of runs was made by the present authors for a study of the effect of O_2 on the distribution of the nitroparaffins formed in the nitration of propane. The data are shown in Figures 3 and 4. The curves in Figure 3 show that as the O_2/C_3H_8 ratio is increased, other factors remaining constant, the mole distribution ratios of 2NP decrease, of NM increase, and of 1NP and NE increase slightly. The qualitative effect of increased O_2/C_3H_8 ratio is the same regardless of whether halogen is present or absent. Figure 4 shows that the effect of increased O_2/C_3H_8 ratio is to decrease the C/NO_2 ratio of the product nitroparaffins.

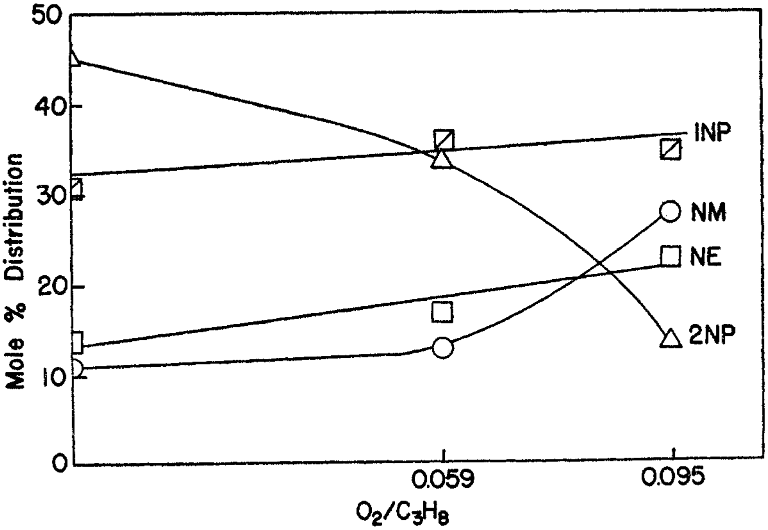

FIGURE 3. EFFECT OF O_2/C_3H_8 RATIO ON THE MOLE-PERCENT DISTRIBUTION OF THE PRODUCT NITROPARAFFINS.

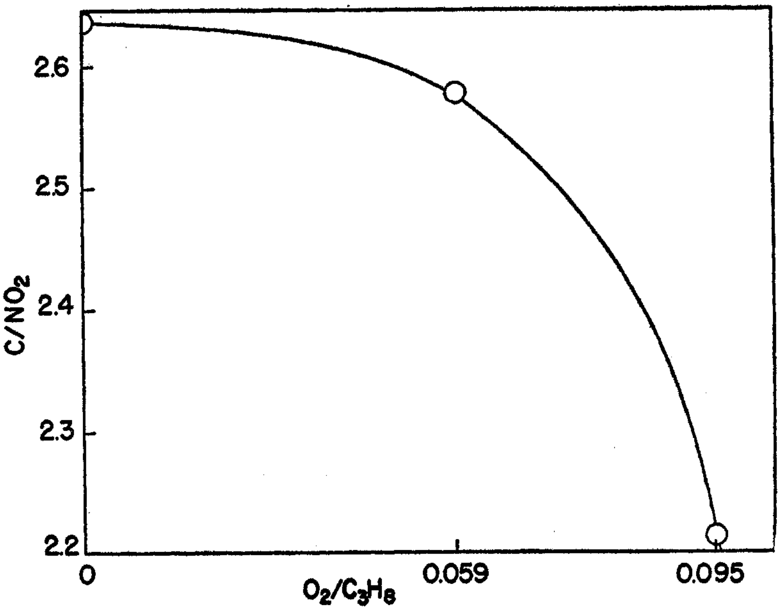

FIGURE 4. EFFECT OF O_2/C_3H_8 RATIO ON THE C/NO_2 RATIO OF THE PRODUCT NITROPARAFFINS.

These trends are governed by similar changes in ratios to those induced by higher temperatures. The curves in Figure 3 therefore take about the same directions as in Figure 1 although there are differences in shapes which result from differences in the degrees to which the ratios are affected. Thus increased O_2/C_3 ratios affect the degree of degradation of propyl radicals to lower alkyl radicals far more than they affect the ratio of 1-propyl/2-propyl radicals produced. It may reasonably be assumed, however, that oxygen is somewhat less selective than other radical-producing agents present in its attack on propane which results in a higher 1-propyl/2-propyl radical production. It may also be assumed that oxygen exerts a powerful degradative effect on both propyl radicals leading to increased amounts of both methyl and ethyl radicals. These assumptions suffice to explain semi-quantitatively the changes in nitroparaffin distributions observed.

EFFECT OF HALOGENS ON THE DISTRIBUTION OF THE NITROPARAFFINS

Halogens, especially chlorine, have been in use for some time as catalysts in vapor phase nitration. The essential function of these halogens is to increase the concentration of alkyl free radicals in the reaction mixture. Kohn (10) has shown that the conversions to and yields of nitroparaffins obtained are dependent upon the concentration of the chlorine when the O_2/HNO_3 ratio is 1.0.

A series of runs was undertaken to study the effect of| increased Cl_2/C_3H_8 ratio, in the absence of oxygen, on the vapor phase nitration of propane. The results of these runs are shown in Figure 5.

It is seen that the effect of an increased Cl_2/C_3H_8 ratio in the absence of

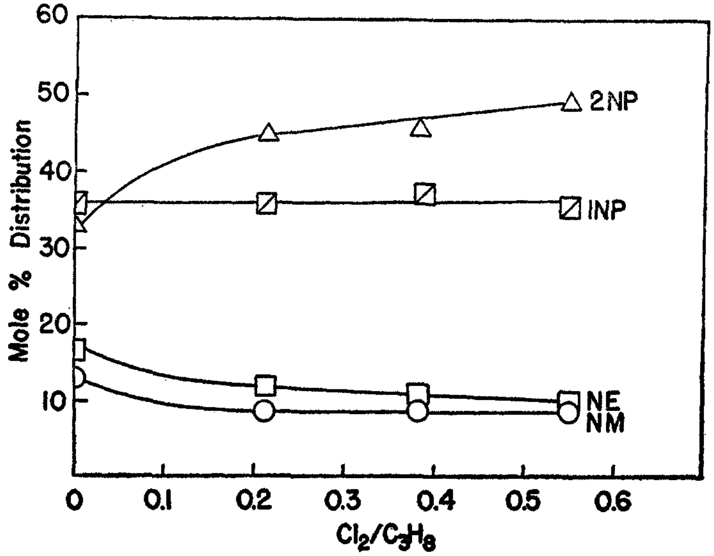

FIGURE 5. EFFECT OF Cl_2/C_3H_8 RATIO (O_2 ABSENT) ON THE MOLE-PERCENT DISTRIBUTION OF THE PRODUCT NITROPARAFFINS.

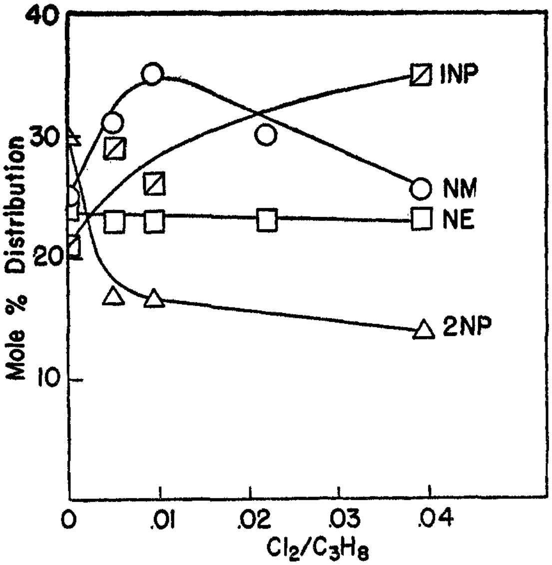

FIGURE 6. EFFECT OF Cl_2/C_3H_8 RATIO (O_2 PRESENT) ON THE MOLE-PERCENT DISTRIBUTION OF THE PRODUCT NITROPARAFFINS,

oxygen is to decrease the NM and NE, and to increase the 2NP, leaving the 1NP relatively unchanged. These results indicate increased selectivity of nitration. The explanation lies in the fact that increased Cl_2/C_3H_8 ratio leads to the formation of more isopropyl and *n*-propyl radicals. But since chlorine is quite selective in its attack upon propane, the increase in the concentration of isopropyl radicals exceeds that of the *n*-propyl radicals. This result is manifested in a slight increase in 2NP relative to 1NP.

The effect of increased Cl_2/C_3H_8 ratio in the presence of oxygen is of a radically different nature. From Figures 6 and 7, the net effect appears to be to decrease the 2NP, increase the 1NP, and to leave relatively unchanged the NE. The NM rises to a maximum at a Cl_2/C_3H_8 ratio of 0.01 and then decreases gradually through the remainder of the curve. The effect on the distribution and on the C/NO_2 ratio of the first small increase in the Cl_2/C_3H_8 ratio from 0 to 0.005 should be noted. This effect is almost that which would be expected from a large increase in the O_2/C_3H_8 ratio (see Figure 3); so it is apparent that small amounts of chlorine promote the effect of oxygen in the vapor phase nitration system. The same oxygen-promoting effect is also observed when bromine is used in place of chlorine. It should be noted that HBr has been recommended recently as a catalyst in the oxidation of hydrocarbons (5).

The curves in Figures 6 and 7 can be explained as follows: First, the small amounts of chlorine catalyze or promote the effect of oxygen resulting in a decrease in 2NP and an increase in 1NP and NM. However, as the halogen concentration increases relative to the oxygen concentration the normal effect of halogen (see Figure 5) begins to supersede that of oxygen, and the 1NP and 2NP curves level off and the NM curve drops. The NE is relatively unaffected

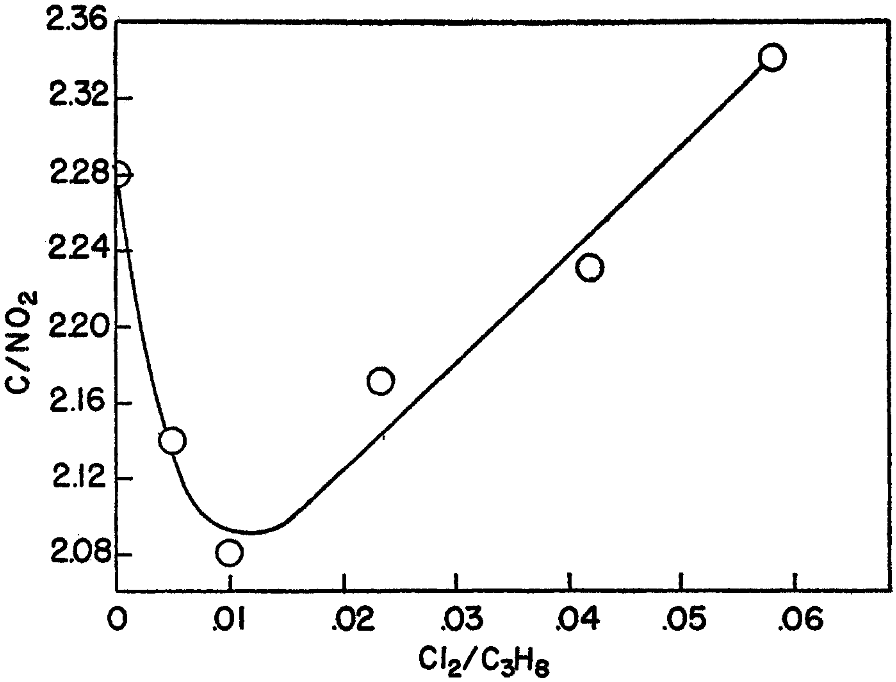

FIGURE 7. EFFECT OF Cl_2/C_3H_8 RATIO (O_2 PRESENT) ON THE C/NO_2 RATIO OF THE PRODUCT NITROPARAFFINS.

THE "1/2" RATIO

In their studies of chlorination Hass, McBee, and Weber (9) showed that the attack of chlorine at different positions on a hydrocarbon molecule could be calculated. From their curves the ratio of 1-propyl chloride/2-propyl chloride formed at 423° would be about 59/41. It is interesting to compare these figures with similar ones obtained in nitration. Since, however, nitration processes lead to extensive degradation of the hydrocarbon nitrated and produce lower nitroparaffins in substantial quantities it is necessary to employ a ratio determined by adding the nitropropanes to the lower nitroparaffins produced. Thus we have postulated above that NE arises primarily from degradation of 2-propyl radicals. Hence the sum of 1NP + NE would represent the degree of attack at the 1-position of propane while the sum of 2NP + NM would represent the degree of attack at the 2-position of propane. The ratio 1NP + NE/2NP + NM, hereafter referred to as the 1/2 ratio, would then be comparable to the Hass, McBee, and Weber ratio calculated for the chlorination of propane. The 1/2 ratio appears to average about 54/46 for nitration with HNO_3 at 423° with no catalysts present. This ratio is apparently increased by increases in the reactor temperature or the oxygen content (halogens present or absent). The ratio is decreased by increases in the surface to volume ratio, the hydrocarbon to nitric acid ratio, or the halogen content (oxygen absent). Ratios as high as 68/33 and as low as 35/65 have been obtained with various combinations of catalysts and conditions (7).

It is perhaps useless to attempt to place these influences on a more quantitative basis since each one is materially affected by changes in the others. However it is useful to know the general effect created by any change in conditions so that it may be counteracted or augmented as desired by other changes. It is also gratifying that these trends correlate with the proposed mechanisms of nitration and increase confidence in their value.

CONCLUSIONS

It is evident from the data presented that the distribution of nitroparaffins obtained in the vapor phase nitration of alkanes may be materially altered by changes in the conditions of nitration. Factors of greatest importance seem to be the reactor temperatures, the reactant ratios, and the presence of catalysts such as oxygen and halogens. Extreme variations for the individual nitroparaffins obtained with propane from this and previous publications (10, 11) range between the following values for mole percent distribution: NM, 9% to 49%; NE, 6% to 36%; 2NP, 5% to 45%; and 1NP, 9% to 35%. It is probable that even greater variations could be obtained if desired by proper combinations of the individual factors reported.

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