



Generation of methylene by the liquid phase oxidation of isobutene with nitrous oxide

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ABSTRACT

The application of nitrous oxide as an alternative oxidant provides new opportunities for selective oxidation of olefins. Here, we studied for the first time the thermal oxidation of isobutene with N_2O in the liquid phase. The study revealed that the oxidation proceeds *via* 1,3-dipolar cycloaddition of N_2O to the C=C bond by two routes forming unstable 4,5-dihydro-[1,2,3]-oxadiazole intermediates. The main route (the contribution of 91%) includes the addition of the N_2O oxygen to the second carbon atom in olefin. In this case, the oxadiazole decomposes with the C–C bond cleavage yielding acetone, methylene ($:CH_2$), and N_2 . The methylene then readily reacts with isobutene and benzene (solvent). The minor route involves the addition of the N_2O oxygen to the first carbon atom and the oxadiazole decomposition with a hydrogen shift leading to isobutanal and N_2 .

The main distinctive feature of the studied reaction is the formation of methylene in high yield.

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1. Introduction

Selective oxidation of olefins to ketones or aldehydes remains one of the most challenging problems. For example, the well-known Wacker process is used for the production of only acetaldehyde or acetone *via* the liquid phase oxidation of ethylene or propylene, respectively, with oxygen in the presence of a homogeneous $PdCl_2/CuCl_2$ catalyst in the HCl medium.^{1,2} The disadvantages of the process include the formation of chlorinated by-products and acid wastes, corrosion activity of the catalyst, and difficult recovery and purification of the target products. A similar oxidation of other olefins proceeds less selectively.

The application of nitrous oxide (N_2O) as an alternative oxidant instead of molecular oxygen opens new opportunities for selective oxidation of olefins. In recent decades, an increased interest in this field was additionally stimulated by the necessity to utilize N_2O anthropogenic emissions, since nitrous oxide is considered as a strong greenhouse gas and ozone-depleting compound.^{3–7}

Generally, the oxidation of organic compounds with N_2O is thermodynamically favorable.⁸ In addition, according to thermodynamic calculation, a release of the O atom from N_2O is

energetically more profitable ($\Delta_r G^0_{298} = 30.5$ kcal/mol) than from O_2 ($\Delta_r G^0_{298} = 55.3$ kcal/mol).^{8,9} However, the N_2O molecule is kinetically rather stable to decomposition up to ~ 1000 °C due to the high activation barrier of this reaction (50–60 kcal/mol).¹⁰ So, the involvement of N_2O in oxidations commonly requires its activation by catalysts. Such heterogeneous catalysts have been found, for example, for the gas phase oxidation of benzene and other aromatic compounds to phenols,^{11–14} oxidation of methane^{15–19} and ethane^{20–22} to alcohols and aldehydes, and epoxidation of propylene and 1-butene.^{23–27} Complexes of metals are also able to catalyze, for example, the epoxidation of olefins^{28,29} and oxidation of alcohols to aldehydes and ketones with nitrous oxide.^{30–35} Meanwhile, rates of these liquid phase reactions are not sufficiently high.

Another possibility to involve N_2O in oxidations is based on its ability to react as a 1,3-dipole with various dipolarophils such as olefins and alkynes.^{36–38} Reactions of this type with olefins, which proceed thermally without a catalyst and give ketones and aldehydes, have been discovered more than 60 years ago.^{39,40} However, the new interest in such oxidations emerged only in early 2000s, when they were performed in the liquid phase at 423–553 K with a higher selectivity that often exceeded 90%.^{41–43}

The very high selectivity of such reactions is due to the fact that N_2O reacts only with the double bonds of olefins and is inert toward other bonds. According to experimental data^{39–44} and quantum-

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chemical modeling,^{44–46} the reaction proceeds by the non-radical mechanism including 1,3-dipolar cycloaddition of N₂O to the olefin double bond with the formation of unstable 4,5-dihydro-[1,2,3]-oxadiazole intermediate (Scheme 1). Its subsequent decomposition with the release of N₂ leads to ketone or aldehyde. Since in many cases the main oxidation products are ketones, reactions of this type were called the ketonization reactions.^{44,47}

Depending on orientation of N=N–O molecule relative to the double bond upon cycloaddition, the reaction can proceed by different routes. Besides, the route involving the cleavage of the C–C bond in the oxadiazole cycle (the cleavage route) is also an important feature of the reaction.^{39,43,44} Carbonyl product formed by this route contains fewer carbon atoms than the parent olefin.

We demonstrated earlier that the contribution of different reaction routes and, accordingly, the composition of the resulting products depend on the olefin structure.^{43,47,48} For example, for 1,2-disubstituted internal olefins, the contribution of the cleavage route to the total oxidation rate is much smaller as compared to mono-substituted terminal olefins.^{43,48} So, in the first case the main oxidation products are ketones, while 1-olefins give a mixture of ketone, aldehydes, and cyclopropane derivatives. Besides, in our previous work,⁴⁹ the effect of cis/trans isomerism on the mechanism of 1,2-disubstituted olefins oxidation with N₂O was revealed using experimental and theoretical approaches.

At the same time, the liquid phase oxidation of terminal olefins having the 1,1-disubstituted double bond by nitrous oxide has not been studied earlier. Therefore, the goal of our study was to clarify the reaction mechanism for this important class of olefins by the example of isobutene oxidation in terms of regioselectivity of N₂O cycloaddition to the double bond, the contribution of different reaction routes, and the composition of products by applying both experimental and quantum-chemical methods.

2. Results and discussion

2.1. Liquid phase oxidation of isobutene with N₂O

Liquid phase oxidation of olefins with nitrous oxide is carried out in the batch reaction system that includes liquid and gas phases. In the case of olefins having different physical properties (boiling point, saturated vapor pressure, solubility, etc.), their amounts in the liquid phase, where the reaction proceeds,^{41,42} will differ even under similar conditions (temperature, pressure, etc.). Thus, it is usually impossible to compare quantitatively the data on oxidation of different olefins, particularly, their reactivity toward N₂O.

However, the oxidation of butene isomers, which differ in the double bond position and substitution degree but have close physical properties, can be performed under similar reaction conditions. This makes it possible to make a correct comparison of the results and reveal the effect of olefin structure on the reaction mechanism and composition of products.

In our earlier work, the liquid phase oxidation of 1-butene and 2-butene with nitrous oxide in a benzene solution at 453–513 K was studied in detail.⁴⁸ In the case of 2-butene, which contains the internal 1,2-disubstituted double bond, the reaction runs mostly without cleavage of the C–C bond in the oxadiazole intermediate

and results in the formation of methyl ethyl ketone (MEK) as the main product (~84 mol %) and a small amount of isobutanal (~3.3 mol %).⁴⁸ The reaction with the cleavage yields acetaldehyde (~7.4 mol %) and ethylidene (:CH–CH₃). Ethylidene then reacts with 2-butene and benzene to form the oxygen-free products: 1,2,3-trimethylcyclopropane (~3.9 mol %) and 7-methylcyclohepta-1,3,5-triene (~0.2 mol %), respectively. The total fraction of carbonyl products is ca. 95 mol %.

Upon oxidation of 1-butene having the terminal mono-substituted double bond, the reaction without cleavage yields MEK (~33.8 mol %) and butanal (~12.8 mol %).⁴⁸ The reaction with the cleavage gives propanal (~30 mol %) and methylene (:CH₂), which reacts with 1-butene and benzene to produce ethylcyclopropane (~13 mol %) and cycloheptatriene (~9 mol %). The total fraction of carbonyl products in this case is ca. 76 mol %.

Table 1 illustrates the results of isobutene oxidation under the same conditions. Similar to 1-butene, isobutene contains the terminal double bond. However, this bond is 1,1-disubstituted owing to the presence of two CH₃ substituents at the second carbon atom. One can see that the oxidation of isobutene yields only two carbonyl compounds: isobutanal (**1**) (~5 mol %) and acetone (**2**) (~50 mol %); their total fraction among all the products is ca. 55 mol %. In addition, 1,1-dimethylcyclopropane (**3**) (~26 mol %) and cycloheptatriene (**4**) (~16 mol %) are among the reaction products. As in the case of 1- and 2-butenes,⁴⁸ the ratio of products is virtually independent of temperature.

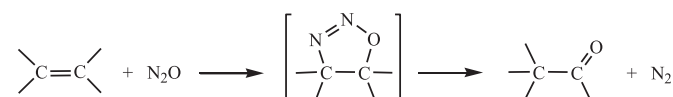
The composition of products formed upon oxidation of isobutene (Table 1) agrees well with the mechanism of 1,3-dipolar cycloaddition of N₂O to the double bond of olefins.^{39,44–46} Scheme 2 shows that, depending on the regioselectivity of the cycloaddition, two isomers of oxadiazole intermediate (**I** and **II**) can form in this case. Respectively, two main reaction routes (R_I and R_{II}) can be implemented.

The formation of isobutanal **1** in the course of reaction shows that intermediate **I** decomposes only without cleavage of the C–C bond in the oxadiazole cycle (pathway 1). This pathway is accompanied by the release of N₂ molecule and transfer of H atom to the adjacent carbon atom (the 1,2-hydrogen shift or H-shift). Similar to monosubstituted terminal olefins,^{39,43,44} the oxidation of isobutene does not produce formaldehyde **5**, which could be expected in the case of cleavage of the C–C bond in intermediate **I** (pathway 2). Quantum-chemical simulation of the reaction between 1-hexene and N₂O also indicates that the contribution of such pathway to the total oxidation rate for terminal olefins should be very small (~0.25%).⁴⁴

In intermediate **II**, oxygen adds to the second carbon atom, which has two methyl substituents. Hence, in this case, the C=O group can be formed only *via* the transfer of the CH₃ group to the adjacent C atom in the C–C bond (the 1,2-CH₃ shift or CH₃-shift) (pathway 3) or *via* the cleavage of this bond (cleavage pathway 4). The presence of acetone **2** as the main carbonyl product shows that intermediate **II** decomposes mostly with the cleavage of the C–C bond (pathway 4). A possible reason is that the CH₃-shift is quite a slow process. According to experimental data on the oxidation of 2-butene,⁴⁸ the rate of CH₃-shift is more than an order of magnitude lower as compared to the H-shift. Thus, in the case of isobutene, the contribution of the pathway with the CH₃-shift (pathway 3), which should give methyl ethyl ketone **6**, is very small. This agrees with the absence of MEK among the products.

As seen from Scheme 2, the cleavage pathway 4 should yield methylene (:CH₂) together with acetone. Owing to the high reactivity typical of carbenes,^{50,51} methylene then reacts with isobutene (reaction 5) and benzene (reaction 6) to produce 1,1-dimethylcyclopropane **3** and cycloheptatriene **4**, respectively.

Quantum-chemical calculations (see Section 2.2) predict that



Scheme 1. The formation and decomposition of 4,5-dihydro-[1,2,3]-oxadiazole intermediate upon N₂O interaction with olefins.

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