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

# NITRATION STUDIES. III. EFFECT OF OXYGEN ON THE VAPOR PHASE NITRATION OF PROPANE WITH NITROGEN DIOXIDE[1]

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Extensive work on the vapor phase nitration of propane with nitrogen dioxide was carried out by Dorsky (3). He found that nitrations with nitrogen dioxide are favored by long contact times and low temperatures compared to nitration with nitric acid. Alexander (2) studied the nitration of propane with nitric acid extensively and showed that the presence of oxygen increased the conversions materially. He also made two preliminary runs using nitrogen dioxide and oxygen and showed that an increase in conversion resulted. There remained to be investigated the full extent of the beneficial effects of oxygen on the nitration of propane with nitrogen dioxide. Neither of the above investigators determined the yields of their products based on propane. Addison (1), however, showed that the use of oxygen in the nitration of butane with nitric acid tended to decrease the yields of nitroparaffins and to increase the yields of by-products based on the hydrocarbon. If the same were to apply to nitrations with nitrogen dioxide, the beneficial effects of increased conversions based on nitrogen dioxide would be overbalanced. If on the other hand the yields based on propane were not materially affected or were improved, then the use of oxygen would be desirable and the rising cost of propane would be of less concern. The present investigation was designed to determine which of these result would be obtained.

*Apparatus.* The apparatus consisted of a metering system for the reactants, a reactor, and a condensing system. The flow control for the propane and the oxygen was provided by jet 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. Nitrogen dioxide was metered through a conventional orifice meter because of the low cylinder pressure available.

The reactor used was made of 14 mm. O.D. Pyrex tubing wound on mandrels of 8 and 10 inches in diameter. Two coils, one of each diameter, were fitted together concentrically and sealed together at the bottom. The reactor had a volume of 2 liters. The heating of the reactor was accomplished with a molten salt ($KNO_3$ and $NaNO_3$) bath provided with immersion heaters operated by an automatic temperature controller.

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

*Product analysis.* The total liquid product was extracted with ether to separate the aqueous and non-aqueous materials. Any aldehydes present in each layer were determined by the hydroxylamine hydrochloride method (5). The ether layer was treated with sodium

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[1] From the Ph.D. thesis of J. V. Hewett, Purdue University, February 1950.

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bicarbonate to remove acidic materials. The nitroparaffins remaining in the ether layer were determined by a nitrogen analysis on an aliquot portion. The analysis used is a modification of a method described by Somers (4). The reduction of the nitroparaffins and the apparatus were the same as in Somer's method. After reducing the nitroparaffins to amines 30 ml. of distilled water was added and the flask was placed on the apparatus. Then 15 ml. of 30% aqueous NaOH was added. The flask was heated by a micro burner placed about three inches below it for 15 minutes. During the heating period the amines were distilled into 50 ml. of 2% boric acid solution. They were then titrated with 0.01 *N* sulfuric acid using a Bromcresol Green-Methyl Red mixed indicator. The end point was taken as the first extremely faint pink color seen over a white surface.

Carbon dioxide, propylene, ethylene, and carbon monoxide were determined by an Orsat analysis on a sample of the exit gases collected between the water and Dry Ice condensers. Conversions were based on the fraction of the nitrogen dioxide which appeared as nitroparaffins. Yields were based on the propane which reacted. The $C/NO_2$ ratio of 2.85 was assumed for the nitroparaffin mixture in the calculations.

TABLE I

NITRATIONS WITHOUT OXYGEN; EFFECT OF TEMPERATURE

| RUN NO. → | A-7[a] | 248-2 | 300-2 | 325-1 |
|---|---|---|---|---|
| Temp., °C | 248 | 248 | 300 | 325 |
| Contact time, min. | 1.86 | 1.90 | 1.93 | 1.93 |
| Propane/$NO_2$ | 4.00 | 3.85 | 4.17 | 4.20 |
| Conversion,[b] % | 13.4 | 13.7 | 16.1 | 16.6 |
| Yield,[c] % | — | 47 | 49 | 51 |

[a] Dorsky's data (3). [b] Per cent of nitrogen in nitrogen dioxide charged appearing in nitroparaffins in effluent. [c] Yield based upon moles of carbon.

## NITRATION WITHOUT OXYGEN

Previous work on nitrations with nitrogen dioxide did not include determinations of the by-products formed in the nitration reaction. This fact coupled with the lack of information about nitrations with nitrogen dioxide at temperatures between 248 and 500° made a series of runs without oxygen necessary. No runs were made at temperatures in excess of 325° because indications were obtained that higher temperatures would not be beneficial. The data for these runs are given in Table I. They show that even without oxygen much higher yields are possible with nitrogen dioxide than with nitric acid as the nitrating agent using present techniques.

## NITRATION OF PROPANE WITH OXYGEN AT TWO MINUTES CONTACT TIME

A series of runs at different temperatures was made at a contact time of two minutes and with one-half mole of oxygen per mole of nitrogen dioxide. A similar series of runs was made using a full mole of oxygen per mole of nitrogen dioxide. This information together with the data obtained without oxygen shows the variations which take place with changes in temperature and oxygen feed rate when a contact time of two minutes is used. It is to be noted that the use of oxygen lowers the optimum temperature, improves the conversion, and increases the yield. This can be seen in the data presented in Tables II and

III. Note that when the conversion shows a maximum the yield is also high and at or near its maximum.

## NITRATION OF PROPANE AT FOUR MINUTES CONTACT TIME

Experiments were carried out which would furnish for a contact time of four minutes information of the same type as was found for a contact time of two minutes. This information is summarized in Tables IV and V. It was hoped that information at two contact times would show a trend towards an optimum contact time. While the information does seem to be favorable to the longer contact time the difference between the results at the two contact times is not pronounced. Several experiments were carried out at a shorter contact time to check this trend in favor of long contact times.

TABLE II

Nitrations with 0.5 Mole of Oxygen per Mole of Nitrogen Dioxide at 2 Minutes Contact Time; Effect of Temperature

| RUN NO. → | 255-1 | 275-2 | 300-3 | 325-2 |
|---|---|---|---|---|
| Temp., °C | 255 | 275 | 300 | 325 |
| Contact time, min | 1.98 | 2.06 | 2.01 | 1.95 |
| Propane/$NO_2$ | 4.28 | 4.36 | 4.17 | 4.27 |
| Conversion (N), % | 12.9 | 18.8 | 28.9 | 19.9 |
| Yield (Based on Propane), % | 60 | 57 | 58 | 43 |

TABLE III

Nitrations with 1.0 Mole of Oxygen per Mole of Nitrogen Dioxide at 2 Minutes Contact Time; Effect of Temperature

| RUN NO. → | 255-4 | 275-1 | 300-5 | 325-3 |
|---|---|---|---|---|
| Temp., °C | 255 | 275 | 300 | 325 |
| Contact time, min | 1.89 | 2.05 | 1.92 | 2.07 |
| Propane/$NO_2$ | 4.40 | 4.54 | 4.18 | 4.37 |
| Conversion (N), % | 13.4 | 25.5 | 16.4 | 13.6 |
| Yield (Propane), % | 37 | 62 | 50 | 40 |

TABLE IV

Nitrations with 0.5 Mole of Oxygen per Mole of Nitrogen Dioxide at 4 Minutes Contact Time; Effect of Temperature

| RUN NO. → | 245-1 | 255-2 | 275-3 | 300-6 |
|---|---|---|---|---|
| Temp., °C | 245 | 255 | 275 | 300 |
| Contact time, min | 3.84 | 4.39 | 4.17 | 3.98 |
| Propane/$NO_2$ | 3.70 | 4.30 | 3.68 | 3.62 |
| Conversion (N), % | 16.9 | 21.5 | 18.2 | 16.5 |
| Yield (Propane), % | 66 | 60 | 60 | 53 |

### NITRATION OF PROPANE AT 1.5 MINUTES CONTACT TIME

The runs at 1.5 minutes contact time were all made with a full mole of oxygen per mole of nitrogen dioxide. The information from these runs again shows very little advantage of one contact time over another, but the longer contact times are somewhat favored. This effect is more pronounced in the yield figures. The data for these runs is presented together with the data from the runs at the other two contact times in Tables VI and VII. The tables show the effects of varying the contact time. It can be seen that the optimum temperature is lower at the longer contact time.

TABLE V

NITRATIONS WITH 1.0 MOLE OF OXYGEN PER MOLE OF NITROGEN DIOXIDE AT 4 MINUTES CONTACT TIME; EFFECT OF TEMPERATURE

| RUN NO. → | 255-3 | 275-4 | 275-9 | 275-7 |
|---|---|---|---|---|
| Temp., °C. | 255 | 275 | 275 | 275 |
| Contact time, min. | 3.76 | 4.03 | 3.60 | 3.28 |
| Propane/$NO_2$ | 4.30 | 4.50 | 5.20 | 7.30 |
| Conversion, % | 22.6 | 32.6 | 29 | 27.5 |
| Yield, % | 49 | 44[a] | 63 | 65 |

[a] Results from a poor material balance so that moles of off gas have been calculated from weights charged instead of weights recovered.

TABLE VI

VARIATIONS IN CONVERSION WITH TEMPERATURE AND CONTACT TIME

$O_2/NO_2 = 1$

| TEMPERATURE, °C. | CONVERSIONS AT TIMES SHOWN | | |
|---|---|---|---|
| | 1.5 min. | 2 min. | 4 min. |
| 255 | — | 13.4 | 22.6 |
| 275 | 18.4 | 25.5 | 29.0 |
| 300 | 25.4 | 16.4 | 22.5 |
| 325 | 17.1 | 13.6 | — |

### NITRATION OF PROPANE AT THREE MINUTES CONTACT TIME

The information already obtained was used to pick the conditions for a single run at a contact time of three minutes, 285°, and three-quarters of a mole of oxygen per mole of nitrogen dioxide. This run resulted in a conversion of 29% and a yield of 71%, the highest yield and nearly the highest conversion obtained in this investigation.

### BY-PRODUCTS

High yields of nitroparaffins reduce the importance of the nature of the by-products in nitrogen dioxide nitrations as compared with nitric acid nitrations using present techniques. Carbon dioxide and carbon monoxide constitute the main by-products with carbon dioxide predominating. The yields of propylene, ethylene, and carbonyl compounds are of minor significance under good operating conditions and usually total less than 10% based on the propane when optimum yields of nitroparaffins are obtained.

### NITROGEN BALANCE

Analyses of the off-gases showed that about 3% of the nitrogen dioxide charged is converted to elementary nitrogen in the nitration process. This is considerably less than that produced in nitrations with nitric acid (about 20%) and constitutes a definite advantage of nitrogen dioxide in vapor phase nitrations.

TABLE VII

Variations in Yield with Temperature and Contact Time

$O_2/NO_2 = 1$

| TEMPERATURE, °C. | YIELDS AT CONTACT TIMES SHOWN, % | | |
|---|---|---|---|
| | 1.5 min. | 2 min. | 4 min. |
| 255 | — | 37 | 49 |
| 275 | 55 | 62 | 63 |
| 300 | 49 | 50 | 48 |
| 325 | 35 | 40 | — |

TABLE VIII

Effect of Catalysts on Nitrations with Nitrogen Dioxide

| CATALYST → | NONE | $Fe_2O_3$ | $B_2O_3$ | 1-PROPANOL[a] |
|---|---|---|---|---|
| Temp., °C | 275 | 275 | 263 | 275 |
| Contact time, min | 2 | 2 | 2 | 2 |
| Propane/$NO_2$, moles | 4 | 4 | 4 | 4 |
| Oxygen/$NO_2$, moles | 1 | 1 | 1 | 1 |
| Conversion (N), % | 25.5 | 1.4 | 20.0 | 19.7 |
| Yield (Propane), % | 62.0 | 4.0 | 51.0 | 61.0 |
| BYPRODUCTS (EXPRESSED AS A PERCENTAGE OF YIELDS IN UNCATALYZED NITRATION) | | | | |
| Carbon dioxide | 100 | 318 | 114 | — |
| Propylene | 100 | 300 | 300 | — |
| Ethylene | 100 | 175 | 93 | — |
| Carbon monoxide | 100 | 157 | 102 | — |

[a] Four % of total charge.

### EFFECT OF CATALYSTS

Many previous attempts have been made to find solid catalysts for vapor phase nitration with nitric acid. In every case investigated in these laboratories added substances have either been inactive or have lowered the conversions markedly. However, it was thought worthwhile to study a few possible catalysts in nitrations with nitrogen dioxide. A temperature in the lowest part of the effective range, 275°, a contact time of two minutes, and the following catalysts were used: ferric oxide, boric oxide, and 1-propanol. The results are shown in an abbreviated form in Table VIII. It is evident that none of these substances has a beneficial result on the nitration reaction.

## CONCLUSIONS

Nitrations with nitrogen dioxide probably proceed by most of the reactions which occur in nitrations with nitric acid. However, in the absence of added catalysts, the original attack on the hydrocarbon molecule must be by the nitrogen dioxide molecule itself. If this attack is assumed to proceed as follows

$$RH + \cdot NO_2 \rightarrow R\cdot + HNO_2$$

$$HNO_2 \rightarrow H_2O + NO + NO_2$$

it is evident that part of the nitrogen dioxide is consumed in creating the necessary free alkyl radicals, and that the conversion based on nitrogen dioxide cannot rise above 67%. Other factors also operate to limit this conversion which reaches a maximum value under the conditions we have studied of about 17%.

The introduction of oxygen into the nitration reactor provides another agent for producing free alkyl radicals, and hence prevents losses of nitrogen dioxide otherwise resulting from this process. The conversions based on nitrogen dioxide therefore increase in the presence of oxygen and reach a maximum value of about 32% at 275° with one mole of oxygen per mole of nitrogen dioxide.

The yields based on hydrocarbons are normally high, about 50%, in nitrations with nitrogen dioxide. However the yields are even higher, about 65%, when oxygen is present in the feed under optimum conditions. This points to a more efficient utilization of the hydrocarbon, probably because there are fewer lower oxides of nitrogen (especially nitric oxide) present when oxygen is employed, and hence fewer opportunities for conversion of the hydrocarbons to by-products.

In the final analysis, oxygen improves both the yields and conversions of nitrogen dioxide nitrations, but the conversions are still not as good as those obtained in nitric acid nitrations in the presence of oxygen. Furthermore the long contact times necessary at the low temperatures which are optimum for nitrogen dioxide nitrations remain a serious disadvantage.

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## SUMMARY

The conversion obtainable in the vapor phase nitration of propane with nitrogen dioxide at practical contact times may be substantially increased by the addition of oxygen to the reaction mixture. The optimum conversion obobtainable at two minutes contact time with oxygen is appreciably higher than at contact times up to and including fourteen minutes without oxygen. The

use of oxygen improves the yield of nitroparaffins based on propane over that obtainable without oxygen by increasing the conversion to nitroparaffins more than the conversion to by-products. The yield based on propane is much higher using nitrogen dioxide as the nitrating agent than that obtained using nitric acid as the nitrating agent and the present nitration techniques. In addition to the high yields based on propane, nitrations using nitrogen dioxide may be carried out so as to achieve high yields based on the nitrating agent.

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