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## Abstract

## Full Text

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# ON THE DIRECTION OF THE REACTION OF THE SIMPLEST $\alpha$-OLEFINS WITH LIQUID DINITROGEN TETROXIDE

*(Presented by Academician M. I. Kabachnik on January 25, 1964)*

The reaction of aliphatic unsaturated compounds with dinitrogen tetroxide has been studied by a number of authors ($^1$). The reaction of olefins (including isobutylene) with dinitrogen tetroxide in ether medium was investigated in especially great detail by Levy and Scaife ($^2$). All these authors showed that the interaction of olefins with dinitrogen tetroxide leads mainly to the formation of nitro compounds. Investigations carried out recently by Shenbrun, Gardner ($^3$), and by us ($^4$) have shown that isobutylene reacts with liquid dinitrogen tetroxide in the absence of a solvent or in nitric acid medium at low temperatures with the formation not of nitro compounds, but of $\alpha$-nitroisobutyric acid as the main final reaction product, which is readily hydrolyzed to $\alpha$-hydroxyisobutyric acid (yield 80%). The latter, in the presence of a catalyst (calcium phosphates), is smoothly dehydrated to methacrylic acid (yield more than 90%). The same authors ($^{3,4}$) proposed a reaction mechanism according to which the primary intermediate product of the reaction is isobutylene nitrosonitrate (see Scheme 1). Isobutylene nitrosonitrate I, through a series of transformations, leads to the formation of $\alpha$-nitroisobutyric acid V. Having shown that what takes place here is not a nitration reaction but a nitrosation reaction, the authors, however, did not substantiate the reaction mechanism experimentally.

**Fig. 1.** Characteristic region of the IR spectrum. Products of the reaction of isobutylene (a) and the dimer of isobutylene nitrosonitrate II (b) with dinitrogen tetroxide

In the present communication, results are given for the experimental substantiation of the mechanism of this reaction, as well as a generalization of the

Figure 2

Figure 2: Figure 2

mechanism using other simplest $\alpha$-olefins as examples. Besides isobutylene, the olefins used were propylene, $\alpha$-butylene, 2-methylbutene-1, 2-methylpentene-1, and methallyl chloride. The reaction of isobutylene with dinitrogen tetroxide was studied in especially great detail. The primary and intermediate products of the reaction of isobutylene with dinitrogen tetroxide were investigated spectroscopically and polarographically.

For the experimental study of the reaction mechanism, the postulated primary reaction products were specially synthesized: isobutylene nitrosonitrate II (in the form of a dimer), by the method proposed by Sidorenko ($^5$), and the tautomeric compound, the oxime of $\alpha$-nitroisobutyric aldehyde III, by the interaction of isobutylene with amyl nitrite and nitric acid according to Ipat' ev ($^6$). The presumed primary product of the reaction of isobutylene with dinitrogen tetroxide—isobutylene nitrosonitrate I (in monomeric form)—cannot be synthesized because of its extreme instability; therefore, its dimer II was used in the study.

In the reaction products obtained by the interaction of isobutylene with dinitrogen tetroxide, $\alpha$-nitroisobutyraldehyde IV, $\alpha$-nitroisobutyric acid (V), and the anhydride of $\alpha$-nitroisobutyric acid VII were detected and identified (see Scheme 1, Table 1). The same products were also found when dimer II was treated with dinitrogen tetroxide. The spectra obtained proved to be identical (Fig. 1, Table 1). Complete identity of the IR spectra of the reaction "oil" obtained in both cases makes it possible to conclude that the primary act in the interaction of isobutylene with dinitrogen tetroxide is a nitration reaction, i.e., the formation of isobutylene nitrosonitrate.

**Fig. 2.** Characteristic region of the IR spectrum. **a**—products of the reaction of dinitrogen tetroxide with an excess of liquid isobutylene; **b**—the same reaction products, heated to 80°; **c**—$\alpha$-nitroisobutyric acid V introduced into the reaction products

Dimer II is readily converted into monomeric form I on heating or on dissolution; in this process the monomeric form is distinguished by extreme instability and passes into the tautomeric form—oxime III. The dimer II synthesized by us, as shown polarographically (appearance of a characteristic wave with potential $\varphi_{1/2} = -0.97$ V at pH 2.06) and spectroscopically (appearance of a band at 1740 cm$^{-1}$), even at room temperature is converted at a high rate into the oxime of $\alpha$-nitroisobutyraldehyde III, as well as into $\alpha$-nitroisobutyraldehyde IV. Oxime III cannot be detected in the reaction products, since in the medium of dinitrogen tetroxide it is rapidly converted into aldehyde IV. When the oxime III specially synthesized by us was treated with dinitrogen tetroxide at low temperature, aldehyde IV and acid V were found in the reaction products, and

Fig. 3. Characteristic region of the IR spectrum of intermediate products (before hydrolysis) of the reaction of $\alpha$-olefins with nitrogen tetroxide: a—isobutylene, b—propylene, c—$\alpha$-butylene, d—2-methylbutene-1, e—2-methylpentene-1, f—methallyl chloride.

Figure 3: Fig. 3. Characteristic region of the IR spectrum of intermediate products (before hydrolysis) of the reaction of $\alpha$-olefins with nitrogen tetroxide: a—isobutylene, b—propylene, c—$\alpha$-butylene, d—2-methylbutene-1, e—2-methylpentene-1, f—methallyl chloride.

not even traces of unreacted oxime III were detected. This makes it possible to assert with confidence that aldehyde IV is formed from oxime III upon its further oxidation.

The products of the reaction of isobutylene with dinitrogen tetroxide contain a considerable amount of the anhydride of $\alpha$-nitroisobutyric acid VII. We have shown spectroscopically that the anhydride is formed from a compound having a characteristic absorption band near 1555 $cm^{-1}$. The reaction "oil" containing such an absorption band can be obtained only at low temperature ($-10°$) and with a short reaction time. The compound with an absorption band at 1555 $cm^{-1}$ can be specially obtained by treating liquid isobutylene with dinitrogen tetroxide at low temperature. Even at room temperature this substance rather rapidly passes into the anhydride of acid VII, as evidenced by the gradual decrease of the absorption band at 1555 $cm^{-1}$ and the increase of the absorption band at 1840 $cm^{-1}$, characteristic of anhydride VII. Polarographic analysis of this substance showed that it contains a nitro group. We proposed that the substance with the characteristic absorption band at 1555 $cm^{-1}$ may be the corresponding nitrolic acid, namely $\alpha$-nitro-$\alpha$-methylpropylnitrolic acid VI. A qualitative test (appearance of a red coloration with alkali) confirmed the presence of a nitrolic acid. Polarographic analysis of the reaction "oil" containing nitrolic acid VI, and of a specially synthesized product—6,6-nitroiminocyclohexane-1-carboxylic acid,

obtained by oxidation of cyclohexanol with nitric acid (7), at pH 10.5 showed identity of the half-wave potentials.

It was further shown that, in the formation of anhydride VII, in addition to acid VI, $\alpha$-nitroisobutyric acid V also takes part. Heating the "oil" containing acid VI did not lead to the formation of anhydride VII; however, the addition of acid V to the "oil" even at room temperature leads to the formation of anhydride VII, as evidenced by the appearance in the spectrum of the "oil" of an absorption band at 1840 $cm^{-1}$ (Fig. 2).

Fig. 3. Characteristic region of the IR spectrum of intermediate products (before hydrolysis) of the reaction of $\alpha$-olefins with nitrogen tetroxide: *a*—isobutylene, *b*—propylene, *c*—$\alpha$-butylene, *d*—2-methylbutene-1, *e*—2-methylpentene-1, *f*—methallyl chloride.

Upon hydrolysis, $\alpha$-nitroisobutyric acid V, $\alpha$-nitroisobutyric aldehyde IV, and the anhydride of $\alpha$-nitroisobutyric acid VII are readily converted into the final product of the reaction—$\alpha$-hydroxyisobutyric acid VIII.

The results of the experiments performed make it possible to propose the following mechanism for the reaction of isobutylene with liquid nitrogen tetroxide (Scheme 1).

Liquid nitrogen tetroxide, in the absence of a solvent (for example, ether), apparently reacts in the nitrosonitrate form ($NO^+$ and $NO_3^-$). In the interaction of isobutylene with liquid nitrogen tetroxide or with a mixture of nitrogen tetroxide and nitric acid, nitrosonitrate I is formed, which at low temperature can give dimer II. Nitrosonitrate I passes into its tautomeric form—the oxime of $\alpha$-nitroisobutyric aldehyde III—and into nitrolic acid VI. Oxime III is oxidized by an excess amount of nitrogen tetroxide to $\alpha$-nitroisobutyric aldehyde IV. Aldehyde IV under the reaction conditions is further oxidized to $\alpha$-nitroisobutyric acid V. Nitrolic acid VI with acid V gives the anhydride of $\alpha$-nitroisobutyric acid VII. Anhydride VII passes into acid V. Upon hydrolysis of IV, V, VII, and also VI, $\alpha$-hydroxyisobutyric acid VIII is formed—the final product of this reaction. Acetic acid IX is obtained upon hydrolysis of I, II, or V.

Next we investigated the products of the interaction of a series of $\alpha$-olefins with nitrogen tetroxide, followed by hydrolysis. In this process the corresponding hydroxy acids were isolated (in 50-70% yield based on reacted olefin), which in a number of cases were dehydrated to the corresponding substituted acrylic acids. The products obtained and their constants are given in Table 1. On the basis of the final reaction products, it may be assumed that the mechanism of interaction of the $\alpha$-olefins studied with nitrogen tetroxide is general. To confirm this assumption, it was···

**Table 1**

**Compounds obtained and their constants**

| Name of compound | Constants | Functional groups and bonds | Frequency of characteristic vibrations in the IR region, $cm^{-1}$ |
|---|---|---|---|
| **Interaction of isobutylene with nitrogen tetroxide at** $-5 \div 0°$; $V_{\mathbf{vol.}}$ **2-3 l/h** | **Interaction of isobutylene with nitrogen tetroxide at** $-5 \div 0°$; $V_{\mathbf{vol.}}$ **2-3 l/h** | **Interaction of isobutylene with nitrogen tetroxide at** $-5 \div 0°$; $V_{\mathbf{vol.}}$ **2-3 l/h** | **Interaction of isobutylene with nitrogen tetroxide at** $-5 \div 0°$; $V_{\mathbf{vol.}}$ **2-3 l/h** |
| Isobutylene nitrosonitrate II | M.p. 105° | $ONO_2NO$ | 16501550 |

| Name of compound | Constants | Functional groups and bonds | Frequency of characteristic vibrations in the IR region, $\text{cm}^{-1}$ |
|---|---|---|---|
| $\alpha$-Nitroisobutyric aldehyde IV | B.p. 48°/15; $d_4^{20} = 1.1730$; $n_D^{20} = 1.4220$ | $ONO_2C{=}O$ | 16501740 |
| $\alpha$-Nitroisobutyric acid V | M.p. 79° | $ONO_2C{=}O$ | 16501730–1725 |
| Anhydride of $\alpha$-nitroisobutyric acid VII | $d_4^{20} = 1.3930$; $n_D^{20} = 1.4438$ | $ONO_2C{=}OC{=}O$ | 16501840–18351730–1725 |
| $\alpha$-Hydroxyisobutyric acid VIII | B.p. 100°/5. M.p. 78° | OH | 3605 |
| Methacrylic acid X | B.p. 87.5°/20; $d_4^{20} = 1.0160$; $n_D^{20} = 1.4314$ | – | – |
| **Interaction of propylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **3-4 l/h** | **Interaction of propylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **3-4 l/h** | **Interaction of propylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **3-4 l/h** | **Interaction of propylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **3-4 l/h** |
| $\alpha$-Nitropropionic acid | B.p. 94°/3; $d_4^{20} = 1.3610$; $n_D^{20} = 1.4359$ | $ONO_2C{=}O$ | 16501725 |
| Lactic acid<br>Acrylic acid | Obtained as 90%<br>B.p. 58°/35; $d_4^{20} = 1.0497$; $n_D^{20} = 1.4162$ | $C{=}OOH$ | 17303605 |
| **Interaction of** $\alpha$**-butylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **2-3 l/h** | **Interaction of** $\alpha$**-butylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **2-3 l/h** | **Interaction of** $\alpha$**-butylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **2-3 l/h** | **Interaction of** $\alpha$**-butylene with nitrogen tetroxide at** $0 \div +15°$**;** $V_{\textbf{vol.}}$ **2-3 l/h** |
| $\alpha$-Nitrobutyric acid | B.p. 108–110°/6; $d_4^{20} = 1.2689$; $n_D^{20} = 1.4351$ | $ONO_2C{=}O$ | 16501730 |

| Name of compound | Constants | Functional groups and bonds | Frequency of characteristic vibrations in the IR region, cm$^{-1}$ |
|---|---|---|---|
| **Interaction of 2-methylbutene-1 with nitrogen tetroxide at** 0 ÷ +10° | **Interaction of 2-methylbutene-1 with nitrogen tetroxide at** 0 ÷ +10° | **Interaction of 2-methylbutene-1 with nitrogen tetroxide at** 0 ÷ +10° | **Interaction of 2-methylbutene-1 with nitrogen tetroxide at** 0 ÷ +10° |
| $\alpha$-Hydroxy-$\alpha$-methylbutyric acid | B.p. 109°/9; m.p. 69.2° | C=O | 1730 |
| $\beta$,$\beta$-Dimethylacrylic acid | B.p. 83°/8; $d_4^{20} = 0.9956$; $n_D^{20} = 1.4468$ | – | – |
| **Interaction of 2-methylpentene-1 with nitrogen tetroxide at** 0 ÷ +10° | **Interaction of 2-methylpentene-1 with nitrogen tetroxide at** 0 ÷ +10° | **Interaction of 2-methylpentene-1 with nitrogen tetroxide at** 0 ÷ +10° | **Interaction of 2-methylpentene-1 with nitrogen tetroxide at** 0 ÷ +10° |
| $\alpha$-Hydroxy-$\alpha$-methylvaleric acid | B.p. 127°/10; m.p. 37.3° | C=O | 1730 |
| 2-Methyl-3-ethylacrylic acid | $d_4^{20} = 1.0898$; $n_D^{40} = 1.4340$B.p. 92°/9; $d_4^{20} = 0.9751$; $n_D^{20} = 1.4513$ | – | – |
| **Interaction of methallyl chloride with nitrogen tetroxide at** 0 ÷ +15° | **Interaction of methallyl chloride with nitrogen tetroxide at** 0 ÷ +15° | **Interaction of methallyl chloride with nitrogen tetroxide at** 0 ÷ +15° | **Interaction of methallyl chloride with nitrogen tetroxide at** 0 ÷ +15° |
| $\beta$-Chloro-$\alpha$-hydroxyisobutyric acid | M.p. 105° | – | – |

A spectroscopic study of the reaction products (before hydrolysis) was carried out. As the results of the investigation showed, the external appearance of all spectra is identical (Fig. 3). These data agree well with the results of polarographic analysis of the reaction products carried out in alkaline medium (pH 11.2). On all polarograms, distinct waves were obtained with half-wave potentials belonging to the corresponding nitrolic acids ($\varphi_{1/2} = -0.51$—$-0.63$ V), $\alpha$-nitro acids ($\varphi_{1/2} = -0.94$—$-1.22$ V), and nitroaldehydes ($\varphi_{1/2} = -1.41 \div 1.65$ V).

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## CITED LITERATURE

1. N. Ya. Demyanov, K. V. Sidorenko, ZhRKhO, **41**, 832 (1909). A. Schärschmidt, T. Hoffmeier, Ber., **58**, 1047 (1937); A. Michael, G. H. Carlson, J. Org. Chem., **5**, 1 (1940).
2. N. Levi, C. W. Scaife, J. Chem. Soc., 1942, 52, 1946, 1093.
3. F. Schoenbrunn, J. Gardner, J. Am. Chem. Soc., **82**, 4905 (1960).
4. B. F. Ustavshchikov, M. I. Farberov, V. A. Podgornova, Neftekhimiya, **2**, 4, 592 (1962).
5. K. V. Sidorenko, ZhRFKhO, **38**, 955 (1906).
6. V. I. Ipat' ev, A. A. Solonina, ZhRFKhO, **33**, 496 (1901).
7. H. C. Godt, J. F. Quinn, J. Am. Chem. Soc., **78**, 1461 (1956).

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