At  $t_n = 133^\circ F$ , a = 0.785, b = 1.163,  $t_m = 134.8^\circ F$ ,  $L_n =$  $192.1, L_m = 284.4;$ 

	~	—Above Kn or	Feed-	Mole	wor	-Below	Feed	Mole
	d or $w$	$K_m$	lm	%	$(l_n + f)$	$K_m$	$l_m$	%
$C_3H_8$	5.0	2.31	2.6	1.3	7.6	2.35	3.8	1.4
iso-C4H10	17.7	1.136	39.6	20.3	0.2	1.157	56.5	20.5
iso-C <sub>4</sub> H <sub>8</sub>	17.9	1.000	65.4	33.5	11.7	1.017	93.3	33.9
$n-C_4H_{10}$	12.0	0.883	87.2	44.8	27.4	0.910	121.1	44.0
.iso-C <sub>5</sub> H12	0.4	0.41	0.2	0.1	0.4	0.41	0.6	0.2
			195.0	100.0			275.3	100.0

This result is reasonably satisfactory, and it can be assumed that  $a = \frac{195}{247.6} = 0.787$  or L/D = 3.70/1. It appears from the results that slightly less than 12.0 moles per hour of *n*-butane will be in the overhead at minimum reflux.

As a matter of interest, the value of  $r_{Diik}$  would have to be at least  $11 \times 14 \times 29.6/14 \times 25 \times 17.9 = 0.727$  in order to prevent *n*-butane from entering the overhead. In the present case this would mean that the overhead would contain 24.3 moles per hour of isobutylene.

The distribution for total reflux is calculated below, using values of  $\alpha$  at 135° F.:



$$l_D = 1.64; \ l_D = 1.73$$

These results, while not in extremely good agreement are within the slide-rule accuracy of the calculation.

Comparing the results of the calculations on the basis of minimum reflux and total reflux, it appears that much more *n*-butane will be in the distillate in the former condition than in the latter. Since actual operations are usually carried out at a reflux ratio close to the minimum, there will be an appreciable quantity of n-butane in the overhead from an operating tower. The empirical methods of obtaining actual decks for this case have not been fully tested, and plate-to-plate calculations are preferable.

#### Conclusion

The approximate method of calculating the minimum reflux for multicomponent mixtures has been shown to yield results in good agreement with the results from plate-to-plate calculations. It has also been shown to give results comparable with those of other methods but seemingly more accurate and to be applicable to the determination of the distribution of a third component of the feed. The fractionation at total reflux is superior to that at minimum reflux as indicated by the comparative separations of the third component.

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## Nitration of Propane by

A careful study has been made of the nitration of propane by nitrogen dioxide over a wide temperature range in order to compare this nitrating agent with nitric acid, which is employed commercially. Contrary to the reports of certain other investigators, nitrogen dioxide and nitric acid yield the same nitroparaffins although conversions are lower with the former reagent.

THE first vapor-phase nitration of a saturated hydrocarbon was reported from this laboratory in 1934 (2). The nitrating agent was nitric acid vapor. Sometime afterward, Urbanski and Slon (4) published a series of articles describing the nitration of methane, propane, n-pentane, n-hexane, n-heptane, n-octane, and n-nonane by nitrogen dioxide in the vapor phase in glass apparatus. Yields with methane were reported as "insignificant", but the higher

<sup>1</sup> Present address, Ethyl Gasoline Corporation, Baton Rouge, La.

#### H. B. HASS, JULIAN DORSKY<sup>1</sup>,

AND E. B. HODGE • Purdue University, Lafayette, Ind.

Nitrogen Dioxide

hydrocarbons were said to be converted to mixtures of monoand dinitroparaffins at 200° C. in a ratio of about 60 to 40. Although minor amounts of secondary nitroparaffins were reported to be present, the principal products were believed to be the primary isomers, and such derivatives as 1,3-dinitropropane and 1,6-dinitrohexane were stated to compose the main dinitro fractions. Since nylon could easily be made from 1,6dinitrohexane by reducing one half to 1,6-hexanediamine, hydrolyzing the other half to adipic acid by the action of sulfuric acid, and condensing the amine and acid, it seemed that in spite of certain internal evidence of mistaken identification, the work of Urbanski and Slon would be worth verifying. [Urbanski and Slon reported that their "1-nitropropane" boiled at 121°. 1-Nitropropane boils at 132° while 2-nitropropane boils at 120°. Similarly, they reported their September, 1941

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FIGURE 1. APPARATUS FOR VAPOR-PHASE NITRATION OF PROPANE WITH NITROGEN DIOXIDE

- Hot water bath
- $1/_4$ -inch stainless steel union for disconnecting NO<sub>2</sub> cylinder from apparatus R
- 1/4-inch Hancock stainless steel needle valve for control of NO2 flow C.
- D. Packing gland connecting 1/4-inch stainless steel tubing from NO2 cylinder to glass flowmeter (1/s-inch Super-Cutno packing used)
- E, G, J, P. Two-way stopcocks
- Trap for NO<sub>2</sub> flowmeter fluid F
- Chamber for mixing NO2 and C3H8 Η.
- Packing gland connecting glass mixing chamber and 1/4-inch stainless steel tube leading I. to reaction chamber K. Packing gland for thermocouple well
- Spray cooler L.

U.

V.

- Reducing union from 5/8-inch reaction chamber to 3/8-inch condenser tubing М.
- Condenser cooled with tap water N.
- Three-way stopcock 0.
- Q, R. Receivers cooled with ice water
- Receivers cooled with solid CO<sub>2</sub>-CHCl<sub>3</sub>-CCl<sub>4</sub> mixture S, T.
  - Υ. Reaction chamber Pentane thermometer
  - Magnesia insulation Z. Thermocouple wells 1. 2.
- W. Heating element х.
- NO<sub>2</sub> flowmeter
- Molten lead bath
- C<sub>3</sub>H<sub>8</sub> flowmeter

"1-nitropentane" boiling at 164-5°. 1-Nitropentane boils at 172° while the secondary isomers boil at 152°. Only color reactions, molecular weights, and per cent nitrogen were given as evidence for the structure of the dinitroparaffins, evidence which indicated only that some (perhaps small) concentration of primary nitro group was present.]

A study of the conditions of temperature and contact time best suited to the production of nitroparaffins from nitrogen dioxide and propane was made over a wide temperature range. The reaction was studied in two nitrators, one fabricated from 18-8 stainless steel which covered a temperature range from 425° to 600° C. and a second made of Pyrex glass which was used at 248° C. The reason for not using a temperature lower than 248° was that even here the reaction was so slow as to require a contact time of 14.2 minutes for substantially complete reaction of the nitrogen dioxide. This is impractically long for commercial vaporphase operation. Also, analyses confirmed a previous finding (1) that at successively lower temperatures smaller proportions of primary nitro derivatives are formed.

#### **Stainless Steel Nitrator**

Propane was nitrated in the vapor phase by nitrogen dioxide at temperatures ranging from about 425° to 600° C, in the apparatus shown in Figure 1.

Liquid nitrogen dioxide, which was supplied by the Commercial Solvents Corporation in stainles the commercial coveras of portation in stands steel (type 347) cylinders, was vaporized and mixed with the proper proportion of commercial propane (95 per cent pure) in the mixing chamber, H. The flows of propane and nitrogen dioxide were regulated with needle valves and measured but of the proper properties. Note: by calibrated glass capillary flowmeters. Nitric acid saturated with nitrogen dioxide was used as the flowmeter liquid for nitrogen dioxide. The mixture of reactants passed into the reaction chamber, which was fabricated of stainless steel. A vertical piece of  $\frac{5}{8}$ -inch pipe surrounded by a molten lead bath was used as a reaction chamber. It was necessary to wash the walls of the chamber with sodium hydroxide solution (25 per cent) after each run in order to obtain re-producible results. The bath was heated electrically, and the temperature controlled to  $\pm 2^{\circ}$ С. by a thermoregulator. A thermocouple well extended into the reaction chamber from the top through a gastight packing gland. On leaving the chamber the reaction mixture was cooled rapidly by a spray of cold water which impinged on the pipe at L. Further cooling was effected in the stainless steel condenser, N, and some of the product collected in receiver Q, which was cooled with ice water. Three other receivers were used, R, S, and T. The first was immersed in an ice bath, and the next two were cooled by a mixture of chloroform, carbon tetrachlo-ride, and solid carbon dioxide. The gas leav-ing the apparatus was kept between  $-30^{\circ}$  and  $-40^{\circ}$  C. to assure almost complete recovery of nitro compounds without condensation of much tended into the reaction chamber from the top nitro compounds without condensation of much

propane. The rapid flow of gas past the thermocouple in the reaction chamber and radiation from the hot walls of the chamber caused a discrepancy between the couple temperature and that of the gas. It was therefore necessary to estimate the actual reaction temperature. The bath tem-peratures were measured within 2° C. The difficulty in estimating the reaction tempera-ture is shown in Figure 2 where the temperature of the thermosure is the meating the meature. of the thermocouple in the reaction chamber is plotted against distance in the chamber for three conditions of gas flow.



The mole ratio of hydrocarbon to nitrogen dioxide was maintained as closely as possible to 4:1. This mixture was found to be nonexplosive. The approximate ratio was determined from the flowmeter readings, but the exact composition of the mixture was determined by analysis. A sample of the gas was collected in a one-liter glass bulb; the nitrogen dioxide was determined by absorption in alkali and the propane determined from the pressure in the bulb after the absorption.

#### **Results of Nitration in Steel Apparatus**

Propane was nitrated in the apparatus at five different bath temperatures. To avoid possible reaction between nitroparaffin and nitrating agent during distillation, the reaction product was diluted with water; the mixture was then distilled, and the nitroparaffins were separated as an oil from the distillate. Several runs were made using different exposure times at each bath temperature; a curve was constructed for each temperature with total moles of reactants (nitrogen dioxide plus propane) per hour plotted against the conversion—i. e.,

### $\frac{\text{moles nitro product} \times 100}{\text{moles NO}_2 \text{ sent into reactor}}$

The mixture of nitro compounds was weighed and assumed to be nitropropane. An analysis was made later. The curves are reproduced in Figure 3. At all bath temperatures except the lowest, the curves show that the maximum conversion for that temperature was obtained. (The curve for the lowest temperature,  $505-510^{\circ}$  C., could not be completed because of the limitations of the apparatus.) However, extrapolation from the completed curves indicates that the highest conversion obtained at 505-510° C. was probably close to the maximum obtainable. Over the range of bath temperatures studied, from 790-795° to 505-510° C., the maximum conversion varied from 4 per cent at the highest to about 9 per cent at the lowest bath temperature. The bath temperatures were not identical with the reaction temperatures, and it is estimated that the highest bath temperature corresponded to a reaction temperature of about 600° C., while the lowest bath temperature corresponded to a reaction temperature of about 425° C.



FIGURE 3. VARIATION OF CONVERSION WITH GAS FLOW IN STEEL NITRATOR



FIGURE 4. HEATING BATH AND REACTION CHAMBER OF LOW-TEMPERATURE NITRATION APPARATUS

A. Inlet for NO<sub>2</sub>-C<sub>3</sub>H<sub>8</sub> mixture
B. Cover
C. Heater
D. Sil-O-Cel insulation
D. Thermocouple wells
F. Reaction chambers
G. Preheater
H. Oil bath
I. Stirrer

A study of the precision of the results obtained in the stainless steel nitrator was made by making three sets of duplicate runs over a wide range of conditions. The average deviation from the mean for each set was about 2 per cent.

Some weeks after the data had been obtained in the stainless steel nitrator, it was desired to make some additional runs. The apparatus did not behave normally and only erratic results were obtained. All attempts to restore the reaction chamber to its original condition were unsuccessful. Such changes had previously been experienced with stainless steel reactors at Purdue and also at the Commercial Solvents Corporation. It is possible that prolonged heating of the stainless steel produced a change in its structure. In any event, the change appeared to favor oxidation at the expense of nitration.

#### **Glass** Nitrator

Propane was nitrated at 248° C. in the apparatus shown in Figure 4:

Only the glass reaction chamber and the heating bath are sketched. The propane and nitrogen dioxide feed system, and the condensing system, except for the steel condenser which was omitted, were identical with that used with the stainless steel nitrator (Figure 1). The glass nitrator was designed to permit the reaction to proceed isothermally at the bath temperature. A preheating coil of 5-mm, glass tubing preceded the chamber proper. Temperature measurements made at the junction of the preheating coil and reaction chamber showed that the reactant gases reached the bath temperature before they entered the chamber. The volume of the preheater was never more than 1.5 per cent of the total reaction volume. During the course of a reaction chamber and found to be that of the bath.

The reaction chamber was constructed from approximately 37-cm. lengths of glass tubing 6.5 and 7.5 cm. in diameter. In the course of the work the reaction volume was increased from 1052 to 2100 to 5450 and finally to 11,730 cc. by adding reaction tubes in series as shown in Figure 4. The tubes were all clamped together, and each was fitted with a glass thermocouple well which entered from the top.

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#### **Results of Nitration in Glass Apparatus**

The percentage of nitrogen dioxide converted to nitropropane was determined in the glass nitrator at  $248 \pm 2^{\circ}$  C. at a number of contact times from 0.725 to 14.2 minutes. The procedure used in the stainless steel nitrator was followed with a few variations. The propane and nitrogen dioxide flows were read from the meters directly, and a separate analysis of the mixture was not necessary. The large volume of the reaction chamber made it necessary to sweep the chamber with the reaction mixture for about half an hour before each run. Fourteen runs were made at different contact times in the glass nitrator. The results are shown in Figure 5, where the percentage of nitrogen dioxide converted to nitropropane is plotted against contact time in minutes. The conversion increased from 6.6 per cent at a contact time of 0.725 minute to 26 per cent at 14.2 minutes. The conversion-contact time curve does not show a maximum, but the flattening of the curve at contact times above 6 minutes and the fact that substantially no nitrogen dioxide remained in the exit gas from the run made at the longest contact time (14.2 minutes) indicate that the maximum conversion or a value very near it had been obtained. Since one of the essential reagents had been entirely consumed, it is unreasonable to suppose that a higher contact time would have increased the conversion.

Three sets of duplicate runs were made in the glass nitrator at different contact times. In each set conditions were reproduced closely and the yields compared. The average deviation from the mean for each set was about 3.5 per cent.

The reaction appeared not to be influenced by the glass surface. This was believed to be an indication that the vapor-phase nitration of propane with nitrogen dioxide is homogeneous.

#### Analysis of Product

The vapor-phase nitration of propane with nitrogen dioxide produced a mixture of nitroparaffins along with other prod-



FIGURE 5. VARIATION OF CONVERSION WITH CON-TACT TIME IN GLASS NITRATOR AT  $248 \pm 2^{\circ}$  C. Reaction-chamber volume in liters: O = 1.052,  $\blacksquare = 21.00$ , = 5.450,  $\bigcirc = 11.73$  ucts which presumably resulted from the simultaneous oxidation and cracking reactions. High temperature favored the formation of the by-products such as aldehydes, olefins, and carboxylic acids resulting from the side reactions. At the contact time necessary for maximum conversion even at 248° C. the oxidation reaction was still appreciable. This was evidenced by the fact that 5 per cent of the reaction product at this temperature consisted of aldehydes.

In some of the runs at high temperatures, particularly those at a bath temperature of  $790-795^{\circ}$  C., a white crystalline substance separated out in the condensing system. The





crystals were identified as ammonium nitrate, and their presence indicates that ammonia was formed during the reaction.

The mixture of nitro compounds obtained from the reaction product at several temperatures was separated in a modified Podbielniak rectifying column. The rectification curves are reproduced in Figure 6. About one gram of boric acid was added to each batch of nitroparaffin rectified. This addition prevented decomposition during the distillation. The relative proportions of the various nitroparaffins produced varied with the reaction temperature. This variation was in accordance with the previous observation that high temperature favors the formation of the lower nitro compounds (nitromethane and nitroethane) and primary substitution products (1-nitropropane) at the expense of secondary and/or tertiary isomers (2-nitropropane). The compositions of the nitroparaffin mixtures analyzed expressed as percentage of total nitroparaffin are as follows:

•	250° C.	505–510° C. <sup>a</sup>	790–795° C.ª
Nitromethane, % Nitroethane, % 1-Nitropropane, % 2-Nitropropane, %	$, \begin{array}{c} 14\\3\\11\\72\end{array}$	15 15 15 55	23.5 23.5 29.5 23.5
<sup>4</sup> Bath temperature.			

These data are plotted in Figure 7. At  $250^{\circ}$  C. 2-nitropropane predominated in the product (72 per cent). The proportion of this substance decreased at higher temperatures, and at 800° C. (bath temperature) it was only 23.5 per cent. The proportion of the other three nitroparaffins, nitromethane, nitroethane, and 1-nitropropane, increased as the reaction temperature was raised. The increase was most rapid in the case of 1-nitropropane and nitroethane.

#### Analysis of Nitromethane–Nitroethane–2-Nitropropane Mixture

The vapor-phase nitration of propane with nitrogen dioxide at 250° C. produced a mixture of nitroparaffins. The rectification of this mixture in the modified Podbielniak column effected the separation of nitromethane, 2-nitropropane, and 1-nitropropane. Nitroethane was not separated by the rectification, but its presence was suspected because it was found in the reaction product that resulted from nitration at higher temperatures. Since nitroethane (b. p. 114° C.) and 2-nitropropane (b. p. 120° C.) boil only 6° C. apart, and only a small amount of nitroethane (less than 5 per cent) was present in the mixture, it is not surprising that no separation was made.

The presence of nitroethane in the reaction mixture produced at  $250^{\circ}$  C. was demonstrated by the use of the colorimetric method of Scott and Treon (3). The method was applied to the fraction of the rectification product which boiled between nitromethane and 2-nitropropane. The mixture, then, contained nitromethane, nitroethane, and 2nitropropane.

The analytical procedure is based on the formation of a persistent pink coloration when an excess of hydrochloric acid containing ferric chloride is added to an alkaline solution of a primary mononitroparaffin. Nitromethane does not produce a color under these conditions, while 2-nitropropane does form a color that fades rapidly.

A standard aqueous solution of the unknown mixture was prepared containing about 10 mg. of nitroparaffins per ml., and also three separate standard solutions of the nitroparaffins each containing about 5 mg. of nitroparaffin per ml. These standard solutions were used to make up a number of solutions for comparison in a Duboscq colorimeter. The procedure of Scott and Treon (3) was followed except that the solutions for comparison were diluted to 50 instead of 25 ml., and a filter was not used with the colorimeter. The unknown was compared with solutions containing the three nitroparaffins, nitroethane alone, and nitroethane and 2-nitropropane. The color formed by the unknown persisted after 24 hours, showing definitely the presence of nitroethane, and comparison in the colorimeter indicated that about 25 per cent of it was nitroethane. Since the original portion taken for analysis was 10 per cent of the total reaction product, approximately 3 per cent of the total was nitroethane.



FIGURE 7. VARIATION OF COMPOSI-TION WITH TEMPERATURE

In their report on the vapor-phase nitration of propane with nitrogen dioxide, Urbanski and Slon (4) stated that the product of the vapor-phase nitration of propane with nitrogen dioxide at 200° C. was a mixture of equal amounts of 1nitropropane and 1,3-dinitropropane. The analysis of the reaction product formed at 250° C. in the present work demonstrated the absence of any dinitroparaffins. Besides the dinitropropane, Urbanski and Slon reported only the presence of 1-nitropropane. The results of this research showed that the principal product (72 per cent) at  $250^{\circ}$  C. was 2-nitropropane, and that 1-nitropropane, nitromethane, and nitroethane were also produced. The predominance of the secondary nitroparaffin in the product at lower temperatures was substantiated by runs made at higher temperatures. In this research the reaction products were carefully rectified in a column, the efficiency of which is attested by the relatively sharp breaks shown in the rectification curves. Urbanski and Slon did not describe their distillation apparatus. The dinitro compound was not distilled but supposedly remained as residue in the flask. A Dumas nitrogen analysis which was low (19.39 per cent found, 20.89 per cent theoretical) and a positive nitrolic acid test for the primary nitro group were used to identify the residue as 1,3-dinitropropane. Urbanski and Slon were apparently unaware of the use of boric acid as an aid in the distillation of the nitroparaffins. They therefore presumably encountered decomposition during the distillation. Such decomposition would have complicated the identification of any dinitro compounds in the distillation residue.

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# The Absorption of Olefins from **Ethylene-Nitrogen and Propylene-**Nitrogen Mixtures

#### E. R. GILLILAND AND J. E. SEEBOLD

Massachusetts Institute of Technology, Cambridge, Mass.

The similarities in physical properties of the olefinic and of the paraffinic constituents of cracked petroleum refinery gases renders their separation difficult and expensive. The high reactivity of the unsaturated molecular structure of the olefins suggests the possibility of exploiting the chemical dissimilarities of the components to effect a less expensive recovery. To this end, a tower 3 inches in diameter and 10 feet high, packed with <sup>3</sup>/s-inch Raschig rings, was constructed to study the absorption of the lower olefins in acid solutions of cuprous chloride. The operation of this tower at temperatures of 15° to 30° C. (59° to 86° F.) and pressures of 50 to 250 pounds per square inch, using

N RECENT years the development of the synthetic chemical branch of the petroleum industry has brought with it a recognized need for a simpler and more effective method of separating the chemically unsaturated constituents from cracked refinery gases. While the unsaturated components can in some cases be successfully subjected to chemical reaction while mixed with inactive gases, it is generally profitable, and frequently imperative from a technical point of view, first to isolate the olefin itself in a concentrated form, then to proceed further with the synthetic operations, and thus gain the advantages of using a pure raw material at the beginning. The reduction in operating pressures, equipment sizes, and yield losses, and the improvement of final product quality will ordinarily justify economically the preliminary extraction of the active constituents from the crude gases.

Present methods of separation include, in the main, highpressure distillation at low temperatures and absorption in organic solvents. These methods of recovery involve considerable capital investment, as well as operating expense, largely because their effectiveness resides in the relatively small differences in the physical properties of the olefinic and aliphatic ethylene-nitrogen and propylene-nitrogen gas mixtures containing about 30 per cent olefin, successfully demonstrated the effectiveness of cuprous salt solutions for olefin extraction. Eighty per cent of the ethylene entering the experimental absorber was extracted at moderate operating conditions.

The height of the absorber equivalent to one transfer unit (H. T. U.) was about 3 feet at liquid rates approximating 5000 pounds per hour per square foot of tower cross section. Liquid film resistance to the diffusion of a complex, coppercontaining addition ion controls the absorption rate, diffusion and rapid chemical reaction occurring simultaneously in the liquid film.

constituents of the various gaseous mixtures available. The rapid growth in the importance of the light unsaturated hydrocarbons as raw materials for a host of industrial organic syntheses, resulting in such diversified products as alcohol, ethers, esters, oxides, acids, and halides, greatly increases the desirability of reducing the initial cost of processing the crude gas. The highly reactive nature of the unsaturated structure of the olefins occurring in the gases suggests the application of some chemical reaction to bring about the desired recovery.

The success of such a chemical recovery process depends upon locating an agent which will (a) react with the olefins rapidly and to a significant degree under moderate, easily obtainable conditions, preferably differing in the extent of reaction with different olefins, (b) liberate the chemically unaltered olefin under other moderate and readily established conditions, and (c) will itself be easily regenerated in its original form to be recycled through the process. The choice of materials which approach these conditions is rather limited. Ethylene, for example, will react with many common substances to form various ethylene derivatives, but these deriva-