[Contribution from the Department of Chemistry, Purdue University and the Purdue Research Foundation]

NITRATION STUDIES. II. EFFECT OF OXYGEN ON THE VAPOR PHASE NITRATION OF BUTANE[1]

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In an investigation of the effects of various gases on the vapor phase nitration of propane, Hass and Alexander (1) discovered that the addition of oxygen to the reaction mixture caused an increase in the conversion of nitric acid to nitroparaffins. The production of oxygenated by-products was noted but no determination was made of the type of compounds produced or of the amounts of each formed. In fact, in all previous studies of vapor phase nitration, attention has been directed almost exclusively to an investigation of the type and quantity of nitroparaffins produced. The lack of data on the nature and yields of by-products has delayed elucidation of the detailed mechanism of the reaction. Since oxygen increases the production of these by-products, a study of them becomes important from an economic standpoint as well as desirable from the theoretical viewpoint.

Butane was chosen for this investigation since it has not been given the same amount of attention accorded the lower hydrocarbons. It is interesting to note that data by Hass and Hodge (2) show that, as the homologous series of normal paraffins is ascended from methane to butane, nitration becomes easier.

Apparatus. The apparatus was similar to that used by Hass and Alexander (1) and consisted of a metering system for the reactants, a gas preheater, a reactor, and a condensing system. The flow control for the butane and oxygen was provided by orifice type flow meters operated with the ratio of upstream to downstream pressure above the critical pressure ratio. Thus the flow was independent of small pressure fluctuations in the reactor. Nitric acid was forced from a liquid reservoir through a calibrated jet into the preheater by a controlled pressure of nitrogen.

The preheater consisted of a coil of 10 mm. I.D. Pyrex glass tubing 250 cm. long with an opening 60 cm. from the outlet for the injection of the nitric acid. This was immersed in a salt-bath maintained at a temperature of 265° by stainless steel strip heaters.

Two reactors were used. The first consisted of a coil of 10 mm. Pyrex glass tubing, 880 cm. long, and having a diameter of 20 cm. The second was made so that it could be packed for studies on the effect of the surface to volume ratio. It consisted of three 90-cm. lengths of 20 mm. I.D. Pyrex glass tubing. Each was bent into the form of a U and the three were connected in series by tubes sealed near the top of each leg. Packing was introduced through the ends of the tubes which were sealed off before operation. The three packings used were $\frac{3}{16}$ and $\frac{1}{8}$ inch Pyrex glass helices and Pyrex glass wool. The temperature of both reactors was maintained with the aid of an automatic controller.

The exit gases were cooled by passage through a water condenser to remove the majority of the liquid products and then through a Dry Ice-trichloroethylene trap to remove gaseous products and excess butane. Any gases remaining uncondensed were passed through a wet test gas meter to measure their volume and were then collected over water or vented as desired.

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Product analysis. The total liquid product was extracted with ether to separate the aqueous and non-aqueous materials. The aldehydes present in each layer were determined by the hydroxylamine hydrochloride method. The ether layer was extracted with sodium bicarbonate to remove acidic materials. The nitroparaffins remaining in the ether layer were determined by a nitrogen analysis on an aliquot portion.

Propene and butene, ethylene, carbon monoxide, and carbon dioxide were determined by an Orsat analysis on a sample of the exit gases.

Conversions are based on the fraction of the nitric acid charged which appeared as nitroparaffins. Yields are based on the butane which reacted. The C/NO_2 ratio of 2.85 was assumed for the nitroparaffin mixture in these calculations.

NITRATION OF BUTANE WITHOUT OXYGEN

Earlier work on the nitration of butane was of an exploratory nature. Hence a study of the effect of oxygen, different surface to volume ratios, and diluents required first an investigation of the results obtainable with nitric acid alone. Since the contact time, mole ratio of hydrocarbon to nitric acid and pressure had been arbitrarily chosen to conform to earlier studies, the one remaining variable was temperature.

TABLE I

NITRATION OF BUTANE WITHOUT OXYGEN; EFFECT OF TEMPERATURE

(Contact Time = 1.6 Seconds; 10 mm. I.D. Coil Reactor)

RUN NO. →	42	10	41	HODGE[a]
C_4H_{10}/HNO_3	15.0	12.3	15.0	14.0
Temp., °C	405	425	435	420
Conversion,[b] %	15	36	22	37
MOLES FORMED[c]				
RNO_2	0.10	0.29	0.14	
$>C{=}O$	0.06	0.06	0.10	
$C_3H_6 + C_4H_8$	0.10	0.11	0.14	
C_2H_4	0.10	0.18	0.12	
CO	0.13	0.07	0.13	
CO_2	0.10	0.26	0.07	
Butane consumed, moles[d]	0.31	0.55	0.41	

[a] Approximately 3 seconds contact time (2). [b] Based on nitric acid charged. [c] Corrected to moles per 10 moles of butane charged. [d] Calculated from the carbon content of the products.

Experiments carried out at 405°, 425°, and 435° served to determine the optimum temperature. The data from these experiments are given in Table I. A plot of conversion against temperature (Figure 1) shows that the best results are obtained at a temperature of 425°.

From the actual quantities of materials produced as listed in Table I, it can be seen that temperature has a marked effect on the production of nitroparaffins. This reaches a maximum and subsequently decreases with increasing temperature. No substantial variations are noted in the productions of the various by-products.

The optimum temperature effect observed in the production of nitroparaffins has previously been explained in two ways. One is that as the temperature is increased, decomposition of nitroparaffins begins to take place, thus reducing the amount found in the product. However, Taylor and Veaselovsky (6) found that the half-life of nitromethane at 420° is 4 minutes. Even assuming a much greater degree of instability for the higher members of the series, pyrolysis should be negligible at a contact time of 1.6 seconds. Hence this explanation seems inadequate to account for the facts.

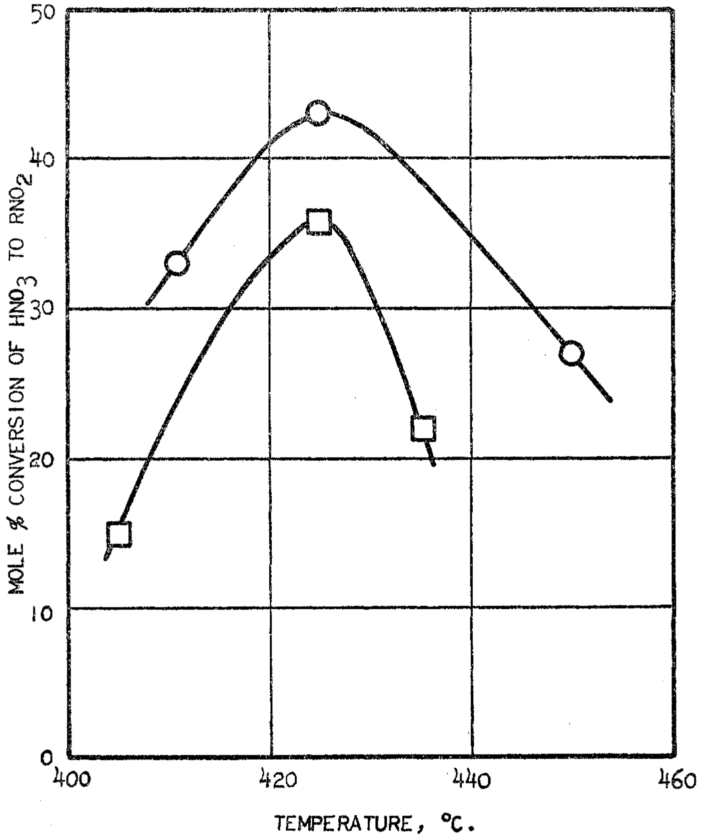

FIGURE 1. EFFECT OF TEMPERATURE ON THE NITRATION OF BUTANE AT 1.6 SEC. CONTACT TIME. Conditions: Ratio C_4H_{10}/HNO_3 = 15; 10-mm. I.D. reactor; ○ = run without oxygen; □ = run with 2 moles O_2/mole HNO_3.

Alternatively it has been suggested that competing side reactions with higher activation energies and involving organic materials become more prominent at the higher temperatures. Such reactions would be expected to produce increasing amounts of by-products as the temperature increases. This is not the case however. It may be calculated from Table I that the change with temperature in the amounts of olefins, carbonyl compounds, and carbon oxides produced, when calculated on the basis of grams of carbon involved, does not compare with the change in butane consumed. Actually the decrease in moles of nitroparaffins produced is approximately equal to the decrease in moles of butane reacting. It may be concluded that a decrease in conversion by competing side reactions involving organic materials, which become pronounced at the higher temperatures, is not supported by experimental evidence.

It is now believed that the optimum temperature effect is associated with the maintenance of proper balance between the reacting radicals as explained in the previous paper in this series, and with the decreased stability of the nitrating agent at the higher temperatures.

TABLE II

NITRATION OF BUTANE WITH OXYGEN; EFFECT OF TEMPERATURE

(Contact Time = 1.6 Seconds; 10 mm. I.D. Coil Reactor)

RUN NO. →	12	11	13
C_4H_{10}/HNO_3	15	15	15
O_2/HNO_3	2	2	2
Temp., °C	411	425	450
Conversion,[a] %	33	43	27
Yield, %	17.4	24.0	15.6
MOLES FORMED			
RNO_2	0.26	0.27	0.17
$> C{=}O$	0.73	0.68	0.49
$C_3H_6 + C_4H_8$	0.73	0.37	0.61
C_2H_4	0.31	0.25	0.11
CO	0.10	0.45	0.26
CO_2	0.31	0.17	0.21
Butane consumed, moles	1.38	1.06	1.01

[a] Based on nitric acid charged.

NITRATION OF BUTANE WITH OXYGEN

The initial experiments with oxygen were performed at three different temperatures to determine the variation in optimum temperature as oxygen was added. The results given in Table II show a maximum conversion of 43% which represents a significant increase over the conversion obtained under comparable conditions without oxygen. When these conversions are plotted against temperature (Figure 1) it is seen that the optimum temperature is still in the neighborhood of 425°.

Since it was demonstrated that the optimum temperature does not vary appreciably with the addition of oxygen, the remaining experiments were performed at a temperature of 425°. The data given in Table III show the effects on yields and conversions of varying the amount of oxygen added to the nitration mixture.

Figure 2, which shows the relation between conversion and the amount of

TABLE III

NITRATION OF BUTANE; EFFECT OF OXYGEN AT CONSTANT TEMPERATURE

(Contact Time = 1.6 Seconds; 10 mm. I.D. Coil Reactor)

RUN NO. →	10	16	11	14
C_4H_{10}/HNO_3	12.3	13.5	15.5	13.2
O_2/HNO_3	0	1	2	3
Temp., °C	425	425	425	425
Conversion, %	36	42	43	26
Yield, %	48	32	24	10
MOLES FORMED				
RNO_2	0.29	0.32	0.27	0.20
$> C{=}O$	0.06	0.37	0.68	0.96
$C_3H_6 + C_4H_8$	0.11	0.33	0.37	1.16
C_2H_4	0.18	0.16	0.25	0.31
CO	0.07	0.51	0.45	0.78
CO_2	0.26	0.05	0.17	0.38
Butane consumed, moles	0.55	0.93	1.06	1.93

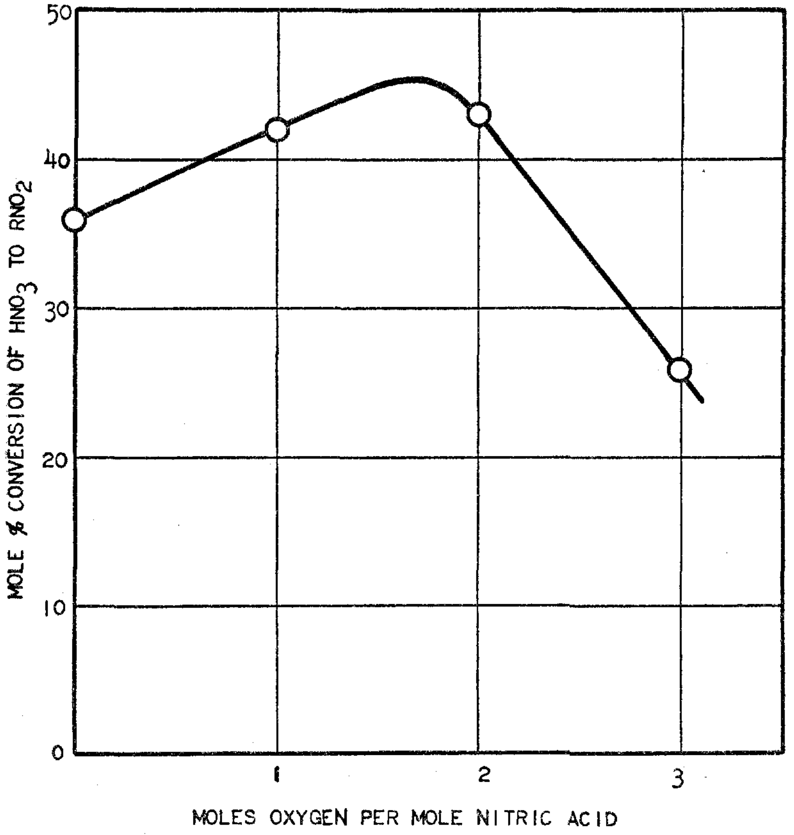

FIGURE 2. NITRATION OF BUTANE; VARIATION OF CONVERSION WITH OXYGEN AT 425°. Conditions: Ratio C_4H_{10}/HNO_3 = 15; Contact time = 1.6 sec.; 10-mm. I.D. reactor.

oxygen added reveals that the highest conversion obtainable in this reactor is 44% at a temperature of 425° with a mole ratio of butane/oxygen/nitric acid of 15/1.6/1.

The yield, based on the amount of butane consumed, is shown in Figure 3 to decrease nearly linearly with the amount of oxygen employed. Thus it is obvious that the increase in conversion observed upon adding oxygen is attained only at the sacrifice of a considerable amount of hydrocarbon through side reactions. The serious nature of this aspect is evident when it is noted that at the oxygen value for maximum conversion, only 26% of the butane reacting is converted to nitroparaffins.

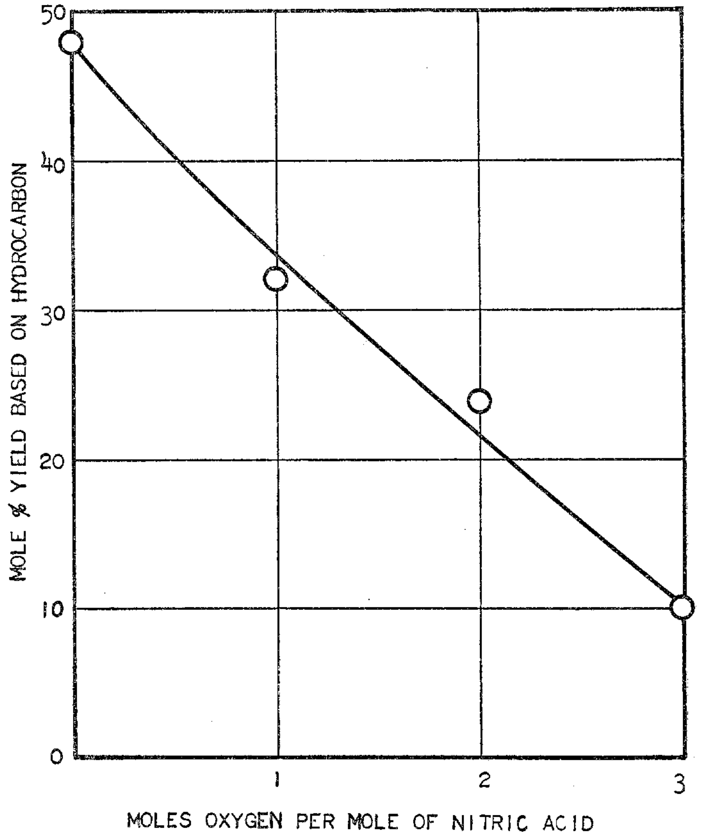

FIGURE 3. NITRATION OF BUTANE; VARIATION OF YIELD WITH OXYGEN AT 425°. Conditions: Ratio C_4H_{10}/HNO_3 = 15; Contact time = 1.6 sec.; 10-mm. I.D. reactor.

The actual amounts of products from each reaction are given in Table III. The formation of carbonyl compounds is proportional to the amount of oxygen added. The olefins and the carbon monoxide appear to increase slowly at first, but finally show an abrupt rise. It is interesting to note that the amounts of carbon dioxide pass through a minimum at the same point where the nitroparaffins show a maximum.

This maximum in the production curve of nitro compounds in the presence of increasing amounts of oxygen is somewhat puzzling unless it is assumed that vapor phase nitration is a free radical process. A portion of the alkyl radicals react with the nitrating agent to produce nitroparaffins. However, the reaction of alkyl radicals with oxygen also occurs with extreme ease. Thus when the oxygen content of the reaction mixture is increased, a portion of the free radicals previously available for nitration is removed by reaction with oxygen and is converted to by-products.

The presence of olefins in the exit gases, regardless of the oxygen content of the reaction mixture, is evidence of the presence of free alkyl radicals. The formation of olefins from saturated hydrocarbons by a free radical process is a well known phenomenon and in this case indicates that a certain number of the free radicals undergo olefin formation before an effective collision with a nitrating agent can take place. It is readily seen that if the number of free radicals is increased beyond the optimum while maintaining the same concentration of nitrating agent, the formation of olefins should become greater. The effect of oxygen is postulated as that of a free radical-forming agent, and it may be noted that the predicted rise in olefin production does occur upon increasing the amount of oxygen added.

The total amount of butane consumed in the experiments conducted at various temperatures while using a reaction mixture having a butane/oxygen/nitric acid ratio of 15/2/1 is given in Table II. An examination of these figures shows that the total amount of reaction again decreases with increasing temperature as was observed previously in the corresponding experiments without oxygen. In this case no maximum is observed, although one must appear at lower temperatures than those studied, since, obviously, if a sufficiently low temperature were chosen, the amount of material reacting could be made as small as desired. The decrease in butane consumed is probably attributable here to smaller fragmentation of each molecule of butane which reacts (compare next section).

EFFECT OF OXYGEN ON THE NITROPARAFFINS PRODUCED

The nitroparaffins formed in Runs 11 and 12 were dried and fractionated in a four-foot column packed with a nichrome wire spiral. As can be seen in Table IV, when the O_2/HNO_3 ratio is changed from zero to two, the amounts of the nitrobutanes formed are decreased significantly, while the amounts of the nitromethane and nitroethane are increased by a factor of two. The data from Runs 11 and 12 show that temperature also has an effect on product distribution.

EFFECT OF SURFACE ON NITRATION

Schechter (3) first mentioned the possible influence in the nitration reaction of the surface to volume ratio in the reactor. However his sole concern was apparently with heat transfer. If one views the nitration reaction as a free radical process, which, in the presence of oxygen involves certain chain mechanisms, then it becomes obvious that extended surface could be important for still other reasons.

The packed reactor described above was used to investigate these effects using varying amounts of oxygen and surface to volume ratios of 20, 28, and 300. While the heat transfer area was probably not completely constant in this series of experiments, it was considerably lower than that existing in the 10 mm. I.D. coil reactor of the earlier experiments. Consequently, no direct comparison may be made between the two sets of data.

TABLE IV

NITRATION OF BUTANE; EFFECT OF OXYGEN ON TYPE OF NITROPARAFFINS

RUN NO. →	HODGE[a]	11	12
C_4H_{10}/HNO_3	14	15.6	12.7
O_2/HNO_3	0	2	2
Temp., °C	420	425	411
MOLE PER CENT			
CH_3NO_2	10	22	19
$C_2H_5NO_2$	13	30	32
1-$C_3H_7NO_2$	8	5	11
2-$C_4H_9NO_2$	45	27	21
1-$C_4H_9NO_2$	24	16	17

[a] Data taken from Hass and Hodge (2).

TABLE V

NITRATION OF BUTANE; EFFECT OF OXYGEN WITH VARYING SURFACE/VOLUME RATIOS

(Temperature = 425°; Contact Time = 1.6 Seconds)

RUN NO. →	18	21	25	22	31	30	28	29	34	35	32	26	33
S/V Ratio	20				28				300				
C_4H_{10}/HNO_3	12.0	16.0	14.3	15.9	16.2	15.6	13.8	14.1	15.6	15.5	15.7	14.8	14.6
O_2/HNO_3	0	1	2	3	0	1	2	3	0	0.5	1	1.25	2
Conversion,[a] %	27	33	42	39	25	39	39	30	20	33	44	41	34
Yield,[b] %	38	30	22	13	44	36	23	12	37	46	45	38	20
MOLES OF PRODUCTS[c]													
RNO_2	0.21	0.21	0.28	0.25	0.16	0.25	0.28	0.21	0.13	0.21	0.28	0.28	0.24
$> C{=}O$	0.14	0.32	0.58	0.90	0.09	0.30	0.58	0.81	0.05	0.18	0.32	0.41	0.63
$C_3H_6 + C_4H_8$	0.15	0.21	0.59	0.93	0.09	0.21	0.48	0.82	0.10	0.09	0.14	0.18	0.44
C_2H_4	0.08	0.13	0.20	0.51	0.06	0.12	0.28	0.59	0.07	0.05	0.03	0.12	0.29
CO	0.33	0.30	0.39	0.67	0.14	0.29	0.43	0.83	0.24	0.18	0.23	0.28	0.49
CO_2	0.08	0.06	0.10	0.07	0.06	0.04	0.11	0.07	0.04	0.09	0.12	0.06	0.07
Butane consumed, moles	0.51	0.64	1.18	1.76	0.34	0.68	1.13	1.67	0.32	0.42	0.58	0.68	1.07

[a] Based on the amount of nitric acid charged. [b] Based on butane consumed. [c] Corrected to a total butane flow of 10 moles.

The results from these experiments are given in Table V. A comparison of the conversions obtained without oxygen with S/V ratios of 20, 28, and 300 shows that conversion actually decreases as the amount of surface increases. That this is not due to the favoring of some other reaction over nitration is demonstrated by comparing the total amount of butane consumed in each case. This value decreases from 0.51 mole to 0.32 mole while the conversion decreases from 27% to 20%. It will be noted that the value of 27% obtained with an S/V ratio of 20 in the packed reactor is much lower than the 36% conversion reported for the 10 mm. I.D. coil reactor. Since, in the latter case, the S/V ratio is 4/1, a portion of this decrease must be due to the surface effect. However, it is felt that to some (and perhaps a major) extent the poorer heat transfer in the packed reactor is responsible.

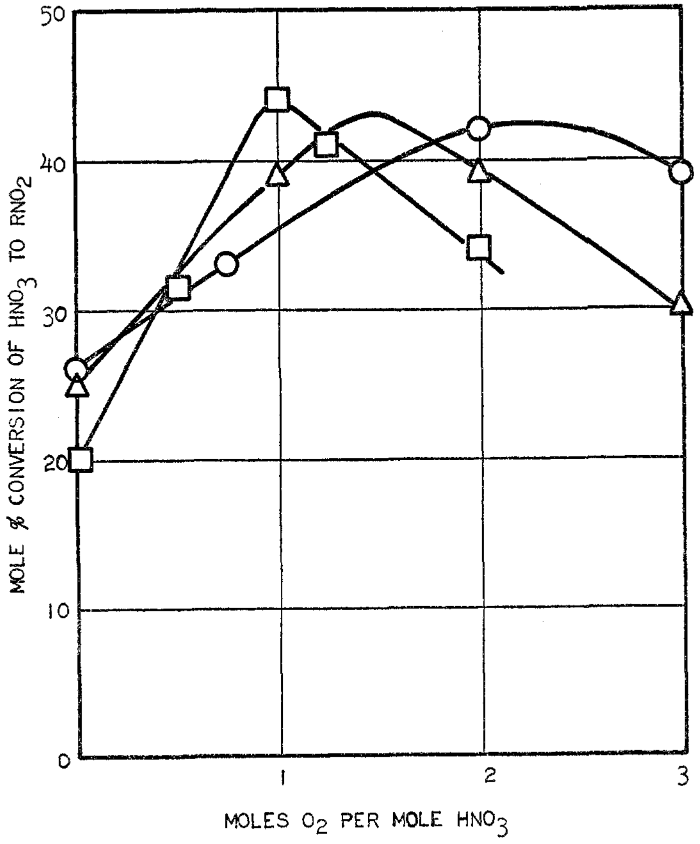

FIGURE 4. EFFECT OF OXYGEN ON CONVERSION WITH DIFFERENT SURFACE/VOLUME RATIOS. Conditions: 425°; Contact time = 1.6 sec.; ○, S/V = 20; △, S/V = 28; □, S/V = 300

In each case, as oxygen was added, the conversion rose to a maximum value and then fell off. These results are given graphically in Figure 4. The maximum values were 42.5% at S/V ratios of 20 and 28, and 44% with S/V ratios of 300. Hence no significant increases in maximum conversion in the presence of oxygen are noted with a change in surface. On the other hand, a marked change in the quantity of oxygen required to give the optimum conversion is noted.

It would be expected that a decrease in the amount of oxygen would increase the yield based on hydrocarbon. Figure 5 shows a comparison of the yields obtained by varying the ratio of oxygen with the three packings. Considerable differences are noted between the yields at S/V ratios of 20, 28, and 300. The peak yield obtained when the S/V ratio is 300 is quite unusual. It is the first case in which an actual increase in yield of nitroparaffins was obtained upon adding oxygen and also the first case in which maxima in both the yields and conversions occurred with equal amounts of oxygen. In the past the chief objection to the use of oxygen has been that the maximum yields were obtained at different oxygen/hydrocarbon ratios than were the maximum conversions. Evidently a large S/V ratio brings these two maxima together at the same oxygen content of feed gas.

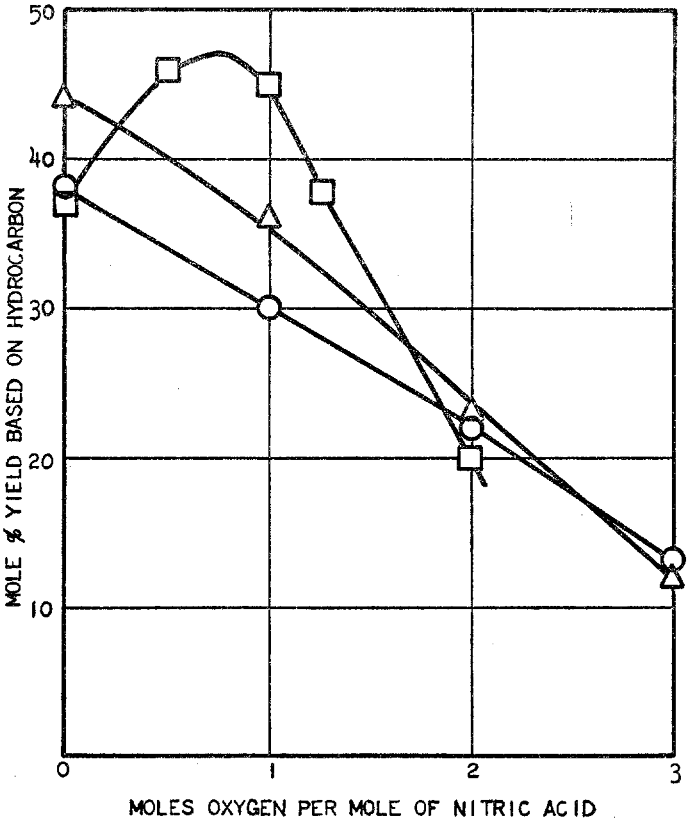

FIGURE 5. NITRATION OF BUTANE; EFFECT OF OXYGEN ON YIELD WITH DIFFERENT SURFACE/VOLUME RATIOS. Conditions: 425°; Contact time = 1.6 sec.; ○, S/V = 20; △, S/V = 28; □, S/V = 300

While all of the mechanisms by which surface exercises its effect are obscure, certain conclusions may be drawn from an examination of the quantities of products obtained in the above experiments (see Table V). A rather large portion of the butane is converted to butenes and propene, thus making this one of the greatest sources of loss. Figure 6 shows how this loss varies with oxygen for each packing. In each case there is a gradual increase in loss until the O_2/HNO_3 ratio reaches a value of approximately one. At this point the rate of increase in this loss becomes much larger. This same effect was noticed when using the 10-mm. coil reactor. It probably indicates the ability of the nitrating agent to utilize a relatively high portion of the free alkyl radicals formed by oxidative attack until a certain concentration of these radicals is reached. After that point, a much larger percentage of these radicals simply undergoes decomposition to form olefins. It can be seen that a higher S/V ratio causes a general decrease in losses as olefins. Referring now to Figure 7, it is seen that the total amount of

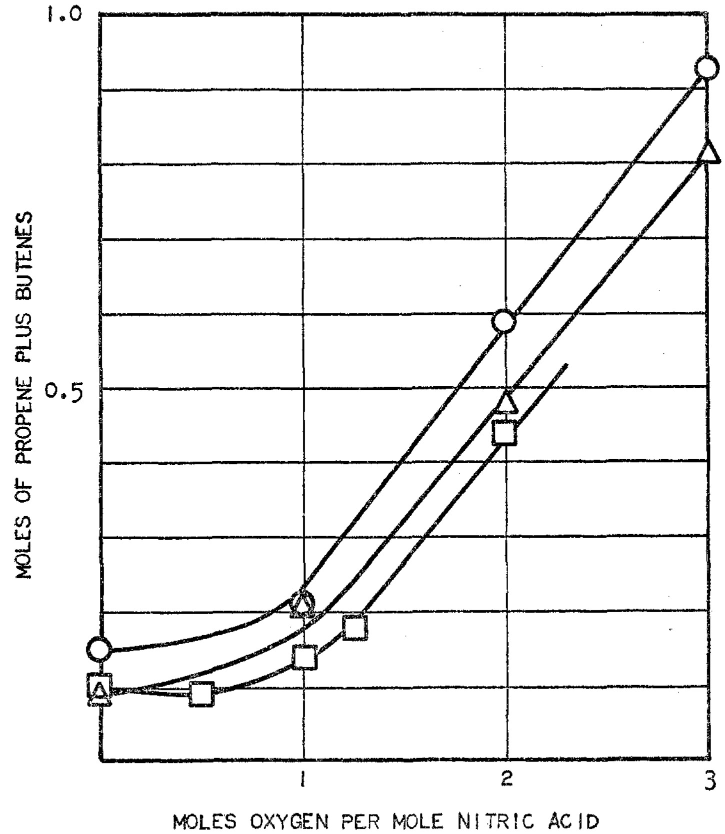

FIGURE 6 EFFECT OF OXYGEN ON FORMATION OF PROPENE AND BUTENES WITH VARIOUS SURFACE/VOLUME RATIOS. Conditions: Contact time = 1.6 sec.; C_4H_{10}/HNO_3 = 15; ○, S/V = 20; △, S/V = 28; □, S/V = 300

butane reacting increases with oxygen, but that the increase is less the greater the S/V ratio. It has previously been proposed that such a decrease in the amount of butane reacting is due to chain stopping with less total production

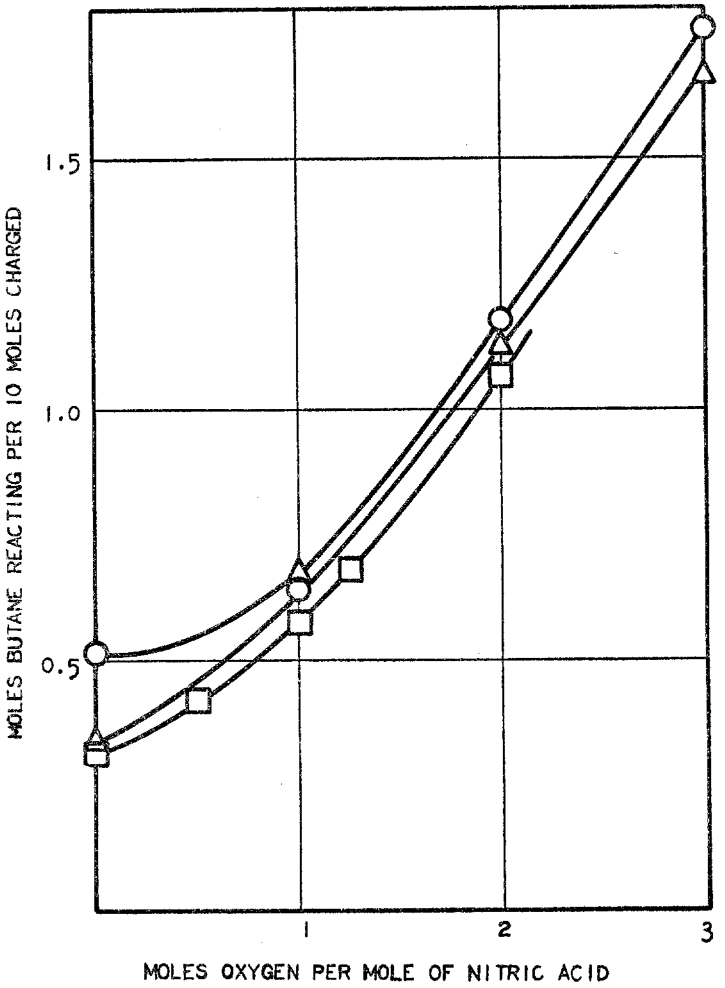

Figure 7. Effect of Oxygen on Amount of Butane Reacting Using Various Surface/Volume Ratios. Conditions: Contact time = 1.6 sec.; C_4H_{10}/HNO_3 = 15; Temperature = 425°; ○, S/V = 20; △, S/V = 28; □, S/V = 300

of free radicals. Hence the decrease in olefin formation observed upon increasing the surface is simply a reflection of a lower rate of free radical formation.

The data given in Table V show that production of nitroparaffins goes through a maximum with increasing oxygen. These maxima are the same height regardless of the S/V ratio but occur with less oxygen as the S/V ratio increases. Since the total number of free radicals present is decreased by more surface, the fact that the same number of free radicals are converted to nitroparaffins must mean that their reaction to form oxygenated materials is a chain reaction which is hindered by surface. Such a reaction would presumably involve OH or O_2H radicals as chain carriers and would be stopped on the walls.

THE USE OF STEAM AS DILUENT

In the foregoing section it was pointed out that an excess of free radicals is probably formed when oxygen is added to the nitration mixture to the extent of two moles for each mole of nitric acid.

The fact that conversion does not increase greatly under these circumstances indicates that an insufficient amount of the nitrating agent is present at the time the extra free radicals are available. This could stem from either of two factors: (a) decomposition of nitric acid in other ways, or (b) production of free radicals over such a short period of time that the actual nitrating agent (presumably NO_2) is not formed fast enough to utilize them before they undergo other change. The obvious solution to the difficulty in the latter case would be to add an inert diluent to the mixture since this would effectively decrease the concentration of alkyl radicals present at any given point. It would not, however, influence materially the total quantity of alkyl radicals formed before the end of the nitration tube is reached. The most likely choice of diluent would seem to be steam. It is inert, cheap, has a high heat capacity, and is already being introduced as water in the 70% nitric acid.

TABLE VI

NITRATION OF BUTANE IN THE PRESENCE OF OXYGEN; USE OF STEAM AS DILUENT

(Contact Time = 1.6 Seconds)

RUN NO. →	11	25	17	20
S/V	4	20	4	20
C_4H_{10}/HNO_3	15.6	14.8	14.6	14.0
O_2/HNO_3	2	2	2	2
C_4H_{10}/H_2O	9.6	9.1	1	1
Conversion, %	36	42	55	54
Yield, %	24	22	30	35
MOLES FORMED				
RNO_2	0.26	0.28	0.36	0.39
$> C{=}O$	0.68	0.58	0.82	0.88
$C_3H_6 + C_4H_8$	0.37	0.59	0.41	0.25
C_2H_4	0.25	0.20	0.10	0.08
CO	0.45	0.39	0.47	0.41
CO_2	0.17	0.10	0.10	0.05
Butane consumed, moles	1.06	1.18	1.12	1.02

Work by Hibshman (4) on the nitration of ethane without added oxygen shows that increasing the dilution of the nitric acid has an adverse effect on conversion. Under these conditions, however, the ratio of free radicals to nitrating agent does not reach an optimum value. Hence, a diluent which decreases the rate of free radical formation would not be expected to increase but rather to decrease the conversion. With excess oxygen present, however, the ratio of free radicals to nitrating agent may exceed the optimum value. A diluent present in suitable amounts would decrease this ratio to the optimum value and thereby lead to increased conversions.

To test this reasoning, two experiments were carried out using equimolar amounts of hydrocarbon and steam. In each case the butane/oxygen/nitric acid ratio was about 14/2/1. One was performed in the 10-mm. coil which has an S/V ratio of 20. Other pertinent information along with the results are given in Table VI. Also included for comparison are Runs 11 and 25 which are equivalent in all respects except they were performed without added steam. An improvement in both conversion and yield was obtained as a result of the addition of steam. Increasing the S/V ratio caused a further improvement in yield although the conversion was not appreciably affected.

An examination of the products shows that the steam increases the amount of aldehydes produced but that the total amount of olefins formed decreases. This decrease, while small in the S/V = 4 reactor, becomes considerable when the S/V ratio is raised to 20. In either case the actual number of moles of nitroparaffins produced shows a substantial rise which is greater than the increase brought about by any other single variable.

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SUMMARY

The optimum conversion based on nitrating agent in the vapor phase nitration of butane may be increased substantially by the addition of oxygen to the reaction mixture. Under ordinary conditions, this addition of oxygen decreases greatly the ultimate yield based on hydrocarbon. However, increasing the ratio of surface to volume in the reactor makes possible slightly higher conversions based on nitric acid and produces striking improvements in the yield based on butane consumed. The use of steam as a diluent in the presence of oxygen also mitigates the harmful effect of the oxygen and aids in raising the conversion still further.

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