NITRATION STUDIES. IV. EFFECT OF BROMINE IN THE VAPOR PHASE NITRATION OF PROPANE[1]

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According to the general mechanisms developed (2) for vapor phase nitration processes a balance must be maintained between free alkyl radicals and nitrogen dioxide radicals to obtain optimum yields of nitroparaffins. Several means are available for controlling the concentrations of free alkyl radicals and for materially improving the nitration yields and conversions. Thus it was shown (1) that (a) addition of oxygen, (b) dilution with steam, and (c) use of high surface to volume reactors have favorable effects in the nitration of butane. Of these factors the most important is the use of oxygen, but unfortunately its advantages are accompanied by certain disadvantages, especially the formation of larger amounts of oxygenated organic substances (aldehydes, acids, carbon oxides). This lowers the yields and conversions which might be obtained if the oxygen served only to generate free alkyl radicals and did not in part remain combined with them.

In seeking a substitute for oxygen which would avoid this difficulty, our attention was drawn to the halogens, especially bromine. Bromine is known to attack hydrocarbons at elevated temperatures by processes which involve free alkyl radical formation and which lead to alkyl bromides. However at the temperatures of nitration alkyl bromides decompose to olefins and hydrogen bromide (4). The olefins are nitratable and the hydrogen bromide is reoxidizable to free bromine. Hence it would appear that bromine would be able to act as a generator of free radicals but would not remain combined with them to the same extent as does oxygen. The cycle, in an abbreviated form, might be represented as follows:

1. $Br_2 \rightleftarrows 2\ Br\cdot$

2. $C_nH_{2n+2} + Br\cdot \rightarrow C_nH_{2n+1}\cdot + HBr$

3. $C_nH_{2n+1}\cdot + Br_2 \rightarrow C_nH_{2n+1}\ Br + Br\cdot$

4. $2\ C_nH_{2n+1}\ Br \rightarrow C_nH_{2n} + C_nH_{2n+1}\cdot + HBr + Br\cdot$ (4)

5. $HBr + [O] \rightarrow HO\cdot + \cdot Br$

From these equations it can be seen that the alkyl radicals necessary for nitration would be produced by a process which is more nearly a true catalysis than with oxygen and that smaller amounts of bromine would be needed.

The present paper reports the results of experiments designed to study the effects of bromine and to apply the various factors found useful in the nitration

TABLE I

NITRATION OF PROPANE WITH NITRIC ACID

RUN NO. →	9	14	15	16	17	18	20	21	22	24	27
Temp., °C	423	423	423	423	423	423	425	418	414	419	419
Surface/volume of reactor, $cm.^{-1}$	28	28	28	28	28	28	28	28	28	28	4
Contact time, sec.	1.8	1.8	1.9	1.8	1.5	1.7	1.6	1.7	1.7	1.6	1.6
MOLE RATIOS REACTANTS											
C_3/O_2	5.1			5.1	8.2	11.5	9.8	12.9	12.9	7.0	7.0
C_3/HNO_3	16.8	20.4	22.8	16.5	9.9	10.6	11.7	13.7	13.7	4.2	4.2
O_2/HNO_3	3.3	0.0	0.0	3.1	1.2	0.9	1.2	1.1	1.1	0.60	0.60
H_2O/HNO_3	15.0	15.0	15.0	15.0	15.0	15.0	1.4	1.4	1.4	1.4	1.4
Br_2/HNO_3	0.0	0.0	0.015	0.015	0.015	0.015	0.0028	0.0028	0.0028	0.0069	0.0057
CONVERSION (N), %	61.7	23.0	27.7	46.0	47.7	43.2	52.7	53.2	48.1	19.6	5.4
YIELDS (Propane), %											
RNO_2	37.6	27.4	50.0	33.2	55.5	57.0	43.1	59.4	61.0	26.0	5.1
CO_2	0.8	2.7	0.0	0.5	0.0	0.2	3.0	0.5	2.2	0.7	2.2
C_3H_6	26.6	24.3	4.5	16.1	9.7	7.3	13.6	7.7	20.2	15.3	26.0
C_2H_4	0.8	23.4	15.0	7.6	4.1	7.8	8.5	6.1	0.0	14.0	28.5
CO	9.3	12.6	19.5	13.3	3.6	1.0	9.7	2.0	0.6	21.6	19.6
Carbonyl compounds	25.1	9.5	11.0	29.4	27.0	26.6	22.2	24.3	15.9	22.4	18.1

of butane to the nitration of propane. Both nitric acid and nitrogen dioxide have been used as nitrating agents and the results compared and contrasted.

Procedure. The apparatus and procedures for the nitric acid nitration of propane were similar to those described previously (1) for the nitration of butane. The bromine was dissolved in the nitric acid and introduced into the reactor in this form. An approximately saturated solution was used, which gave a Br_2/HNO_3 mole ratio of 0.015. In some experiments this saturated solution was diluted with nitric acid to give a lower mole ratio. The most pertinent data are assembled in Table I.

TABLE II

NITRATION OF PROPANE WITH NITROGEN DIOXIDE

RUN NO. →	2	3	4	9	11	12
Temp., °C	300	325	300	325	325	350
Surface/volume of reactor, cm.$^{-1}$	3.6	3.6	3.6	3.6	3.6	3.6
Contact times, min	2.0	2.0	2.0	2.0	2.0	2.0
FLOW RATE, MOLES						
C_3H_8	4.2	4.2	8.0	4.2	4.2	8.0
NO_2	1.0	1.0	1.0	1.0	1.0	1.0
O_2	0.5	0.5	1.0	0.5	0.5	0.6
Br_2	0.0	0.0	0.0	0.0	0.031	0.033
I_2	0.0	0.0	0.0	0.0085	0.0	0.0
CONVERSION (N), %	26.4	26.5	24.4	25.6	27.4	19.5
YIELDS (propane), %						
RNO_2	46.3	41.7	45.3	50.9	50.2	24.2
CO_2	30.5	21.5	30.4	23.9	22.3	16.3
C_3H_6	5.5	4.8	2.4	10.0	6.8	8.1
C_2H_4	0.0	0.6	3.0	1.0	2.7	0.0
CO	13.6	22.1	6.9	5.2	14.2	48.7
Carbonyl compounds	4.1	9.1	12.2	9.2	3.9	2.9
DISTRIBUTION OF RNO_2,^{a} weight—%						
CH_3NO_2	28.0	32.9	38.6	35.3	36.6	—
$C_2H_5NO_2$	8.6	9.0	9.6	9.1	6.0	—
$CH_3CH_2CH_2NO_2$	17.2	15.6	11.7	11.8	15.9	—
$CH_3CHNO_2CH_3$	45.6	41.9	39.5	43.2	40.6	—
C/N ratio calc'd	2.20	2.09	1.97	2.04	2.05	2.05^b

^{a} By mass spectrographic analysis.

^{b} Nitroparaffin sample from Run 12 lost before mass spectrographic analysis. C/NO_2 ratio assumed to be 2.05 (by analogy with Run 11) for calculation of yields.

The apparatus and procedures for the nitrogen dioxide nitration of propane were similar to those employed previously (3), but the reactor was newly constructed of twin spirals of 14 mm. O.D. glass tubing arranged concentrically and sealed together at the bottom. The total tube had a capacity of 2200 cc. Bromine and iodine were introduced into the propane feed from tared tubes thermostatically controlled to deliver the desired amount of halogen through vaporization into the propane stream. The most pertinent data obtained are assembled in Table II.

Discussion of results in the nitration of propane with nitric acid. It is readily apparent that bromine brings about a marked improvement in yields and con-

versions in the nitration of propane and that optimum results are also greatly dependent on other variables. A comparison of Runs 14 and 15 shows that a mere 0.015 mole of bromine per mole of nitric acid raises the yield from 23% to 50% and the conversion from 23% to 28%. Neither of these runs contained added oxygen. However, Runs 16, 17, and 18 show that even better results are obtained when both oxygen and bromine are added simultaneously, the yield
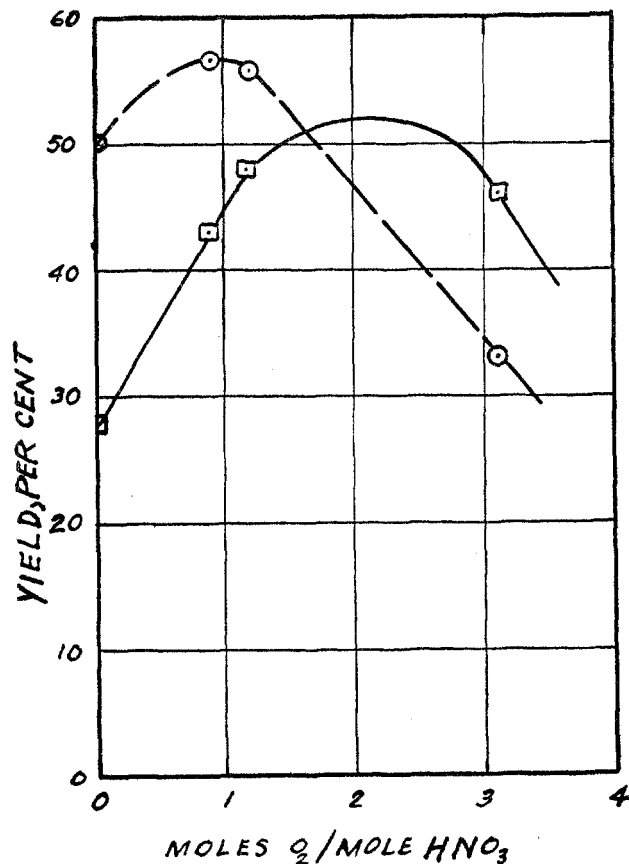

FIGURE 1. EFFECT OF VARYING THE OXYGEN FEED IN THE NITRATION WITH BROMINE. Conditions: 425°, Br_2/HNO_3 = 0.015, contact time of 1.7± sec. Propane yield = ⊙; Nitrogen conversion = ⊡.

based on propane reaching a peak of 57% and the conversion based on nitric acid reaching a peak of 48%. A comparison of these same runs shows too that the beneficial influence of oxygen reaches a peak at an oxygen/nitric acid/propane mole ratio of 1 or 2/1/10 depending on whether the yield (1 mole O_2) or the conversion (2 moles O_2) is being considered. This relationship is more clearly defined in the graph of Figure 1.

The advantageous effects of oxygen may be attributed in part to its utilization (rather than nitric acid) in the reoxidation of hydrogen bromide to free

bromine as shown in Equation 5. Too much oxygen is obviously harmful, Run 16, since an oxygen/nitric acid/propane ratio of 3/1/5 leads to a yield of only 33%. With no bromine, Run 9, this same ratio gives a very high conversion, 62%, although the yield is still low, 38%.

Runs 20, 21, and 22 were made in an attempt to adjust all of the known factors to optimum values and obtain highest yields and conversions. It is evident that the steam diluent may be eliminated, the amount of bromine decreased materially, and the temperature decreased ten degrees without undue losses occurring. Peak yield, 61%; peak conversion, 53%.

Run 24 compared with Run 22 shows the deleterious effect of a sharp decrease in the propane/nitric acid ratio. There is a large decrease in nitroparaffins and a large increase in oxidation products which accompanies this change. Similarly, Run 27 compared to Run 24 shows the further deleterious effect of employing a nitration reactor tube with a low surface/volume ratio.

The various changes made in the runs of Table I bring about appreciable changes in the ratios of byproducts produced, as well as in the amounts of nitroparaffins obtained. Thus it is evident that the use of oxygen strongly favors the formation of carbonyl compounds. The yields for carbonyl compounds are somewhat arbitrarily calculated on the basis of 1.2 carbon atoms per oxygen atom, since formaldehyde is the chief but not the only carbonyl compound present. The yields of nitroparaffins are calculated on the basis of 2.85 carbon atoms per NO_2 group for the sake of comparison with previous results reported from this laboratory. Present practice is to determine this value for each run with the aid of mass spectrographic analyses, and later results will be reported on this basis. Indications are that the value 2.85 is probably a litle too high on the average.

Figure 2 shows a graph of variations in amounts of products produced with different amounts of oxygen and in the presence of bromine. It will be noted that the moles of carbonyl compounds (principally aldehydes) and the moles of nitroparaffins reach a peak almost simultaneously and that the amounts of carbon monoxide pass through a minimum at about the same time. The amounts of carbon dioxide and of the two principal olefins, ethylene and propylene, rise continuously and do not reach a peak throughout the range studied.

Discussion of results in the nitration of propane with nitrogen dioxide. Vapor phase nitration using nitrogen dioxide contrasts with vapor phase nitration using nitric acid in various ways of which the more important to the present discussion are summarized below:

CONTRASTING FACTORS	NO_2	HNO_3
Yields on alkane	higher	lower
Conversions on nitrogen	lower	higher
Optimum temperature	lower	higher
Optimum contact time	longer	shorter
By-products:		
Carbon oxides	higher	lower
Olefins	lower	higher
Carbonyl compounds	lower	higher

It was shown previously (3) that the addition of oxygen tended to minimize these differences. In so far as nitrogen dioxide nitrations are concerned the addition of oxygen greatly lowered the contact times required and increased the yields and conversions. It did not however increase the conversions sufficiently to make the process competitive with the nitric acid process.
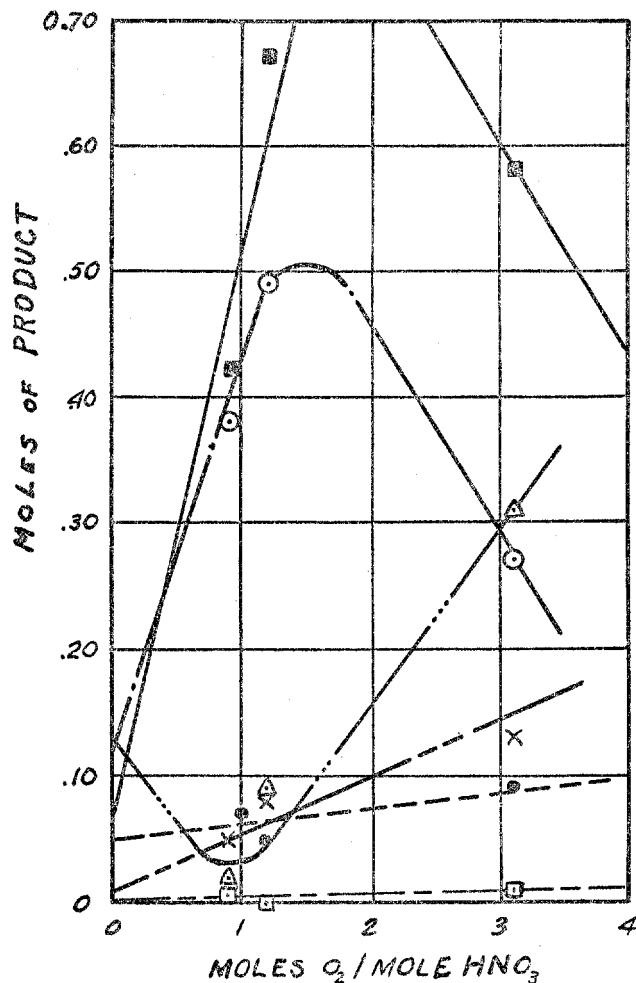

FIGURE 2. VARIATION IN MOLES OF PRODUCT WITH OXYGEN FEED WITH BROMINE. $\odot$ = RNO_2; $\square$ = CO_2; $\times$ = Propylene; $\bullet$ = Ethylene; $\triangle$ = CO; $\blacksquare$ = Aldehydes.

The addition of bromine in Run 11 and of iodine in Run 9 apparently caused a considerable further increase in nitration yield but no appreciable increase in conversion. Nitration with nitric acid therefore remains the more practical process. A peak yield of 50.9% and a peak conversion of 27% were obtained with nitrogen dioxide. These compare with 59% and 53% respectively for nitrations

with nitric acid in the presence of both bromine and oxygen (Table I, Run 21). The yields in Table II were calculated from the actual C/N ratio in the nitro paraffins as determined by mass spectrographic analyses. This ratio is probably lower for nitrations with nitrogen dioxide (*ca.* 2.0) than with nitric acid (*ca.* 2.2—tentative). The yields in Table II cannot be compared directly with the yields reported in the preceding paper (3), since the latter were calculated from the C/N ratio 2.85.

Other effects of bromine under optimum operating conditions, Run 11, were (a) to decrease the amount of carbon monoxide produced and the degree of acidity and N_2O_3 content of the condensate, (b) to increase the total amount of off-gas, and (c) to alter slightly the distribution of nitroparaffins formed. The deleterious effect of higher temperature on nitrogen dioxide nitrations is clearly shown in Run 12. At 350° the yield dropped to 31% and the conversion to 20% even though both bromine and oxygen were present.

SUMMARY

Factors influencing the nitration of propane with both nitric acid and nitrogen dioxide have been studied. It has been shown that bromine has a beneficial effect on both the yields and conversions to nitroparaffins using nitric acid and on the yields but not the conversions using nitrogen dioxide. The addition of oxygen and the use of high surface reactors and high propane content feeds augment the effectiveness of the halogen. The favorable influence of bromine has been attributed to its catalytic activity in creating the free alkyl radicals believed to be necessary for nitration. Other results of the use of bromine and of iodine are described.

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