[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY AND THE PURDUE RESEARCH FOUNDATION]

NITRATION STUDIES. V. EFFECT OF CHLORINE IN VAPOR PHASE NITRATION WITH NITRIC ACID[1]

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The work of Bachman, Hewett, and Millikan (4) has shown that the addition of small amounts of bromine or iodine increases the conversion to and yield of nitroparaffins obtained in the vapor phase nitration of propane with nitric acid or nitrogen dioxide. This investigation has demonstrated that chlorine may also be used effectively instead of bromine or iodine. Furthermore, it has been shown that higher percentages of halogen than those previously employed (4) are advantageous, but that eventually decreases in both the yield and the conversion result if the halogen concentration is increased too much. Optimum results have been found to depend upon the nature of the halogen and its concentration, as well as upon variables such as the ratios of the other reactants and the temperature.

Chlorine like bromine probably owes its catalytic effectiveness in nitration to its ability to generate alkyl free radicals which then combine with NO_2 radicals to produce nitroparaffins. It is more efficient in doing this than oxygen not only because it is more reactive towards hydrocarbons but also because it does not remain combined with the organic radicals in the form of by-products to the extent that oxygen does. As more is learned about the complex series of reactions that occur during nitration, it becomes increasingly apparent that optimum results depend upon maintaining a proper balance between the concentrations of NO_2 and free alkyl radicals present in the reaction at any given point. The use of halogens constitutes an important step forward in developing this concept and has led to the highest combination of yields based on hydrocarbon and conversions based on nitrating agent so far obtained.

Chlorine as well as bromine influences the nitration process in other ways besides the yields of and conversions to nitroparaffins. Thus the average C/NO_2 ratio in the nitroparaffins produced and the yields of by-products obtained are materially altered. The explanations and implications of these effects are discussed in later sections.

Apparatus. The apparatus used was identical with that described in the previous papers in this series (2, 3, 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.

Bromine was introduced as a solution in nitric acid or as a gas by passing the propane-oxygen mixture over it in a tared container. The rate of flow of bromine in the latter case was regulated by controlling the temperature of the bromine container.

Product analysis. The product analysis was identical to that described previously (2, 3, 4).

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[1] From the Ph.D. thesis of L. Kohn, Purdue University, June 1951.

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Conversions are based on the fraction of the nitric acid charged which appeared as nitroparaffins. Yields are based on the propane which reacted. The constitution of the nitroparaffin mixture was determined by mass spectrographic analysis.

EFFECT OF PROPANE/NITRIC ACID RATIO IN NITRATIONS IN THE PRESENCE OF OXYGEN

Before beginning a detailed study of the effect of chlorine in vapor phase nitrations it was necessary to make a series of halogen-free runs as a basis for comparison. These were made at several different propane/nitric acid ratios since information on the influence of this ratio was also needed. Previous work in this laboratory indicated that, all other experimental conditions being held constant, the conversions to and yields of nitroparaffins would increase with increasing propane/nitric acid ratio (2, 3).

TABLE I

EFFECT OF PROPANE/NITRIC ACID RATIO IN NITRATIONS IN THE PRESENCE OF OXYGEN

Temp. = 423°. $C_3H_8/O_2 = 10.5$

Contact Time = 1.73 ± .05 Sec. $H_2O/HNO_3 = 1.55^a$

$S/V = 300$ cm.$^{-1b}$

RUN NO. →	31	32	33
REACTANT RATIOS			
C_3H_8/HNO_3	10.3	12.3	16.3
O_2/HNO_3	0.97	1.17	1.56
NITROPARAFFIN PRODUCTS			
Conversion, %	38.9	43.2	47.8
Yield, %	38.3	40.2	41.4
C/NO_2 Ratio	2.28	2.21	2.19
OTHER PRODUCTS, YIELD, %			
Carbon dioxide	3.5	2.9	4.1
Carbon monoxide	6.2	6.2	7.7
Propylene	19.9	14.3	10.7
Ethylene	2.3	3.8	4.2
Carbonyl comp'ds	29.7	32.8	31.9

[a] 69.3% HNO_3 used.

[b] S/V = surface/volume ratio of the reactor.

Runs 31, 32, and 33 (Table I) were performed under favorable reaction conditions and with a near optimum propane/oxygen ratio (10.5 ± 0.2). Since it is possible that halogen affects the reactor surface permanently or semi-permanently, these runs were performed in a new reactor which had never before been used and which had never been in contact with halogens. The results are assembled in Table I. They cannot accurately be compared with the results of previous workers since different reactors were used. However, they lie in the same range and suggest reasonable precision. Furthermore, it should be noted that the yields in the present work are based on mass spectrographic analyses of the nitroparaffin mixture and are therefore considerably more accurate than previous values.

From Figure 1 it is seen that the conversion and yield both increase with increasing propane/nitric acid ratio, but that the change in conversion is more rapid than the change in yield. The increased conversion may be explained by assuming an increased concentration of alkyl free radicals (1) which gives a better balance between these and the NO_2 radicals present. Since increased alkyl radical formation also leads to greater production of oxidation by-products the yield does not increase as sharply as the conversion and even a decrease in yield at very high propane/nitric acid ratios is conceivable.

A striking effect of increased propane concentration is the decrease in propylene production. This may be explained by the probable fact that at high propane/nitric acid ratios there will be increased tendency for propyl free radicals to be converted to other products before they can combine with NO_2 to form nitroparaffins. The decrease in the average carbon chain length of nitroparaffins observed is in accord with this explanation. Propylene is probably formed principally by the reaction $C_3H_7 \bullet \rightarrow C_3H_6 + H \bullet$. Oxidizing agents would favor this reaction by combining with the hydrogen atoms liberated. Hence an increase in the ratio propane/oxidizing agents would be expected to result in decreased propylene formation.

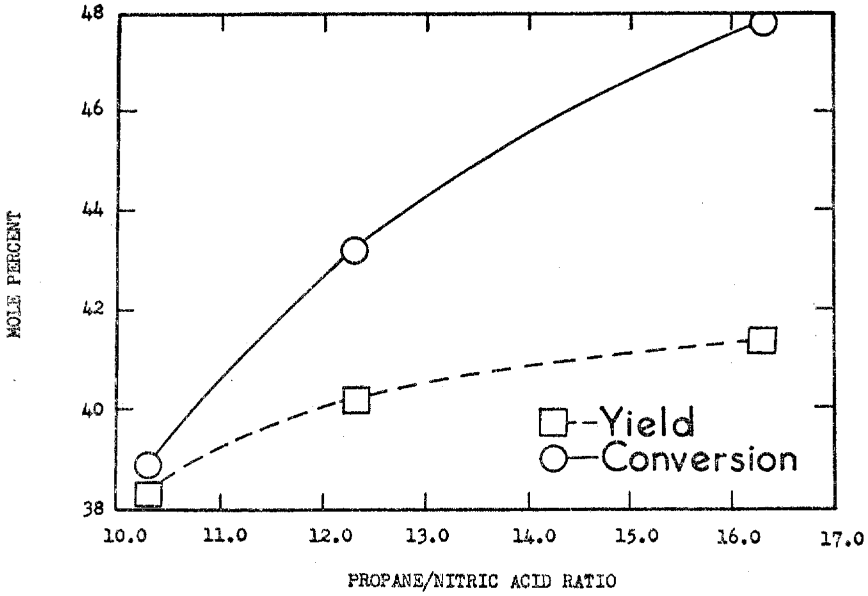

Figure 1. Mole-% Conversion and Yield *vs.* Propane/Nitric Acid Ratio. Conditions: Reaction temperature, 423°; $C_3H_8/O_2 = 10.5$; Contact time = 1.73 ± 0.05 sec.; S/V = 300 cm.$^{-1}$

EFFECT OF BROMINE CONCENTRATION IN NITRATIONS IN THE PRESENCE OF OXYGEN

Previous experiments (4) showed that the addition of small amounts of bromine in the vapor phase nitration of propane in the presence of oxygen causes a notable increase in conversion to and yield of nitroparaffins. In order to determine the effect of variations in the bromine concentration on conversion and yield, a series of runs was performed in which all reaction conditions were held constant at near optimum values. In some cases, a propane/nitric acid ratio higher than the desired 10.5 ± 0.2 was used, but the conversions and yields obtained were reduced to the values which would be expected at a propane/nitric acid of 10.5. This was done by noting the increase in conversion and yield obtained by increasing the propane/nitric acid ratio from 10.5 to the ratio used in the absence of halogen (Figure 1) and subtracting this amount from the experimentally determined conversions and yields. This is, of course, only a good approximation.

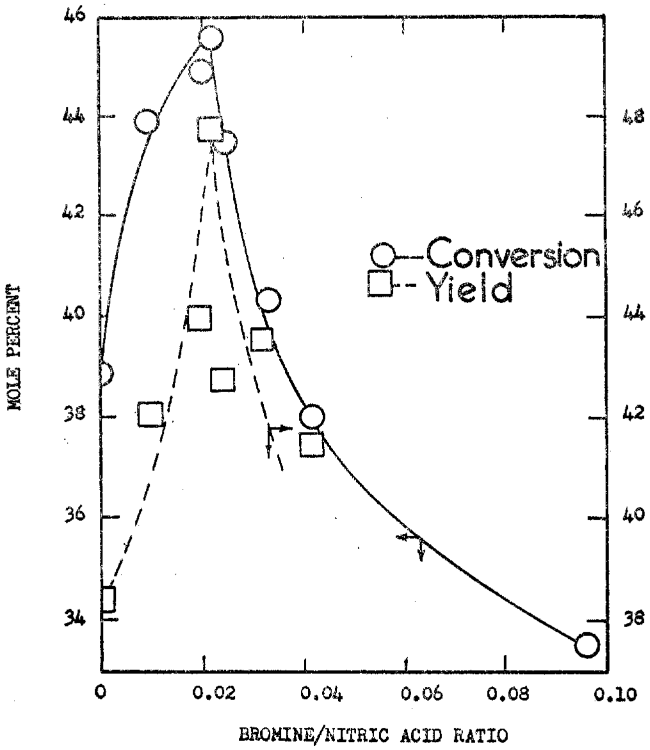

FIGURE 2. MOLE-% CONVERSION AND YIELD *vs.* BROMINE/NITRIC ACID RATIO. Conditions: Reaction temperature, 423°; $C_3H_8/HNO_3 = 10.5 \pm 0.2$; Contact time = 1.69 ± 0.04 sec.; $C_3H_8/O_2 = 10.6$; S/V = 300 cm.$^{-1}$

From Figure 2, it is seen that the conversions and yields increase as the bromine concentration is increased until the peak conversion of 45.6% and yield of 47.8% are obtained at a bromine/nitric acid ratio of 0.022. A further increase in bromine concentration causes a sharp decrease in conversion and yield, and the values at a bromine/nitric acid ratio of about 0.04 are approximately equal to those obtained in the absence of bromine. The conversion is lowered still further by the addition of larger amounts of bromine and a value of 33.5% is obtained at a bromine/nitric acid ratio of 0.096. From this study it is noted that the use of the optimum bromine/nitric acid ratio under the given experimental conditions gives a 6.7% increase in conversion and a 9.3% increase in yield as compared to similar runs without bromine.

Inspection of Table II shows that, in general, the addition of bromine, even in very small concentrations, causes a decrease in the average carbon chain length of nitroparaffins, a decrease in the propylene and carbon monoxide yields, and an increase in the carbonyl compound (aldehydes and ketones) yield.

TABLE II

EFFECT OF INCREASING BROMINE CONCENTRATION IN THE PRESENCE OF OXYGEN

Temp. = 423°. $C_3H_8/O_2 = 10.5$

Contact Time = 1.69 ± .04 Sec. $H_2O/HNO_3 = 1.55^a$

$S/V = 300\ cm.^{-1}$

RUN NO. →	31	66	67[b]	71	68[b]	72[b]	69	73
REACTANT RATIOS								
C_3H_8/HNO_3	10.3	10.7	11.1	10.6	12.0	11.7	10.3	10.7
O_2/HNO_3	.97	1.01	1.05	1.01	1.13	1.11	.98	1.02
Br_2/HNO_3	0	.0091	.0196	.022	.024	.033	.041	.096
NITROPARAFFIN PRODUCTS								
Conversion, %	38.9	43.9	44.9	45.6	43.5	40.3	38.0	33.5
Yield, %	38.3	42.0	44.0	47.8	42.7	43.6	41.5	—
C/NO_2 Ratio	2.28	2.08	2.15	2.00	2.06	2.03	3.03	—
OTHER PRODUCTS, YIELD, %								
Carbon dioxide	3.5	1.5	3.1	4.0	1.7	3.0	3.3	—
Carbon monoxide	6.2	4.4	4.7	5.1	4.9	4.7	4.9	—
Propylene	19.9	7.4	4.7	3.4	8.2	3.6	8.2	—
Ethylene	2.3	1.0	3.1	2.3	1.1	2.4	2.2	—
Carbonyl comp'ds	29.7	39.6	39.6	37.3	39.9	41.6	39.9	—

[a] 69.3% HNO_3 used.

[b] Conversion and yield corrected for C_3H_8/HNO_3 ratio.

EFFECT OF CHLORINE CONCENTRATION IN NITRATIONS IN THE PRESENCE OF OXYGEN

Since chlorine was expected to give results similar to those obtained with bromine, a study was made of the effect of increasing chlorine concentration on the conversions to and yields of nitroparaffins. These runs (Table III) were made under similar experimental conditions and with similar reactant ratios to the previously described runs employing bromine (Table II).

From Figure 2 it is seen that the conversions and yields increase as the chlorine is increased until a peak conversion of 44.8% and a peak yield of 42.5% is obtained at a chlorine/nitric acid ratio of 0.052. A further increase in chlorine concentration causes a reduction in the conversions and yields until values which are about equal to those obtained in the absence of chlorine are found at a chlorine/nitric acid ratio of 0.42. The use of the optimum chlorine/nitric acid ratio gives a 5.9% increase in conversion and a 4.2% increase in yield over those obtained without chlorine.

Inspection of Table III shows that the addition of chlorine causes a decrease in the length of the average carbon chain of the nitroparaffins produced, a decrease in the propylene and carbon monoxide yields, and an increase in the carbonyl compounds yield. In a special run similar to run 48 but with a high Cl_2/HNO_3 ratio of 0.7 an attempt was made to determine qualitatively the ultimate fate of the halogen. Ionic chlorine was found present in copious quantities in the aqueous layer of the product by testing with silver ion. Likewise titration with base showed a large increase in the amounts of strong acids formed during nitrations in the presence of chlorine. These facts indicate that part of the chlorine is eventually converted to hydrogen chloride. Another part is converted to alkyl chlorides, of which 1- and 2-chloropropanes were isolated and identified by means of their boiling points, refractive indices, and solubility characteristics.

TABLE III

EFFECT OF INCREASING CHLORINE CONCENTRATION IN NITRATIONS IN THE PRESENCE OF OXYGEN

Temp. = 423°. $C_3H_8/O_2 = 10.5$

Contact Time = 1.69 ± .04 Sec. $H_2O/HNO_3 = 1.55$[a]

S/V = 300 $cm.^{-1}$ $C_3H_8/HNO_3 = 10.5 \pm .2$

RUN NO. →	31	55	61	51	53	48
REACTANT RATIOS						
O_2/HNO_3	0.97	0.98	1.01	1.00	1.00	1.01
Cl_2/HNO_3	0	0.01	0.052	0.10	0.23	0.42
NITROPARAFFIN PRODUCTS						
Conversion, %	38.9	40.9	44.8	43.3	41.1	39.2
Yield, %	38.3	40.6	42.5	41.2	41.1	36.2
C/NO_2 Ratio	2.28	2.09	2.15	2.11	2.17	2.23
OTHER PRODUCTS, YIELD, %						
Carbon dioxide	3.5	5.1	1.4	2.4	2.5	3.1
Carbon monoxide	6.2	4.6	3.8	2.9	3.5	5.8
Propylene	19.9	7.7	4.3	7.2	4.5	8.1
Ethylene	2.3	2.1	2.9	4.8	5.0	6.3
Carbonyl comp'ds	29.7	40.0	45.2	41.4	43.4	40.5

[a] 69.3% HNO_3 used.

COMPARISON OF EFFECTS OF BROMINE AND CHLORINE

The most striking features to be noted in comparing the beneficial effects of bromine and chlorine in the vapor phase nitration of propane are the differences in the optimum concentrations of the two halogens and the difference in sharpness of the peaks at these optimum halogen concentrations. The optimum bromine concentration is about half that for chlorine, but the decrease in conversion and yield at halogen concentrations slightly greater than the optimum is much more striking in the case of bromine. In fact, a poor bromine/nitric acid ratio of 0.04, which is even less than the optimum chlorine/nitric acid ratio of 0.05, gives a conversion and yield lower than those obtained in the total absence of halogen.

The optimum bromine concentration gives a slightly higher conversion and yield than is obtained at the optimum chlorine concentration, but from a commercial viewpoint the use of chlorine might be preferred because of its wider range of effectiveness and because of its lower cost and ease of handling as compared to bromine. However, the production of hydrochloric acid introduces a more severe corrosion problem.

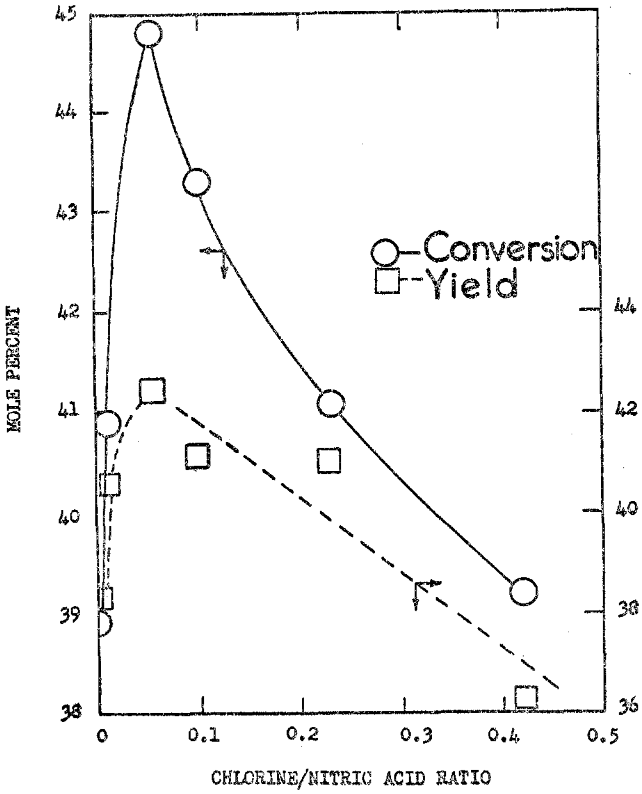

Figure 3. Mole-% Conversion and Yield *vs.* Chlorine/Nitric Acid Ratio. Conditions: Reaction temperature, 423°; $C_3H_8/HNO_3 = 10.5 \pm 0.2$; Contact time = 1.67 ± 0.01 sec.; $C_3H_8/O_2 = 10.6$; S/V = 300 cm.$^{-1}$

Both chlorine and bromine give a lower average nitroparaffin carbon chain length, decreased propylene and carbon monoxide yields, and an increased carbonyl compound yield.

In order to attempt to explain the relative effects of bromine and chlorine on the conversion to and yield of nitroparaffins it is helpful to consider the previously proposed reaction mechanism for the vapor phase nitration of hydrocarbons (1).

The reactions of bromine and chlorine in the reactor are probably the following, in which X_2 represents Br_2 or Cl_2 and R—H any alkane such as propane:

1. $X_2 \rightarrow 2X\cdot$
2. $R{-}H + X\cdot \rightarrow R\cdot + HX$
3. $R\cdot + NO_2\cdot \rightarrow RNO_2$
4. $R\cdot + X_2 \rightarrow RX + X\cdot$
5. $HX + NO_2\cdot \rightarrow X_2 + H_2O +$ lower N oxides
6. $RX + NO_2\cdot \rightarrow X_2 +$ R oxidation products + lower N oxides

Since the desired effect is the production of alkyl free radicals according to reaction 2, it is necessary to regulate the concentration of halogen so that the alkyl free radicals produced react with NO_2 to form nitroparaffins as in 3 instead of reacting with a molecule of halogen as in 4 to form alkyl halides. The hydrogen halides produced in 2 and any alkyl halides produced in 4 are probably oxidized by NO_2 or nitric acid as shown in 5 and 6 to regenerate the halogen at the expense of NO_2 or nitric acid.

Since the conversions to and yields of nitroparaffins obtained depend on the maintenance of an optimum ratio of alkyl/NO_2 free radicals (1) it would be expected, in view of the system of competing reactions, that an optimum halogen concentration should exist. This theoretical viewpoint is confirmed by the experimental data already presented. Additional evidence for the proposed reaction scheme is the observation that the optimum bromine concentration is about one-half the optimum chlorine concentration, and the decrease in conversion with increase in bromine concentration beyond the optimum is much sharper than with chlorine. This results from more rapid oxidation of hydrogen bromide and alkyl bromides as compared to hydrogen chloride and alkyl chlorides under the conditions of nitration. This increases the effective concentration of bromine over that of chlorine for generating alkyl free radicals. Since these oxidations are accompanied by a decrease in NO_2 concentration (see equations 5 and 6), the use of bromine concentrations greater than the optimum value causes a decrease in NO_2 concentration and a more pronounced decrease in conversion than with the same amount of chlorine. It is probable that halogen concentrations greater than the optimum also cause equation 4 to take place to such a degree that the alkyl free radical concentration is actually decreased.

A dark, tarry material which contained both nitrogen and bromine was formed only in the runs containing bromine. This may account for a part of the decreased conversion at bromine concentrations above the optimum. The tar is probably formed by reaction of the reduction products of NO_2 with nitroparaffins and/or carbonyl compounds.

EFFECT OF PROPANE/OXYGEN RATIO IN NITRATIONS IN THE PRESENCE OF BROMINE

The addition of optimum amounts of oxygen in the vapor phase nitration of hydrocarbons considerably increases the conversion to nitroparaffins but decreases their yield (2, 3, 5).

The propane/oxygen ratio must play an important role in the relative amounts of nitroparaffins and oxidation by-products obtained in the vapor phase nitration of propane. The attack of oxygen on propane produces an alkyl free radical. The subsequent fate of this radical determines the relative yields of nitroparaffins and oxidation by-products. Reaction of these radicals with NO_2 gives the desired nitroparaffins, while reaction with oxygen gives chiefly oxygenated by-products.

TABLE IV

EFFECT OF PROPANE/OXYGEN RATIO IN NITRATIONS IN THE PRESENCE OF BROMINE

Temp. = 423°. H_2O/HNO_3 = 1.55[a]

S/V = 28 cm.$^{-1}$ Br_2/HNO_3 = 0.0093

RUN NO. →	29	30
CONTACT TIME, sec.	1.71	1.76
REACTANT RATIOS		
C_3H_8/O_2	17.4	10.6
C_3H_8/HNO_3	18.4	17.2
O_2/HNO_3	1.06	1.62
NITROPARAFFIN PRODUCTS		
Conversion, %	52.8	61.8
Yield, %	51.6	47.5
C/NO_2 Ratio	2.24	2.25
OTHER PRODUCTS, YIELD, %		
Carbon dioxide	1.5	2.1
Carbon monoxide	0	1.1
Propylene	15.4	14.4
Ethylene	1.5	3.2
Carbonyl comp'ds	30.0	31.8

[a] 69.3% HNO_3 used.

It is to be expected that there will be an optimum propane/oxygen ratio at which the amount of nitroparaffins produced is very much higher while the amount of oxidation products is still very low.

The effect of bromine at the optimum propane/oxygen ratio may be predicted by assuming that bromine tends to increase the concentration of alkyl free radicals. This would lead one to expect that even small amounts of bromine would lower the optimum value of the propane/oxygen ratio by decreasing the amount of oxygen required to produce the necessary alkyl free radicals.

Runs 29 and 30 (Table IV) were similar in all respects except that a propane/oxygen ratio of 17.4 was employed in run 29 while a ratio of 10.6 was employed in run 30. A conversion of 52.8% and a yield of 51.6% were obtained in run 29, while a conversion of 61.8% and a yield of 47.5% were obtained in run 30. The lower propane/oxygen ratio used in run 30, therefore, caused an increase in conversion of 9.0% and a decrease in yield of 4.1%. The presence of a more favorable propane/oxygen ratio has been demonstrated, but the most advantageous ratio was not found in all probability. From this work and the previous papers (2, 3) it is likely that the optimum propane/oxygen ratio will be found to lie between 8–12 at this particular bromine/nitric acid ratio. At other bromine concentrations the optimum propane/oxygen ratio may lie at other values.

EFFECT OF ETHYL BROMIDE IN NITRATIONS IN THE PRESENCE OF OXYGEN

At nitrating temperatures alkyl halides decompose thermally (7). The products include hydrogen halides which are readily oxidized by nitric acid or nitrogen dioxide to halogens. Actually, in the presence of nitric acid, halogens are formed from alkyl halides by processes which are probably more complicated than the one outlined above. However, it was anticipated that alkyl halides could be substituted satisfactorily for halogens in the catalyzed nitration of propane.

TABLE V

Effect of Ethyl Bromide in Nitrations in the Presence of Oxygen

Temp. = 424°. C_3H_8/O_2 = 10.0

S/V = 28 cm.$^{-1}$ H_2O/HNO_3 = 1.55[a]

RUN NO. →	24	25[b]
CONTACT TIME, sec.	1.76	1.77
REACTANT RATIOS		
C_3H_8/HNO_3	12.8	13.2
O_2/HNO_3	1.28	1.32
NITROPARAFFIN PRODUCTS		
Conversion, %	48.8	51.3
Yield, %	38.8	43.2
C/NO_2 Ratio	2.23	2.13
OTHER PRODUCTS, YIELD, %		
Carbon dioxide	1.9	0.9
Carbon monoxide	10.2	6.6
Propylene	15.3	10.5
Ethylene	5.5	1.8
Carbonyl comp'ds	28.3	37.0

[a] 69.3% HNO_3 used.

[b] C_2H_5Br/HNO_3 = .0128.

Runs 24 and 25 (Table V) were similar in all respects except that an ethyl bromide/nitric acid ratio of 0.0128 was used in run 25. The addition of ethyl bromide caused an increase in conversion from 48.8% to 51.3% and an increase in yield from 38.8% to 43.2%. The slightly higher propane/nitric acid ratio used in run 25 could only account for a small part of these increases. As was found to be true with the addition of bromine itself, the addition of ethyl bromide causes a decreased average carbon chain length of nitroparaffins, decreased propylene and carbon monoxide yields and an increased carbonyl compound yield.

EFFECT OF VARIATIONS IN NITRATION TEMPERATURE IN THE PRESENCE OF OXYGEN AND CHLORINE

The necessity for careful control of reaction temperature in the vapor phase nitration of hydrocarbons was discovered early in the development of the process and before the use of oxygen-halogen catalysis was known. Hence it was felt to be important to study the effect of variations in temperature in the presence of these catalysts. The quantitative variation of conversion to and yield of nitroparaffins at different temperatures in the nitration of propane with 70% nitric acid in the presence of oxygen and chlorine was determined. Runs 5 and 6 (Table VI) were identical except that a reaction temperature of 423° was employed in run 5 while a temperature of 419° was used in run 6. The temperature decrease of 4° from run 5 to run 6 caused a decrease in conversion from 62.3% to 58.0% but an increase in yield from 37.7% to 43.8%. The increase in yield at a lower temperature may be explained by assuming a decreased loss of propane to oxidation products. This was supported by the higher average carbon chain length of nitroparaffins in run 6 indicating that less oxidative cracking of the hydrocarbon had occurred. The increase in conversion with increasing temperature indicates a more efficient utilization of the nitrating agent. This may be due to an increased rate of production of NO_2 radicals and consequently the establishment of a better balance between the concentrations of the NO_2 and alkyl free radicals.

TABLE VI

EFFECT OF VARIATION IN NITRATION TEMPERATURE IN THE PRESENCE OF OXYGEN AND CHLORINE

$C_3H_8/O_2 = 8.8$. $C_3H_8/HNO_3 = 16.1$

$O_2/HNO_3 = 1.83$. $H_2O/HNO_3 = 1.42^a$

$S/V = 28$ cm.$^{-1}$ $Cl_2/HNO_3 = 0.10$

Contact Time = 1.69 sec.

RUN NO. →	5	6
TEMP., °C	423	419
NITROPARAFFIN PRODUCTS		
Conversion, %	62.3	58.0
Yield, %	37.7	43.8
C/NO_2 Ratio	2.13	2.22
OTHER PRODUCTS, YIELD, %		
Carbon dioxide	2.9	4.1
Carbon monoxide	2.5	1.0
Propylene	19.1	24.7
Ethylene	6.7	2.1
Carbonyl comp'ds	30.9	24.3

[a] 71.1% HNO_3 used.

EFFECT OF NITRIC OXIDE IN NITRATIONS IN THE PRESENCE OF OXYGEN

The inhibitory effect of nitric oxide in the vapor phase nitration of hydrocarbons with nitric acid in the presence of oxygen has been reported by Hass and Alexander (5) and by Hodge (6). Run 34 (Table VII) was performed under reaction conditions and with reactant ratios similar to those used in run 31 (Table I) except that a slightly higher propane/nitric acid ratio and a nitric oxide/nitric acid ratio of 0.009 was used in run 34. The addition of the small amount of nitric oxide caused a reduction in conversion from 38.9% to 34.5% while the yield was only slightly increased from 38.3% to 38.6%. By taking the slightly higher propane/nitric acid ratio used in run 34 into account (Figure 1), it can be calculated that the addition of nitric oxide caused about a 6.3% decrease in conversion and a 0.7% decrease in yield.

TABLE VII

EFFECT OF NITRIC OXIDE IN NITRATIONS IN THE PRESENCE OF OXYGEN

$C_3H_8/O_2 = 10.6$. $C_3H_8/HNO_3 = 11.1$

$O_2/HNO_3 = 1.05$. $H_2O/HNO_3 = 1.55$[a]

$S/V = 300$ cm.$^{-1}$

RUN NO. →	34[b]	39
TEMP., °C	423	421
CONTACT TIME, sec	1.68	1.73
REACTANT RATIOS		
Br_2/HNO_3	0	.007
NO/HNO_3	.009	.007
NITROPARAFFIN PRODUCTS		
Conversion, %	34.5	41.2
Yield, %	38.6	35.6
C/NO_2 Ratio	2.18	2.02
OTHER PRODUCTS, YIELD, %		
Carbon dioxide	3.8	3.4
Carbon monoxide	11.9	5.8
Propylene	10.2	11.7
Ethylene	5.7	4.9
Carbonyl comp'ds	30.9	37.8

[a] 69.3% HNO_3 used.

[b] No halogen used in this reactor prior to this run.

The decrease in conversion obtained on adding nitric oxide merely substantiates earlier observations (5, 6), but the determination of the near constancy of the yield is novel. By assuming that nitric oxide acts as a chain-stopper in the chain reaction between propane and oxygen (8), it can be seen that nitric oxide should decrease the concentration of alkyl free radicals to a value below the optimum, thereby decreasing the conversion. The nitric oxide also combines with a small fraction of the free radicals produced and thus decreases the yield in proportion to its concentration.

Run 39 was similar to run 34 except that it was made at 421° with the addition of sufficient bromine to give a bromine/nitric acid ratio of 0.009. A conversion of 41.2% and a yield of 35.6% were obtained. It is seen that the simultaneous addition of these amounts of bromine and nitric oxide gives a conversion in the range to be expected if neither the nitric oxide nor the bromine were present (compare Figure 1). If run 39 had been performed at 423°, instead of at 421°, a higher conversion would have been expected.

It is apparent that bromine counteracts the inhibitory effect of nitric oxide. The explanation of this may be either that bromine restores the more favorable alkyl radical/NO_2 ratio by increasing the rate of alkyl radical production or that it effectively removes the nitric oxide from the reaction mixture by combining with it or by catalyzing its combination with some other reactant such as oxygen.

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SUMMARY

The conversion to and yield of nitroparaffins obtained from the vapor phase nitration of propane with nitric acid in the presence of oxygen and halogens has been shown to vary considerably with the halogen concentration. An optimum concentration has been found for chlorine and bromine which gives peak conversions and yields considerably higher than those without halogen. The conversions and yields with halogens have also been shown to vary with the propane/nitric acid ratio, the propane/oxygen ratio, and the reaction temperature. It has further been shown that halogens counteract the inhibitory action of nitric oxide on the nitration process.

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