to the formation of electrolytes on reaction with oxygen or with light. An attractive interpretation of the oxygenation reaction assumes that this represents an extreme case of attack on the solvent. Much less extensive attack on other solvents, presumably involving triphenylmethylperoxy radical[26] is well established. The present data suggest that a triphenylcarbonium salt of a dinegative anion is formed. In the absence of knowledge concerning the nature of the anion or even the stoichiometry of oxygen consumption,[27] the system cannot be more completely defined.

The product of irradiation in the absence of oxygen apparently is different from that obtained in other media where triphenylmethane and diphenyl-bis-diphenyleneethane result from induced disproportionation. A reasonable hypothesis is that generation of conducting species in the present case involves attack on the solvent but diagnostic data are not now available.

**Acknowledgment.**—This work was made possible by a Frederick Gardner Cottrell grant by the Research Corporation. Mr. Peter Pappas assisted in some of the experiments. Valuable discussions were held with Dr. George R. Thomas.

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[26] *Cf.* N. N. Lichtin and G. R. Thomas, THIS JOURNAL, **76**, 3021 (1954).

[27] A single rough quantitative oxygenation experiment indicated consumption of 0.7 mole of $O_2$ per mole of hexaphenylethane. Additional experiments by P. Pappas yielded results of poor precision which fell in the range 1 ± 0.5 mole of $O_2$ per mole of hexaphenylethane.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

# The Reaction of Nitric Oxide with Isobutylene

BY JOHN F. BROWN, JR.

RECEIVED NOVEMBER 28, 1956

Nitric oxide containing traces of nitrogen dioxide reacts readily with liquid isobutylene to give nitrogen and a mixture of nitrated products. This mixture is believed to contain β-nitroisobutylene (22%); nitro-*t*-butanol (9%); traces of isobutylene pseudonitrosite, nitro-*t*-butyl nitrate and α-hydroxyisobutyraldoxime; and major amounts (66%) of a substance having the partial structure (nitro-*t*-butyl)$_4$$N_2O_2$. The latter is very unstable and decomposes on standing or gentle warming to give α-nitroisobutylene and N-(nitro-*t*-butyl)-hydroxylamine, which also decomposes on standing or heating. Thus, the net result of treating isobutylene with nitric oxide and then distilling the product is the formation of nitroisobutylenes (74%) and small quantities of substances having nitro-*t*-butyl groups joined to nitro, nitroso, nitrate ester, hydroxyl, hydroxylamino and oximino groups. It is suggested that the (nitro-*t*-butyl)$_4$$N_2O_2$ is representative of the unidentified unstable oils which have frequently been obtained by treating olefins with $N_2O_3$ or $N_2O_4$. A mechanism for the NO–isobutylene reaction is proposed.

In the past, the nature of the reaction between nitric oxide and olefins has been virtually unknown. There are about a dozen references in the technical literature suggesting the possibility of such a reaction, but the only workers to identify any products were Bloomfield and Jeffrey,[1] who obtained 1-nitrocyclohexene and cyclohexene pseudonitrosite from cyclohexene. As late as 1949, an authoritative text stated that reactions between nitric oxide and the normal ethylenic double bond did not occur.[2]

An extensive study of the nitric oxide–olefin reaction has recently been made in this Laboratory. This study established three general characteristics of the reaction. First, the reaction is initiated by nitrogen dioxide. Scrupulously purified nitric oxide can be stored in contact with liquid olefins for days without reaction, but in the presence of traces of $NO_2$, such as are usually present in nitric oxide, reaction occurs readily with many types of olefins and other hydrocarbons.[3] Second, the product of a nitric oxide–olefin reaction is usually a mixture of the crystalline pseudonitrosite (dimeric nitro nitroso adduct) and an unstable liquid mixture which will undergo a "fume-off" or low-order explosion upon attempted distillation. It was found that the decomposition of these liquids could be controlled by steam distillation or passage through a falling film still, but no means of fractionating any significant quantity without decomposition was discovered. Third, the distilled liquid reaction products consist mainly of mixtures of nitroölefins. For example, 1-octene gives 1-nitro-1-octene and 1-nitro-2-octene.[3] In general, the linear olefins give fair yields of both nitroölefins and pseudonitrosites, while the branched olefins give good total yields of nitroölefins but little pseudonitrosite.

It was evident, however, that any detailed understanding of the nitric oxide–olefin reaction would require considerably more information about the nature of the reaction products. The present investigation of the products from the nitric oxide–isobutylene reaction was undertaken in order to obtain such information.

Basically, this objective required that a detailed analysis be made on a complex mixture which was changing composition continually during the course of the analysis. In order to accomplish this, a large batch of nitric oxide–isobutylene reaction product was prepared and the stoichiometry of the reaction determined. The product was fractionated, mainly by distillations under mild conditions, until a large number of fractions representing individual compounds or simple mixtures had been obtained. Analysis of these then permitted a

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[1] G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 120 (1944).

[2] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," The Clarendon Press, Oxford, 1949, p. 213.

[3] C. A. Burkhard, J. F. Brown, Jr., C. S. Herrick, R. L. Myers and D. T. Hurd, Abstracts of Papers, 126th Meeting American Chemical Society, September 12–17, 1954, p. 42-O.

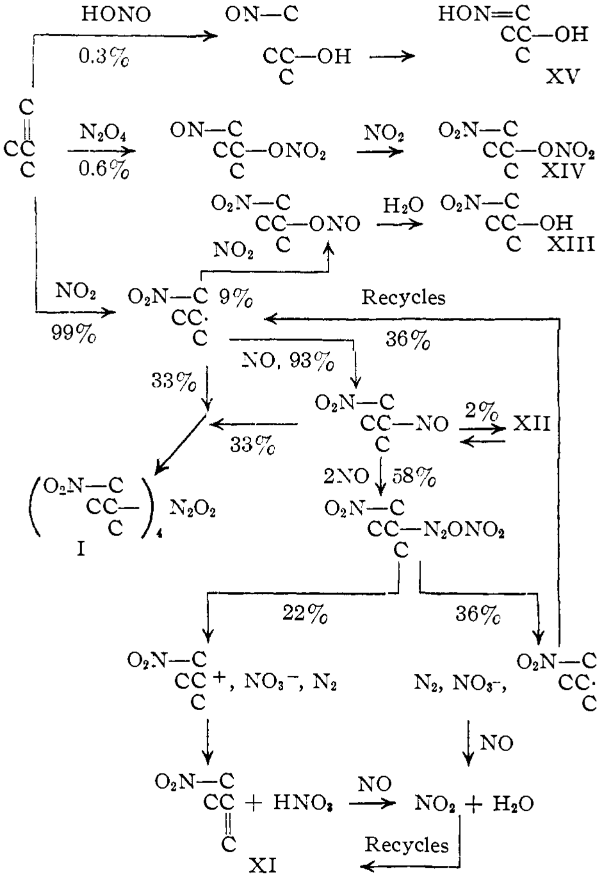

Fig. 1.—Proposed course of the reaction between nitric oxide and liquid isobutylene.

complete identification and estimation of the constituents of the separated fractions. During the fractionation, the refractive indices, infrared spectra and other properties of the mixtures were followed closely in order to detect changes in product composition as they occurred. The nature of the changes that the individual product constituents underwent under the conditions of the fractionation were then determined and used as the basis for estimates of the product composition at earlier stages. Finally, the resulting estimate of the initial product composition was checked by comparing the stoichiometric ratios which it predicted against those actually observed.

## Results

The results of this investigation are summarized in Table I. The composition "after fractionation" shows corrected analytical values for the aggregate composition of 45 liquid and solid organic fractions separate from the crude product. The composition "initially present" represents these values adjusted for all the changes that were observed to be occurring during the fractionation, while that at the "intermediate stage" represents a somewhat hypothetical product in which the decomposition of I, the most sensitive constituent, has gone to completion, while that of II, the next most sensitive, has not yet begun.

The major primary product of the reaction between nitric oxide and isobutylene is a thick, unstable oil having the partial structure (nitro-*t*-butyl)$_4N_2O_2$ (I) and hence referred to as the $R_4N_2O_2$ compound. Upon standing or gentle warming it undergoes elimination and decomposition to give α-nitroisobutylene (1-nitro-2-methyl-1-propene, X) and N-(nitro-*t*-butyl)-hydroxylamine (II).

TABLE I

ESTIMATED COMPOSITION OF THE PRODUCT FROM THE REACTION OF NITRIC OXIDE WITH EXCESS LIQUID ISOBUTYLENE AT 28°

| Compound | Initially present | Intermediate stage | After fractionation |
|---|---|---|---|
| (Nitro-*t*-butyl)$_4N_2O_2$ (I) | 66.4 | .. | .. |
| N-(Nitro-*t*-butyl)-hydroxylamine (II) | .. | 15 | 1.0 |
| O,N-Bis-(nitro-*t*-butyl)-hydroxylamine (III) | .. | .. | 0.4 |
| Nitromethane (IV) | .. | .. | 1.8 |
| Acetone (V) | .. | .. | 0.8 |
| Acetoxime (VI) | .. | .. | 0.2 |
| O-(Nitro-*t*-butyl)-acetoxime (VII) | .. | .. | 2.3 |
| Regenerated isobutylene | .. | .. | *ca.* 1 |
| 1,2-Dinitroisobutane (VIII) | .. | .. | 0.8 |
| Unidentified (IX) | .. | 2 | .. |
| α-Nitroisobutylene (X) | .. | 49 | 49.7 |
| β-Nitroisobutylene (XI) | 21.8 | 21.8 | 24.2 |
| Isobutylene pseudonitrosite (XII) | 2.1 | 2.1 | 2.7 |
| Nitro-*t*-butanol (XIII) | 8.8 | 8.8 | 8.8 |
| Nitro-*t*-butyl nitrate (XIV) | 0.6 | 0.6 | 0.6 |
| α-Hydroxyisobutyraldoxime (XV) | 0.3 | 0.3 | 0.3 |
| Liquids b.p. > 100° (1 mm.) (XVI) | .. | .. | 7.3 |

$$(C_4H_8NO_2)_4N_2O_2 \longrightarrow 3C_4H_7NO_2 + (C_4H_8NO_2)NHOH + (HNO)$$

However, as might be expected for a β-nitroalkylamine,[4] II is also rather unstable and undergoes three further types of decomposition under conditions like those employed in the fractionation. These may be termed disproportionation, dealdolization and reversion to starting materials.

The disproportionation occurs mainly when solutions of II are allowed to stand in the cold and gives the O,N-bis-(nitro-*t*-butyl)-hydroxylamine (III).

$$2(C_4H_8NO_2)NHOH \longrightarrow (C_4H_8NO_2)NHO(C_4H_8NO_2) + NH_2OH$$

Dealdolization occurs on heating and results in a cleavage of the II into nitromethane and acetoxime.

$$(CH_3)_2C(CH_2NO_2)NHOH \longrightarrow CH_3NO_2 + (CH_3)_2C{=}NOH$$

A similar reaction of the dialkylhydroxylamine III gives O-(nitro-*t*-butyl)-acetoxime (VII).

$$(CH_3)_2C(CH_2NO_2)NHO(C_4H_8NO_2) \longrightarrow CH_3NO_2 + (CH_3)_2C{=}NO(C_4H_8NO_2)$$

The reaction termed "reversion to starting materials" is a complex autocatalytic process which is induced by heating with nitrogen oxides. It appears to involve the steps

$$(CH_3)_2C(CH_2NO_2)NHOH + NO_2 \longrightarrow (CH_3)_2C(CH_2NO_2)NO \quad (XII)$$

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(4) A. Lambert and J. D. Rose, *J. Chem. Soc.*, 1511 (1947).

$$(CH_3)_2C(CH_2NO_2)NO \overset{\Delta}{\rightleftarrows} (CH_3)_2C{=}CH_2 + NO + NO_2$$

$$(CH_3)_2C(CH_2NO_2)NO + NO_2 \longrightarrow NO + (CH_3)_2C(CH_2NO_2)NO_2 \quad \text{(VIII)}$$

$$(CH_3)_2C{=}CH_2 + NO \longrightarrow N_2,\ (CH_3)_2C{=}CHNO_2, \text{ etc.}$$

The net result of this process is the formation of gaseous products such as isobutylene, nitrogen and nitric oxide, along with XII, VIII and considerable tar. The thermal dissociation and disproportionation of the pseudonitrosite, represented by the last three equations, was examined independently and found to give good yields of dinitroisobutane VIII, along with regenerated isobutylene, X, $N_2$ and NO.

Finally, it was noted that a little isomerization[5] of the α-nitroisobutylene (X) to the more volatile β-nitroisobutylene (XI) occurred during one distillation in which the base II was present.

By adjusting the values of the final composition listed in Table I for the observed conversions of II and IX into III–X and XVI, of X into XI and of I into II, X and probably IX, the composition listed in Table I as "initially present" was calculated. This composition predicts that the stoichiometric ratios of isobutylene consumed to nitric oxide consumed to nitrogen produced to water produced should be 1.00:2.54:0.58:0.063. The observed values, 1.00:2.50:0.60:0.064, are within experimental error of these and hence provide independent support for the estimated initial composition of the product.

## Discussion

**Relationship to Other Nitrations.**—It would appear from Table I that the products of the nitric oxide–olefin reaction are qualitatively, though not quantitatively, the same as those obtained in other olefin nitrations. Except for the hydroxylamine derivatives, all of the NO–isobutylene reaction products are representative of those obtained by treating isobutylene or other olefins with $N_2O_3$, $N_2O_4$ or nitric acid. Thus, the reaction of $N_2O_4$ with isobutylene in ether gave 54.9% VIII, 36.5% XIII, 2.3% XIV and 8.0% 1,3-dinitro-2-methylpropanol-2, which was stated to have resulted from the further nitration of XI.[6] In addition, the formation of X and of substances giving gaseous decomposition products during distillation was noted. The reaction of $N_2O_3$ with isobutylene in ether gave 24% XII, 14% XIII, 4% of the dinitro alcohol, a little VIII, and a large quantity of an unidentified oil which gave X on treatment with alkali.[6] α-Hydroxyisobutyraldoxime has not been identified in such reaction products, but the corresponding compound, 3-hydroxy-3-methyl-2-butanoxime, has been obtained from 2-methyl-2-butene,[7] and the nitrate ester of α-hydroxyisobutyraldoxime, isobutylene nitrosate, has been obtained by treating isobutylene with $N_2O_4$ in the absence of a solvent.[8] The latter reaction also gave VIII, XII, nitroisobutylene and a very unstable oil which produced diisobutylamine and β-hydroxyisobutylamine upon hydrogenation.

There are no prior reports of any $R_4N_2O_2$ compounds, but many preparations of materials having all of the attributes of I have been described in the literature. The addition of "nitrous fumes" or $N_2O_3$ to an olefin gives good yields of crystalline pseudonitrosites in only a few cases; usually, the major product is a viscous, unstable oil referred to as an "oily nitrosite" or "liquid pseudonitrosite." The fact that such oils form α-nitroölefins on standing or gentle warming has been recognized for those obtained from camphene,[9] β-pinene,[10] styrene,[11] indene,[12] 1-methylindene,[12] 1,1-diphenylethylene[13] and 1-arylcyclohexenes.[14] Since none of these oils were analyzed, none possessed the intense blue color characteristic of tertiary nitroso compounds in solution and no isolated pseudonitrosite has ever been observed to undergo a spontaneous elimination to α-nitroölefin, it seems likely that these oils were not simply different forms of the nitro-nitroso adducts but were instead $R_4N_2O_2$ compounds corresponding to the (nitro-*t*-butyl)$_4N_2O_2$ obtained from isobutylene.

**The $R_4N_2O_2$ Compound.**—The $R_4N_2O_2$ compound is thus of interest not only as the major primary product of the NO–isobutylene reaction but also as a possible example of an unrecognized major product in many $N_2O_3$- and $N_2O_4$–olefin reactions. The formation of such products means that mixtures of $NO_2$, olefin and NO can combine in the ratio 2:2:1, as well as in the known ratios 1:1:1 (giving pseudonitrosites) and 2:1:0 (giving nitrosates, nitro nitrites and dinitro compounds).

The available data do not seem to permit an unambiguous structural assignment to our $R_4N_2O_2$ compound, but a fairly good case can be made for the structure  $\begin{matrix}R\\RO\end{matrix}\!\!>NN<\!\!\begin{matrix}R\\OR\end{matrix}$, which we prefer. It is believed that the compound is formed by a combination of nitro-*t*-butyl radicals and NO in a 2:1 ratio. This could occur by the steps

$$C_4H_8 + NO_2 \longrightarrow \cdot C_4H_8NO_2 \equiv R\cdot$$

$$R\cdot + NO \longrightarrow RNO$$

$$RNO + R\cdot \longrightarrow R\dot{N}OR \longrightarrow (RNOR)_2$$

Several similar processes have been described in the literature. Gingras and Waters found that 2-cyano-2-propyl radicals could combine with NO in a 3:1 ratio to give the trialkylhydroxylamine and with aromatic nitroso compounds to give aryldialkylhydroxylamines.[15] On the other hand, the triarylmethyl radicals produced by reducing triphenylmethane dyes with zinc combined with NO in a 2:1 ratio, especially in the presence of excess reducing agent, giving bis-(triarylmethyl)-hydroxylamines.[16] A 2:1 adduct of triphenylmethyl radicals and NO was obtained once by Schlenk and

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[5] H. Shechter and J. W. Shepherd, THIS JOURNAL, **76**, 3617 (1954).

[6] N. Levy, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948).

[7] M. I. Konovalov, *J. Russ. Phys. Chem. Soc.*, **33**, 48 (1901); H. Weghofer, *Erdöl u. Kohle*, **4**, 1 (1951).

[8] A. Michael and G. H. Carlson, *J. Org. Chem.*, **5**, 1 (1940).

[9] W. Jagelki, *Ber.*, **32**, 1499 (1899).

[10] O. Wallach and E. Isaac, *Ann.*, **346**, 243 (1906).

[11] E. A. Sommer, *Ber.*, **28**, 1328 (1895).

[12] O. Wallach and E. Beschke, *Ann.*, **336**, 1 (1904).

[13] P. Lipp, W. Lüdicke, N. Kalinkoff and A. P. Petkoff, *ibid.*, **449**, 21 (1926).

[14] T. R. Govindachari, B. R. Pai, N. Arumugam and K. Nagarajan, *Chemistry & Industry*, 757 (1954).

[15] B. A. Gingras and W. A. Waters, *J. Chem. Soc.*, 1920 (1954).

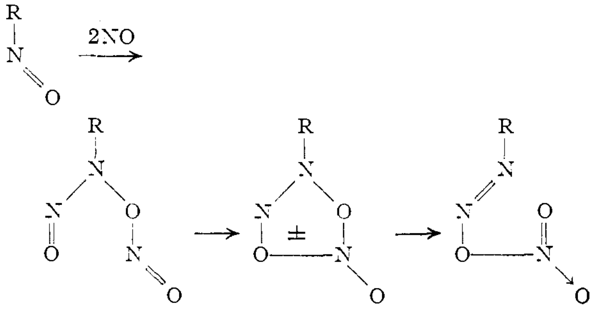
[16] E. Weitz, L. Müller and K. Dinges, *Chem. Ber.*, **85**, 878 (1952).

Mair.[17] The exact structure of none of these 2:1 adducts is known with certainty, but Schlenk and Mair's adduct is clearly different from the N,N(?)-bis-(triphenylmethyl)-hydroxylamine obtained from triphenylcarbinol and hydroxylamine.[18]

**Mechanism.**—The reaction between nitric oxide and isobutylene is remarkable in that under very mild conditions it gives a complex mixture of products, none of which bears much obvious structural relationship to the starting material, nitric oxide. In order to rationalize this fact, it seems desirable to set forth our conception of the mechanism of the reaction, even though much of the detailed evidence in its support must await the publication of our observations on other olefin nitrations. This mechanism, shown in Fig. 1, is based upon the following considerations.

First of all, the need for catalytic quantities of $NO_2$ in the reaction, the structures of the organic products and the similarity of those products to those obtained from $N_2O_3$- and $N_2O_4$-olefin reactions all suggest that these products must be formed *via* such species as $NO_2$, $N_2O_3$, $N_2O_4$, $HNO_2$, etc. The available information on the mechanisms of the reactions of these substances with olefins,[19] as well as our own studies of the stereochemistry of the nitric oxide-cyclohexene reaction products, indicates that products such as VIII, XII and XIII are mainly formed by free radical processes involving addition of $NO_2$ to the double bond, while products such as XIV and XV are formed by ionic processes involving attack of $NO^+$ on the double bond.

The central problem of the mechanism thus becomes that of accounting for the formation of $NO_2$ in the reaction medium. We have proposed[20] that this occurs *via* a diazo nitrate, as shown in Fig. 1. The formation of this diazo nitrate from the pseudonitrosite can be visualized as



We propose further that this intermediate diazo nitrate can decompose by either homolytic or heterolytic bond rupture. The homolytic process regenerates the original radical and hence accomplishes a simple disproportionation of the NO into $N_2$ and $NO_2$, which is a thermodynamically feasible reaction ($\Delta F = -59.6$ kcal.).

$$\begin{array}{c} R\cdot + 3NO \longrightarrow RN_2ONO_2 \\ RN_2ONO_2 \longrightarrow R\cdot + N_2 + NO_3\cdot \\ NO_3\cdot + NO \longrightarrow 2NO_2 \\ \hline 4NO \longrightarrow N_2 + 2NO_2 \end{array}$$

The heterolytic decomposition gives diazonium nitrate, thence carbonium nitrate, thence $\beta$-nitroisobutylene and nitric acid. It also accomplishes a conversion of NO to $NO_2$, but does so less efficiently than the homolytic route.

$$\begin{array}{c} NO_2 + C_4H_8 \longrightarrow R\cdot \\ R\cdot + 3NO \longrightarrow RN_2ONO_2 \\ RN_2ONO_2 \longrightarrow RN_2{}^+NO_3{}^- \longrightarrow R^+NO_3{}^- + N_2 \\ R^+NO_3{}^- \longrightarrow C_4H_7NO_2 + HNO_3 \\ HNO_3 + 0.5NO \longrightarrow 0.5H_2O + 1.5NO_2 \\ \hline C_4H_8 + 3.5NO \longrightarrow C_4H_7NO_2 + 0.5H_2O + 0.5NO_2 + N_2 \end{array}$$

These proposals are based upon the known reactions of nitrosobenzene with 2NO to give benzenediazonium nitrate,[21] of certain triarylmethyl radicals with 3NO to give triarylcarbonium nitrates[16] and upon the formation of $\beta$-nitrocarbonium ion rearrangement products in some other nitric oxide-olefin reactions.[20] Similar mechanisms involving intermediate diazo nitrates have been proposed to account for other unexpected products from the reactions of NO, NOCl and $N_2O_3$ with organic compounds[20] and for the nitric oxide-benzaldehyde reaction.[22]

## Experimental

All melting points are corrected, boiling points are uncorrected. Elementary analyses, done by Mrs. J. Northrop and Mrs. J. Martin, represent single determinations and are reliable to ±0.5%. The C.P. isobutylene and nitric oxide used were purchased from the Matheson Co. Analyses showed that the nitric oxide cylinders used contained 93.0-94.5% NO, 1.5-2.0% $N_2O$, 4-5% $N_2$ and traces of $NO_2$ while the isobutylene was free of non-olefinic constituents.

**General Characteristics of the Reaction.**—Preliminary experiments showed that the nitric oxide and isobutylene would react when the gases were mixed and held in a glass bulb at 24-35°, when the mixed gases were passed through an 18 × 1200 mm. glass tube at 30-60° or when gaseous nitric oxide was passed into liquid isobutylene under pressure. Induction periods were observed in the glass bulb runs unless the liquid products of a previous run were present; once started, the reactions proceeded with a reproducible velocity which was readily followed by the pressure drop. Starting with 200 mm. of isobutylene and 550 mm. of nitric oxide, the roughly third-order reactions had half-times of 5-11 minutes in the range 24-35°. In the 18 × 1200 mm. tube, with a 3:1 NO-isobutylene mixture flowing at 200 ml./min. at 50°, formation of liquid products occurred only in the last 200 mm. of the tube unless a few ml./min. of air were admitted along with the reactants to help catalyze the reaction. The product in each of these cases was a green oil which slowly evolved gas on standing at 0°. Attempts to fractionate these oils by distillation at 10 mm. or by chromatographing over alumina led to low-order explosions or "fume offs." The infrared spectra showed that the products from the reactions of isobutylene vapor contained oxidation products (formic acid, aldehydes and ketones) as well as nitration products (nitrate esters and nitro compounds), while the products from liquid isobutylene contained only nitration products. Effort was therefore concentrated on the latter reaction.

**Liquid Phase Reaction.**—The apparatus used was designed and operated by R. L. Myers and C. S. Herrick. It consisted of a one-liter stainless steel autoclave equipped

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[17] W. Schlenk and L. Mair, *Ber.*, **44**, 1169 (1911).

[18] A. Mothwurf, *ibid.*, **37**, 3150 (1904).

[19] A. I. Titov, *Zhur. Obshchei Khim.*, **16**, 1896 (1946); A. N. Baryshnikova and A. I. Titov, *Doklady Akad. Nauk S.S.S.R.*, **91**, 1099 (1953); H. Shechter and F. Conrad, THIS JOURNAL, **75**, 5610 (1953); J. C. D. Brand and I. D. R. Stevens, *Chemistry & Industry*, 469 (1956).

[20] J. F. Brown, Jr., Abstracts of Papers, 126th Meeting American Chemical Society, September 12-17, 1954, p. 43-O.

[21] E. Bamberger, *Ber.*, **30**, 506 (1897); F. H. Westheimer, E. Segel and R. Schramm, THIS JOURNAL, **69**, 776 (1947).

[22] L. P. Kuhn, Abstracts of Papers, 130th Meeting American Chemical Society, September 16-21, 1956, p. 16-O.

with a stirrer, cooling coil, gas inlet tube, reflux condenser, pressure regulating valve set to hold the internal pressure at 150 p.s.i. and tanks for collecting and measuring the reactant and product gases. In operation, the system was flushed with nitrogen, a weighed quantity of isobutylene admitted to the autoclave and nitric oxide passed in at a rate of 4.8 moles/hr. The product gases passed through the Dry Ice cooled reflux condenser and pressure regulating valve into accumulator tanks. At the end of the run, the apparatus was flushed with a known quantity of nitrogen and the total gaseous product analyzed; except for small quantities of unreacted nitric oxide, nitrous oxide and isobutylene, nitrogen was the sole gaseous product. Next, the autoclave was cooled to −50°, most of the liquid product poured out and the remainder rinsed out with acetone. The liquid product was allowed to come to room temperature, and then finally degassed *in vacuo* by pumping through a −78° trap; the resulting weight loss was taken to represent unreacted isobutylene. In this way, 281 g. (5.01 moles) of isobutylene was treated with 217 g. (7.23 moles) of nitric oxide at 28° to give 121 g. (2.16 moles) of unreacted isobutylene, 3.0 g. (0.10 mole) of unreacted nitric oxide, 48.1 g. (1.72 moles) of nitrogen and 325.7 g. of deep blue-green liquid reaction product, which consisted of a 295.9 g. main portion and 29.8 g. recovered from the acetone rinsings. Thus, the reaction could be estimated to have been proceeding under an NO partial pressure of 0.4 atm. and to have consumed 160 g. (2.85 moles, 57% conversion) of isobutylene and 214 g. (7.13 moles, 99% conversion) of nitric oxide.

**Distillation.**—The conversion of the crude product to distillates suitable for fractionation was carried out only on the main portion of the crude liquid reaction product. This was passed twice through a falling film still[23] maintained at 60° under 5 mm. pressure and the volatiles collected in −78° traps. The two portions of the distillate, 63.5 and 36.7 g., $n^{20}\mathrm{D}$ 1.4450 and 1.4516 on oil phases, both separated aqueous layers on warming to 0° (3.0 ml., $n^{20}\mathrm{D}$ 1.3425, and 0.1 ml., respectively). The aqueous layers were combined, saturated with sodium sulfate, and the 0.1 ml. of oil which separated combined with the other oils to give a total first distillate, which was a blue oil, 97.2 g., $n^{20}\mathrm{D}$ 1.4475. The residue was a viscous green liquid, 195.7 g., $n^{20}\mathrm{D}$ 1.4850. It became somewhat more mobile after standing nine days at 5° and was then passed through the still at 100° under 1 mm. pressure to give a second distillate (blue-green oil, 116.7 g., $n^{20}\mathrm{D}$ 1.4624) and a viscous brown residue (79.0 g., $n^{20}\mathrm{D}$ 1.4838). The latter was extracted with two 350-ml. portions of water, and the aqueous extracts saturated with salt and extracted with ether. This gave 8.2 g. of recovered water-soluble liquid, 12.1 g. of unrecovered water-soluble products and 58.7 g. of water-insoluble residue. An attempt to crystallize the latter from an ether–hexane solution at −78° was unsuccessful, and 5.9 g. of the material was accidentally lost during the solvent removal. The remaining 52.8 g. was distilled in two portions from an oil-bath; gas evolution was noted, but no explosion occurred. This gave a third distillate (43.9 g., $n^{20}\mathrm{D}$ 1.4638, 1.4650 and 1.4492 on successive thirds), a residual tar (5.5 g., b.p. >100° (1 mm.)) and a 3.4-g. loss, presumably due mostly to the gaseous products evolved. In all of these operations, all apparatus used was rinsed with ether after use in order to minimize handling losses.

**Fractionation Procedure.**—In fractionating the first three mixtures obtained from the crude product, effort was made to separate the less stable higher boiling products first, meanwhile accumulating the stabler lower boiling materials (indicated by *) for a single fractional distillation later.

The recovered water-soluble products were distilled to give (a), 5 ml., b.p. <85° (2.5 mm.); (b), 2.7 g., b.p. 85–96° (2.5 mm.); and 0.5-g. residue. Redistillation of (b) in a small molecular still gave (c) 0.6 g., trap condensate; (d) 1.9 g., partially solid; and 0.2 g. of residue. Crystallization of (d) from cold ether gave 0.7 g. of II and mother liquors (d′), $n^{20}\mathrm{D}$ 1.4698.

The first distillate from the falling film still was allowed to stand five days at 0° and then 3.8 g. of crystalline XII removed. Distillation of the mother liquors from a flask held at 35–40° gave distillate (e)*, 49.2 g., very pale blue, $n^{20}\mathrm{D}$ 1.443; and a deep blue residue, 44.2 g., $n^{20}\mathrm{D}$ 1.4591, which deposited 2.2 g. more XII on standing. Another distillation under the same conditions gave (f)*, 27.5 g., $n^{20}\mathrm{D}$ 1.462, and another deep blue residue which deposited 0.7 g. XII on standing. The residual liquid was combined with fraction (a) and the second falling film still distillate and carefully distilled, giving (g)*, 4.5 ml. trap condensate; (h)*, 77.0 g., b.p. 35–40° (4 mm.), $n^{20}\mathrm{D}$ 1.4651; (i), 11.0 g., deep blue, b.p. 40 (4 mm.)–40° (1.5 mm.) $n^{20}\mathrm{D}$ 1.4567; and (j) 47 ml., pale blue residue, $n^{20}\mathrm{D}$ 1.4571. On standing at 5°, (i) deposited 0.3 g. of XII, leaving liquid (i′).

The fraction (j) at this point presumably consisted mainly of II and XIII; a small sample which was not distilled immediately was examined after two weeks storage at 0° and found to be mostly extractable with water. Infrared examination of the water-insoluble portion, (j′) indicated the presence of III, IX, and XIV; VIII could not be detected. The distillation of (j) was commenced under 2 mm. pressure, using a 110° oil-bath. At first, distillation proceeded normally, giving a light blue distillate (b.p. 55° (2 mm.), probably XIII). Then the contents of the pot turned a deep blue-green and a vigorous evolution of gases commenced. The heating bath was removed, but the evolution of gases (estimated at 10 g. from weight loss) continued for several minutes, the pressure remained at 30–60 mm. despite continued pumping, and about 10 ml. of deep blue liquid distilled into the receiver. At the completion of this gas evolution, normal distillation was continued, giving fractions (k)*, 4.5 ml., trap condensate; (l), 17 ml., b.p. 55–75° (2 mm.), but including the deep blue liquid which distilled during the gas evolution; (m), 1.5 g., b.p. 65–85° (1 mm.), $n^{20}\mathrm{D}$ 1.4511; (n), 3.0 g., b.p. *ca.* 85° (1 mm.), $n^{20}\mathrm{D}$ 1.4532; and a clear brown residue, 9.5 g., $n^{20}\mathrm{D}$ 1.4865. On standing at 5°, (*l*) deposited 2.0 g. XII, m.p. 81–82°, leaving mother liquors (l′), $n^{20}\mathrm{D}$ 1.4464. A solution of (n) in ether deposited 1.5 g. of VIII on cooling to −78°, leaving liquid (n’).

The fractions (i′) and (l’) were combined and redistilled, giving (o)*, 1.0 ml., in trap; (p)*, 8 ml., b.p. 40–50° (4 mm.), $n^{20}\mathrm{D}$ 1.4594; (q)*, 7.5 ml., b.p. 50–61° (4 mm.), deep blue, $n^{20}\mathrm{D}$ 1.4483; (r) 9.0 g., b.p. 61 (4 mm.)–50° (1 mm.) almost colorless, $n^{20}\mathrm{D}$ 1.4438; and 0.5 g. of yellow-brown residue. Fraction (r) largely solidified to crystalline XIII after long standing at 5°.

All of the fractions marked * were combined to give a single lot, 173.0 g., $n^{20}\mathrm{D}$ 1.4557, which was distilled through a six-plate column by Mr. E. M. Hadsell. This gave seventeen fractions: (1) trap condensate, 2.0 g., $n^{20}\mathrm{D}$ 1.4127 after removing 0.5 g. water by drying over sodium sulfate; (2) forerun, 1.3 g., b.p. 44.5–47.5° (20 mm.), $n^{20}\mathrm{D}$ 1.4243; (3–4) β-nitroisobutylene (XI), 37.6 g., b.p. 47.5–50.0° (20 mm.), $n^{20}\mathrm{D}$ 1.4326–1.4342; (5–6) intermediate fractions, 22.0 g., b.p. 49 (19 mm.)–55° (11 mm.), $n^{20}\mathrm{D}$ 1.4370–1.4556; (7–14) α-nitroisobutylene (X), 89.8 g., b.p. 55 (11 mm.)–73° (23 mm.), $n^{20}\mathrm{D}$ 1.4695–1.4702; (15) 5.3 g., b.p. 73–86° (23 mm.), $n^{20}\mathrm{D}$ 1.4647; (16) hold-up; 5.0 g., $n^{20}\mathrm{D}$ 1.4472; (17) residue, 7.0 g., $n^{20}\mathrm{D}$ 1.4501; handling loss, 3.0 g. Infrared examination showed that fractions 3–13 contained only X and XI, while 16 and 17 were largely XIII. The blue color, presumably due to traces of XII in the charge, disappeared completely during the course of the three-day distillation. From the plots of b.p. and $n^{20}\mathrm{D}$ *vs.* weight distilled, it was concluded that fractions 1–17 contained 53 g. of XI, 101 g. of X, 2.0 g. of lower boiling material and 14 g. of higher boiling material.

The fractionation of the third crude distillate (43.9 g.) was done separately. Distillation through a short column gave (s), trap condensate, 3.2 g., two phases; (t) 3.8 g., b.p. 51–60° (19 mm.), $n^{20}\mathrm{D}$ 1.4514; (u), 8.4 g., b.p. 60–62° (19 mm.), $n^{20}\mathrm{D}$ 1.4590; (v), 8.2 g., b.p. 61.5° (18 mm.), $n^{20}\mathrm{D}$ 1.4615; (w), 7.9 g., b.p. 61.5–65° (18 mm.), $n^{20}\mathrm{D}$ 1.4614; and residue (x). Fractions (u), (v) and (w) consisted essentially entirely of X and XI. The constancy of their ratio through three successive fractions and the drop in refractive index during the fractionation were interpreted to mean that the known[5] base-catalyzed interconversion of X and XI was effecting a transformation of X to the more volatile XI during the distillation. Fraction (s) smelled distinctly of hydroxylamine, and its vapor gave a weakly alkaline reaction to test paper. It was neutralized with a little sulfuric acid and saturated with sodium sulfate to remove the water, giving (s′), 2.0 g., $n^{20}\mathrm{D}$ 1.3887. On cooling to −78°, a little VI, m.p. and mixed m.p. 59–61.5°, separated from fractions (t) and (u).

The distillation of (x) gave (y), trap condensate, 1.4 ml.; (z), 3.5 g., b.p. 50–65° (5 mm.), $n^{20}\mathrm{D}$ 1.4532; (aa), 3.5 g.,

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[23] N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1094 (1946).

b.p. 65–70° (5 mm.), $n^{20}D$ 1.4489; (bb), 3.5 g., b.p. 70 (5 mm.)–120° (1 mm.), $n^{20}D$ 1.4688; and 0.2 g. of residue. Drying (y) over sodium sulfate gave (y′), 1.0 g., $n^{20}D$ 1.4400. After removing analytical samples, fractions (z) and (aa) were first extracted with 6-ml. portions of water until no further volume change was notable, then shaken with sodium bisulfite solution to remove X and finally dried over sodium sulfate. The proportions of water-soluble, bisulfite-soluble and insoluble materials in (z) and (aa) were 34, 33 and 33%; and 27, 6 and 67%, respectively. About 60% of the water-soluble material was recovered by saturating the solutions with salt and extracting with ether, giving (cc), 1.2 g., $n^{20}D$ 1.4445, which was found to be >95% XIII. The combined insoluble oils, 2.9 g., were distilled through a Holzman column giving (dd), 0.18 g., b.p. 74.5–76° (5 mm.), $n^{20}D$ 1.4532; (ee), pure VII, 1.40 g., b.p. 77° (5 mm.), $n^{20}D$ 1.4460; (ff), 0.84 g., b.p. 77° (5 mm.), $n^{20}D$ 1.4465; and residue, 0.3 g. Finally, fraction (bb) was observed to have deposited some crystals after standing a month at 0°. These were extracted with aqueous sulfuric acid, the extracts made alkaline and extracted with ether to recover 0.4 g. of II, which was considerably less than the content indicated by the infrared spectrum to have been present originally. The acid-insoluble portion was distilled in a small molecular still to give (gg), 2.1 g.; this rapidly deposited crystals of III, 1.0 g., leaving (gg′), 1.0 g., yellowish oil, $n^{20}D$ 1.4655.

The net result of this fractionation was the isolation of all of the stable reaction products listed in Table I except for IV, V, XIV, and XV; and the separation of the crude reaction product into 50 organic fractions which represented either individual compounds or simple mixtures of substances having similar volatilities.

**Analytical Procedures.**—In general, qualitative analyses of the separate product fractions were based upon infrared spectra and the isolation of constituents, while the quantitative analyses were based upon the infrared spectra and other physical properties of the fractions.

First of all, the infrared spectra of authentic specimens of all of the stable product components were determined. The major features of most of these spectra have already been reported and discussed.[24] Next, qualitative analyses of the product fractions were made by comparing their spectra with those of the authentic materials. It was possible to identify all of the bands of the product spectra with bands of the appropriate intensity in the standards; thus the presence of appreciable amounts of stable products other than those listed in Table I could be eliminated.

In making quantitative estimates from the infrared spectra, use was made of the "internal standard" technique in most cases. This took advantage of the fact that most of the products were nitro-*t*-butyl derivatives and hence gave primary nitro $NO_2$ asymmetrical stretching bands near 6.42 $\mu$ which had molar extinction coefficients (in $CHCl_3$) near 550. Thus, the ratio of the intensity of any given band in the sample to that of the 6.42 $\mu$ band, divided by the corresponding ratio in the standard, gave the ratio of that constituent to the total primary nitro content of the sample. The relative content of $\alpha$-nitroisobutylene (X), which was present to a greater or lesser extent in most of the samples analyzed, was estimated from the intensities of its 6.58 and 7.37 $\mu$ bands relative to the 6.42 $\mu$ band, adjusted for the lower extinction coefficients (380 and 280, respectively) of these bands. This method was checked where possible by a comparison of the refractive index of the sample with those of the components. The estimated compositions of fractions (z) and (aa) were checked by selective extraction, as already noted, and that of (d′) was checked by an elementary analysis.

It was thus determined that the compositions of the various fractionated product mixtures were as follows: Fraction c, 0.6 g.: 0.1 X, 0.5 XIII. Fraction d′, 1.2 g.: 0.7 II, 0.5 XV. Fraction m, 1.5 g.: 0.5 VIII, 0.2 X, 0.3 XIII, 0.5 XIV. Fraction n′, 1.5 g.: 0.8 VIII, 0.2 XIII, 0.5 XIV. Fraction r, 9.0 g.: 0.7 VII, 7.0 XIII, 1.3 XIV. Low boilers from fractions 1–17, other than water, 1.5 g.: 0.6 IV, 0.6 V, 0.1 VI, 0.1 X, 0.1 XI. High boilers from fractions 1–17, 14 g.: 13.0 XIII, 1.0 XVI. Fraction s′, 2.0 g.: 1.6 IV, 0.2 V, 0.1 X, 0.1 XI. Fraction t, 3.8 g., 0.3 IV, 0.3 V, 0.2 VI (by isolation), 2.2 X, 0.8 XI. Fractions u, v, w, 24.5 g.: 18.4 X, 6.1 XI. Fraction y′, 1.0 g.: 0.3 IV, 0.5 X, 0.2 XI. Fraction z, 3.5 g.: 1.2 VII, 1.2 X, 1.1 XIII. Fraction aa, 3.5 g.: 2.4 VII, 0.2 X, 0.9 XIII. Fraction bb, 3.5 g.; 1.4 II, 1.2 III, 0.6 VII, 0.3 XVI.

The aggregate weights of the constituents of these mixtures, along with those of X and XI in fractions 1–17, of the II, VIII and XII separated in crystalline form during the fractionation, and of the residues and water obtained are listed in Table II as weights of compounds present "In Fractions."

**Treatment of Losses.**—The total weight of the water and the 45 liquid and solid organic fractions obtained up through fraction bb was 257.8 g. The remainder of the 295.9 g. of crude product taken for fractionation was accounted for by three types of losses. These were unrecovered water-soluble materials lost in the first extraction, 12.1 g.; gases evolved during degradative distillations, 13.4 g.; and mechanical losses due to handling, spillage, sampling, evaporation, etc., 12.6 g.

In order to obtain some understanding of the nature of the unrecovered water-soluble materials, known quantities of the water-soluble products II, XIII and XV were separately run through the water extraction and recovery procedure used. Each was recovered in about 65% yield, which was in line with a previous report of high losses during the extraction of isobutylene nitration products with water.[6] Since 8.2 g. of these products were recovered, this suggests that another 4.4 g. of the same materials were lost in the extraction. This 4.4 g. was assumed to represent 3.0 g. of XIII, 0.7 g. of II, 0.3 g. of XV and 0.4 g. of XVI, on the basis of the contents of these substances in the recovered water-soluble product after fractionation.

TABLE II

PRODUCTS OBTAINED BY FRACTIONATING 295.9 G. OF CRUDE REACTION PRODUCT

| Compound | In fractions, g. | Corrected weight, g. | Mole $C_4$-units |
|---|---|---|---|
| II | 2.8 | 3.6 | 0.0268 |
| III | 1.2 | 1.3 | .0110 |
| IV | 2.8 | 2.9 | ( .0475)[c] |
| V | 1.1 | 1.2 | .0207 |
| VI | 0.3 | 0.3 | .0041 |
| VII | 4.9 | 5.1 | .0585 |
| VIII | 2.8 | 2.9 | .0196 |
| X | 124.0 | 130.1 | 1.2869 |
| XI | 60.3 | 63.3 | 0.6261 |
| XII | 9.0 | 9.4 | .0710 |
| XIII | 23.0 | 27.1 | .2275 |
| XIV | 2.3 | 2.4 | .0146 |
| XV | 0.5 | 0.8 | .0078 |
| XVI | 17.7 | 19.0 | .1880[d] |
| Inorg.[a] | 5.1 | 25.0[b] | .... |
| $C_4H_8$ | ... | 1.5 | .0274 |
| | 257.8 | 295.9 | 2.59 |
| Losses | | | |
| $H_2O$ sol. | 12.1 | | |
| Gases | 13.4 | | |
| Mechan. | 12.6 | | |
| | 295.9 | | |

[a] Inorganic products: $H_2O$, $NH_2OH$, $N_2$, NO, etc. [b] Includes 5.4 g. corrected weight of recovered water, 7.7 g. $H_2O$ water-soluble materials not otherwise accounted for and 11.9 g. of gases not accounted for as isobutylene. [c] In totaling the $C_4$-units, the $C_3$-units in V, VI and VII were counted as $C_4$, while the $C_1$ of IV, obtained in nearly equivalent amount, was not counted. [d] Assumed to have average composition of a nitroisobutylene polymer.

An attempt was made to divide up the 12.6 g. of mechanical losses on the basis of the estimated compositions of the various intermediate fractions on which they were incurred. This indicated that the losses were rather uniformly distributed among the product constituents and hence that the most satisfactory procedure would be to assume that these

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[24] J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).

losses were proportional to the quantities of constituents found present in the 257.8 g. of recovered product fractions. By adding these distributions of the 12.6 g. of mechanical losses and the 4.4 g. of unrecovered water-soluble products to the quantities of constituents present in the recovered fractions, the corrected yield figures shown in the third and fourth columns of Table II were determined.

It was noted that these corrected yields of organic products accounted for 2.56 moles of isobutylene. Since the 295.9 g. of product fractionated had originally come from 2.59 moles of isobutylene (*i.e.*, 2.85 × 295.9/325.7) this left 0.03 mole unaccounted for. This was assumed to represent regenerated isobutylene, lost during the fractionation along with the other gaseous products. However, this yield figure for regenerated isobutylene must be taken only as an order of magnitude, since it represents a small difference between large quantities. The percentage yields listed in the last column of Table I are calculated directly from the molar yields in Table II.

(Nitro-*t*-butyl)$_4$N$_2$O$_2$ (I).—The 29.8-g. portion of the crude reaction product which was not fractionated was kept at 0° for 4 weeks and 0.6 g. of crystalline XII removed. A 14.7-g. portion of the remaining liquid was extracted with four 100-ml. portions of cold water to remove II, XIII and XV, once with a disodium phosphate solution and twice more with water. The remaining oil was devolatilized by very brief stirring at 50° under 0.5 mm. pressure to give 4.0 g. of a concentrate of I. This was a viscous, yellow-brown oil, $n^{20}\text{D}$ 1.4911, which was insoluble in solutions of sodium bisulfite or dilute acids. It was stored at −78° between analyses, the sequence of which was infrared spectrum, ultraviolet spectrum, elementary analyses and molecular weight; during this sequence sufficient decomposition occurred to lower the $n^{20}\text{D}$ to 1.4904.

The usual infrared analysis indicated that the sample contained about 13% X, 12% III, 2% XIV, 2% of a hydroxylic impurity, later identified as XIII, and possibly a little IX. The remaining 65–70% of the sample, namely, I, gave an infrared spectrum which was very similar to those of the other nitro-*t*-butyl derivatives. It showed the strong bands of a primary nitro compound at 6.43, 7.00 and 7.27 μ, but no bands indicative of OH, NH, olefinic CH, C═C, C═N or C═O groups, nor were there any ultraviolet absorption bands above 230 μ. Prominent characterizing infrared bands lay at 7.95, 8.25, 8.70, 10.97 and 13.55 μ. In chloroform solution, the intensities of the 6.43 and 6.58 μ bands ($E^{1\%}_{1\text{cm.}}$) were 40 and 4.9, respectively; on the basis of the previously indicated molar extinction coefficients, this indicated that for each C$_4$-residue in the sample there were 0.85 primary nitro group and 0.15 conjugated nitro group, or a total of 1.00 nitro group per C$_4$-residue. Since each of the identified contaminants contained one nitro group per C$_4$-residue, it follows that Compound I must also have contained one nitro group per C$_4$-residue.

The analysis (found: C, 41.3; H, 6.5; N, 17.7; mol. wt., benzene cryoscopic, 232) corresponded almost exactly with the formula $C_8H_{15}N_3O_5$ for the over-all mixture. Fortuitously, this turned out to be very close to the aggregate elementary composition of the identified contaminants, so that the calculated elementary composition of I would be little affected by small errors in the estimates of the impurity content. At any rate, by allowing for the known contaminants and for the uncertainties resulting from decomposition during analysis and the standard error in the analyses, it was concluded that the analyses fixed the composition of the I contained in the sample within the limits $(C_8H_{15-16}N_3O_5)_{1-2}$.

Assuming that I is not a free radical, the three permissible formulas within these limits are $C_8H_{15}N_3O_5$, $(C_8H_{15}N_3O_5)_2$ and $(C_8H_{16}N_3O_5)_2$. The last formula was supported by three other facts. First, the compound was known to contain 1.0 primary nitro group per C$_4$-residue and to give entirely α-nitroisobutylene and nitro-*t*-butyl derivatives on decomposition. This indicated that all of the C$_4$-residues were present as nitro-*t*-butyl ($C_4H_8NO_2$) groups. Second, the high index and viscosity of the compound, despite the absence of conjugated structures or hydrogen bonding groups such as OH or NH, supported the formulas of higher molecular weight. Third, as already noted, the over-all stoichiometry of the reaction was in support of the conclusion that the major initial product was $(C_8H_{16}N_3O_5)_2$.

The I had a half-life of about three weeks at 0° and a similar stability in dilute chloroform solution at room temperature. Successive infrared spectra on the solution showed the 6.43 μ band of the I decreasing and the 6.58 μ (and other) bands of the X increasing steadily. Complete decomposition resulted when an attempt was made to distil 2.0 g. of the concentrate in a molecular still under a high vacuum at 50°. Infrared analyses indicated that the products had the following compositions: trap condensate (1.2 g., $n^{20}\text{D}$ 1.4673), 1.1 g. of X, 0.1 g. of XI and XIII; liquid distillate (0.4 g.), 0.3 g. of II, 0.05 g. of X, 0.05 g. of XIV; residue, 0.3 g. The decomposition of the 1.3–1.4 g. of I contained in the sample thus gave 0.3 g. of II and 0.9 g. of X, in addition to that already present. The residue gave a little more X on further heating.

To confirm the identification of II in the liquid distillate, the portion remaining after analysis was divided into two 0.1–0.2-g. portions. Both were noted to become partly crystalline on standing a week at 0°. The solid from one was removed and recrystallized twice from chloroform–hexane to give 0.035 g. of II, m.p. and mixed m.p. 56.5–58°. The other was left at 0° for 6 months and then filtered. The solid, 0.11 g., was recrystallized from methanol and found to be III, m.p. 60–61.5°, mixed m.p. with II, 41–51°. The liquid contained VII; however, neither III nor VII could be detected in the original liquid distillate.

N-(Nitro-*t*-butyl)-hydroxylamine (II).—Recrystallization of the crude product from fractions (d) and (bb) from ether or methanol gave white crystals, m.p. and mixed m.p. 57–58°. The infrared spectrum showed the expected bands of primary nitro and hydroxylamino groups.[24]

*Anal.* Calcd. for $C_4H_{10}N_2O_3$: C, 35.8; H, 7.5; N, 20.9. Found: C, 35.9; H, 7.7; N, 21.1.

The compound was synthesized independently by shaking 2.0 g. of X with a solution of 2.0 g. of hydroxylamine hydrochloride and 0.8 g. of sodium hydroxide in 5 ml. of water for a few minutes. The odor of the X disappeared, and on cooling II crystallized out. Extraction of the mother liquors with ether and crystallization of the crude product from the extract at −78° gave 1.8 g. of crude II, m. 46–57°. After two recrystallization from methanol, 1.6 g. (60%) of pure II, m.p. 57–58.5°, was obtained.

The formulation of II as an N- rather than an O-alkyl hydroxylamine was based upon the infrared spectrum, which showed no NH$_2$ deformation band and upon its oxidation to the nitroso compound XII. One gram of II was dissolved in a solution of 2 ml. of concentrated sulfuric acid in 10 ml. of water at 0°, and a solution of 2 g. of sodium dichromate was added dropwise with stirring until the yellow color persisted. The mixture was allowed to stand an hour at 0° to permit the deep blue oil to dimerize and solidify. The crude solid, m. 74–78°, weighed 0.8 g. Recrystallization from carbon tetrachloride gave 0.7 g. (71%) of XII, m.p. 82.5–83.5°. The oxidation could also be effected by $N_2O_4$. When this was added to a solution of II in chloroform at 0°, the deep blue color of the nitroso compound XII appeared instantly. As more $N_2O_4$ was added, however, this pseudonitrosite was oxidized to the dinitro compound[25] and the color disappeared.

The pyrolysis of II was examined by a procedure which we have employed with a variety of unstable olefin nitration products. This consisted of heating 0.1–0.3 g. of the compound in a small test-tube whose bottom was in an oil-bath and whose sides were at room temperature. It was found that working with larger quantities frequently led to uncontrollable decomposition reactions. When 0.276 g. of II was thus heated an hour at 120°, there was a 15% weight loss, apparently due to the volatilization of IV and VI. The residual 0.234 g. of colorless liquid largely crystallized on cooling to give VI, m.p. and mixed m.p. 59–61°. This dealdolization of II to IV and VI appeared to be irreversible; when a mixture of IV, VI and piperidine was allowed to stand several days at room temperature, removal of the volatile reactants *in vacuo* left only a trace of residue, and this was completely unaffected by chromic acid.

The pyrolytic experiment was repeated using 0.148 g. of II, but this time several small (0.5–1.0-mg.) portions of fuming nitric acid were added as an NO$_2$ source. After each addition, a blue-green color appeared, and a steady evolution of gas began and continued for several minutes before subsiding. After an hour, further additions of the acid provoked no additional gas evolution; 3 mg. had been added in all. The tube then contained 0.047 of a brown oil;

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(25) A. Michael and G. H. Carlson, *J. Org. Chem.*, **4**, 169 (1939).

*i.e.*, 70% of the II had been converted to vapors and lost. The residual oil could not be crystallized from solution in a little methanol at −78°, even after seeding with VIII and II. Other strong acids produced no visible effects when added to hot II.

**O,N-Bis-(nitro-*t*-butyl)-hydroxylamine (III).**—The crude product from fraction (gg) was recrystallized from methanol to give large monoclinic tablets, m.p. 61–62.5°. The compound was insoluble in dilute acids, and the infrared spectrum indicated that the NH group was not hydrogen bonded (very sharp band of medium intensity at 3.07 μ). Otherwise, the infrared spectrum was quite similar to that of II.[24]

*Anal.* Calcd. for $C_8H_{17}N_3O_5$: C, 40.8; H, 7.2; N, 17.9. Found: C, 41.4, 40.4; H, 7.0, 6.9; N, 17.9.

The compound was synthesized independently by allowing a mixture of 0.37 g. of II, 2.0 g. of X and 0.01 ml. of triethylamine to stand overnight at room temperature. The amine and unreacted II were then extracted with dilute acid and the excess X evaporated *in vacuo*. Crystallization of the residue from methanol gave a 23% yield of III, m.p. and mixed m.p. 61–62°.

When 0.5 g. of III was heated in a bath at 180° for a few minutes (no discoloration), 0.2 ml. of distillate b. 103–130°, was obtained. This deposited some crystalline VI on cooling and left a liquid indicated by its infrared spectrum to be largely IV. The spectrum of the distillation residue indicated that it contained roughly equal amounts of VII and X.

**Low Boiling Products.**—Nitromethane (IV), acetone (V) and acetoxime (VI) were identified in the various cold trap condensates and fore-runs from their infrared spectra. Commercial samples were used for the infrared reference spectra and mixed m.p. determinations.

**O-(Nitro-*t*-butyl)-acetoxime (VII).**—The pure specimen obtained as fraction (ee) (b.p. 77° (5 mm.), $n^{20}_{\mathrm{D}}$ 1.4460) was a colorless liquid having a pleasant, somewhat camphoraceous odor, which showed the characteristic infrared bands of primary nitro and oxime ether groups.[24] The same material was synthesized independently by allowing a mixture of 3.65 g. (0.05 mole) of VI, 5.05 g. (0.05 mole) of X and 10 drops of triethylamine stand for three days at room temperature. The resulting mixture was extracted with dilute sulfuric acid and with strong sodium bisulfite solution, washed, dried and distilled to give 6.3 g. (72%) of VII, b.p. 77° (5 mm.), $n^{20}_{\mathrm{D}}$ 1.4460.

*Anal.* Calcd. for $C_7H_{14}N_2O_3$: C, 48.2; H, 8.1; N, 16.1. Found: C, 48.5, 49.0; H, 7.7, 8.1; N, 15.9.

**1,2-Dinitroisobutane (VIII).**—The solid obtained from fraction (n) was recrystallized from ether at −78° to give soft, waxy crystals, m.p. 53°, reported[6] m.p. 52–53°. The infrared spectrum[24] showed all the bands expected for this structure.

**Unidentified Products.**—Fraction (j′) showed a strong infrared band at 10.10 μ which was not present in the spectra of any of the redistilled product fractions or identified products. This band was presumed to indicate the presence of an unidentified unstable product component IX, which was probably another nitro-*t*-butyl derivative.

The portion of the crude reaction product which was allowed to stand four weeks at 0° contained some substance, possibly a nitrolic acid, which could be extracted with water or weakly alkaline buffers to give yellow or orange solutions. These solutions were reversibly decolorized by acidification with strong acids. The same behavior was shown by fractions (d′) and (s) (weak test), by specimens of X which had stood in glass bottles for several months (but not by fresh X) and by the crude products of the isobutylene vapor–nitric oxide and the isobutylene–$N_2O_4$ reactions (strong tests).

**α-Nitroisobutylene** (1-Nitro-2-methyl-1-propene, **X**).—The best specimen obtained, fraction 10, was a pale yellow oil, b.p. 64° (18 mm.), $n^{20}_{\mathrm{D}}$ 1.4702; reported[5] b.p. 72° (25 mm.), $n^{20}_{\mathrm{D}}$ 1.4710.

**β-Nitroisobutylene** (3-Nitro-2-methyl-1-propene, **XI**).—The best specimen obtained, fraction 3, was a colorless oil, b.p. 47.5–48.5° (20 mm.), $n^{20}_{\mathrm{D}}$ 1.4326; reported[5] b.p. 56° (25 mm.), $n^{20}_{\mathrm{D}}$ 1.4330.

**Isobutylene Pseudonitrosite, Bis-(1-nitro-2-nitroso-2-methylpropane) (XII).**—The five portions of XII recovered from the crude distillates (m.p. 81–82°) were recrystallized once from ether–acetone to give pure XII as large, clear, orthorhombic tablets, m.p. 85–86°, to a deep blue liquid; reported, m.p. 80–82°,[8] 81°,[6] 87–88°.[26] When dissolved in solvents at room temperature, the solutions were initially colorless, but turned deep blue within a minute or two.

The pyrolysis of XII was conducted as described for II. When 0.200 g. was held at 120°, there was a gradual evolution of gas and fading of the blue color. After 25 minutes, 0.153 g. of light yellow liquid, $n^{20}_{\mathrm{D}}$ 1.4548, remained. The composition estimated from the infrared spectrum was 70% VIII, 20% X and 10% uncertain. Crystallization of a solution of this pyrolysate in methanol at −78° gave 0.080 g. of VIII, m.p. 47–50°. Other runs showed that the composition of the pyrolysate was very little affected by 10° variations in the temperature, by carrying out the pyrolysis under nitrogen or by operating in an evacuated sealed ampoule. In the last case, a mass spectrometric analysis (by F. J. Norton) on the gaseous product showed that it was mainly isobutylene and nitrogen, with lesser quantities of nitric oxide and traces of nitromethane, acetone, etc.

In looking for other possible transformations of XII under the conditions of the product fractionation, a novel reaction with nitric acid was discovered. When 0.2 g. of XII was dissolved in 3 ml. of cold absolute nitric acid, a reddish-brown solution was formed, which soon changed to light yellow. Dilution and washing with water gave an oil which distilled completely to give pure XIV (by infrared), $n^{20}_{\mathrm{D}}$ 1.4500. However, this reaction was markedly inhibited by traces of water and did not occur at all with 70% nitric acid, so that it probably could not have occurred during the product fractionation.

**Nitro-*t*-butanol (XIII).**—This was obtained in >80% purity in fractions (c), (r), 16, 17 and (cc). The sample used for the infrared standard (b.p. 55° (2 mm.), m.p. 24°, $n^{20}_{\mathrm{D}}$ 1.4435) was prepared by the condensation of nitromethane with acetone.[27]

**Nitro-*t*-butyl Nitrate (XIV).**—The isolation of this compound was not undertaken since the infrared identification (in fractions (m), (n′) and (r)) was particularly unambiguous. The strong bands of nitrate esters[24] are detected readily even in dilute solutions, and in XIV there also occurs a rare type of splitting of the nitrate $NO_2$ symmetrical stretching band into a pair of bands at 7.70 and 7.91 μ. The sample used for the infrared standard was prepared by nitrating 1.00 g. of XIII with 4 ml. of absolute nitric acid in 17 ml. of chloroform for 15 minutes at 0°. Extraction with water, solvent removal, further repeated extractions with water and distillation in a small molecular still gave 0.39 g. of XIV, $n^{20}_{\mathrm{D}}$ 1.4500, which solidified completely upon storage in a 5° refrigerator; reported[6] $n^{20}_{\mathrm{D}}$ 1.449, m.p. 6°.

**α-Hydroxyisobutyraldoxime (XV).**—This was detected only in fraction (d′), which was estimated from the infrared spectrum to be a roughly 2:1 mixture of II and XV. However, since the "internal standard" method was not applicable to such a mixture, an elementary analysis was made, which indicated that the actual proportions were about 62 and 38%.

*Anal.* Calcd. for 38% $C_4H_9NO_2$ + 62% $C_4H_9N_2O_3$: C, 40.1; H, 7.5; N, 18.2. Found: C, 40.1; H, 6.7; N, 17.8, 18.2, 18.4.

The specimen used for the infrared standard ($n^{20}_{\mathrm{D}}$ 1.4847) was prepared by the alkaline hydrolysis of the corresponding nitrate ester.[28]

**Calculation of Initial Product Composition.**—In calculating the initial product composition from that of the fractionated products, the major assumption made was that all of the products II through X, along with a little XII, the regenerated isobutylene, and XVI came from I, mostly *via* II, by the paths already indicated in the Results section. This assumption is based upon the observed behavior of compounds I, II, III and XII under conditions like those used in fractionating the product mixture and upon a number of observations made during the fractionation. Two of these seem particularly significant to the assumption in point. First, even though some decomposition of I must have occurred during the falling film distillation at 60°, the first crude distillate contained less than a third of the

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(26) C. C. Price and C. A. Sears, THIS JOURNAL, **75**, 3275 (1953).

(27) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1948).

(28) V. N. Ipatieff and A. Solonina, *J. Russ. Phys. Chem. Soc.*, **33**, 496 (1901).

X ultimately obtained. This is shown by its refractive index and the indices of the mixed nitroisobutylene fractions (e and f) obtained from it. Second, even though all of the intermediate fractions gave high boiling residues upon redistillation, the original distillations of the 295.9 g. of crude product converted all but 5.5 g. to materials b. <100° (1 mm.). This indicates that there was very little or no formation of stable telomeric or condensed products in the original reaction.

The one point left in doubt concerns the origin of the acetone (V) which could have come either from the dealdolization of XIII or the dealdolization of II, followed by reaction of the resulting acetoxime with water and/or nitrous acid. We have arbitrarily selected the latter route in our calculation because of the greater instability of II.

Thus, the initial contents of XIII, XIV and XV were assumed to be the same as the corrected values for those in the final products. The content of XII was taken as the final amount less that formed in the distillation of fraction (j) and the initial content of XI taken as the final content less the 10% formed during the distillation which gave fractions (u-w). The resulting estimate of the initial product composition is shown in Table I.

This estimate means that in our reaction, which consumed 2.85 moles of isobutylene, the initial product mixture should have contained ($^1/_4$ × 1.89) moles of I, 0.62 mole of XI, 0.06 mole of XII, 0.25 mole of XIII, 0.02 mole of XIV and 0.01 mole of XV. The formation of such a mixture would require the consumption of 7.195 moles of NO and would produce at the same time 1.66 moles of $N_2$ and 0.18 mole of water. These are within experimental error of the observed values, namely, 7.13 moles of NO consumed, 1.72 moles of $N_2$ produced and 0.183 mole of $H_2O$ (3.0 g. × 325.7/295.9) removed from the first falling film distillate.

SCHENECTADY, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

# Rates of Acetolysis of *cis*- and *trans*-2-Nitroxycyclohexyl *p*-Bromobenzenesulfonates and *p*-Toluenesulfonates

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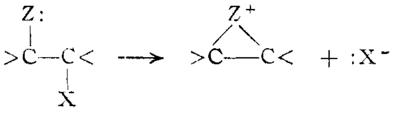
RECEIVED NOVEMBER 6, 1956

The rates of solvolysis of *cis*- and *trans*-2-nitroxycyclohexyl *p*-bromobenzenesulfonates and *p*-toluenesulfonates in acetic acid at 87.9° have been measured. Solvolyses with the *trans* isomers proceed at a rate less than twice that of the *cis* isomers, indicating that the nitroxy group is not an effective anchimeric group. The preparations of these arenesulfonates and of *cis*- and *trans*-1,2-cyclohexanediol mononitrates are described.

Winstein and his co-workers[1] have shown that rate enhancement occurs when a group on a $\beta$-carbon atom participates in solvolysis of another group on the $\alpha$-carbon atom, *viz.*



(1)

For example, the *p*-bromobenzenesulfonate (brosylate) of *trans*-2-acetoxycyclohexanol—where the acetoxy group is sterically situated so as to permit participation as in (1)—solvolyzes in acetic acid 630 times as rapidly as the *cis* isomer (where participation is sterically impossible). In similar fashion *trans*-2-bromocyclohexyl brosylate reacts 800 times as rapidly as the *cis* isomer. These groups therefore are effective participants. However, both *cis* and *trans*-cyclohexanediol dibrosylate react at about the same rate. Thus arenesulfonoxy groups are ineffective in this participation.

The rates of solvolysis of *cis*- and *trans*-2-nitroxycyclohexyl *p*-bromobenzenesulfonate and *p*-toluenesulfonate were determined in acetic acid at 87.9°, substantially as described by Winstein and co-workers.[1] The rate constants are given in Table I (average of two runs), along with data of Winstein for 2-acetoxycyclohexyl and 2-*p*-bromobenzenesulfonoxycyclohexyl brosylates and/or tosylates.

TABLE I

REACTION RATE CONSTANTS FOR ACETOLYSIS OF 2-SUBSTITUTED CYCLOHEXYL *p*-TOLUENESULFONATES AND *p*-BROMOBENZENESULFONATES

| 2-Substituent | Temp., °C. | $10^8k$, sec.$^{-1}$ |
|---|---|---|
| *p*-Toluenesulfonates | | |
| *trans*-Acetoxy | 99.7 | 20,000[a] |
| *cis*-Acetoxy | 99.7 | 53[a] |
| | 88 | *ca.* 18[b] |
| *trans*-Nitroxy[c] | 87.88 | 5.6 |
| *cis*-Nitroxy[c] | 87.88 | 3.9 |
| *p*-Bromobenzenesulfonates | | |
| Hydrogen | 74.95 | 15,000[d] |
| *trans*-Acetoxy | 74.95 | 3750[d] |
| *cis*-Acetoxy | 74.95 | 5.9[d] |
| *trans*-Bromobenzenesulfonoxy | 74.95 | 8.5[d] |
| | 88 | *ca.* 30[e] |
| *cis*-Bromobenzenesulfonoxy | 74.95 | 9.5[d] |
| | 88 | *ca.* 30[e] |
| *trans*-Nitroxy[c] | 87.88 | 13 |
| *cis*-Nitroxy[c] | 87.88 | 7.1 |

[a] Data of Winstein, Grunwald, Buckles and Hansen.[1a] [b] Estimated from data at 100° by assuming rate constant is one-third of value at 100°. [c] Present work; solution contained 0.05*M* sodium acetate and 0.36*M* water. [d] Data of Winstein, Grunwald and Ingraham.[1b] [e] Estimated from data at 75° by assuming rate constant is thrice that at 75°.

It will be noted that the *trans*-nitroxy compounds are less than twice as reactive as the corresponding *cis* compounds and that their rate constants for solvolysis are of the same order of magnitude as the *cis*-2-acetoxy compounds or the 2-arenesulfonoxy compounds. The results indicate clearly that effective participation of nitroxy does not obtain and that an intermediate such as I is not being formed in the rate-determining step in solvolysis. The effect of the nitroxy group appears limited to its inductive effect (similar to the *cis*-acetoxy and the arenesulfonoxy group), which thus slows down the rate significantly with respect to cyclohexyl

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[1] (a) S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, THIS JOURNAL, **70**, 816 (1948); (b) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).