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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.

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 N_2O 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 N_2 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 monosubstituted 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 N_2O 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 N_2O cycloaddition to the double bond, the contribution of different reaction routes, and the composition of products by applying both experimental and quantum-chemical methods.

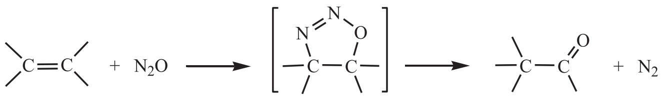
2. Results and discussion

2.1. Liquid phase oxidation of isobutene with N_2O

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 N_2O.

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–CH_3). 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. %.



Scheme 1. The formation and decomposition of 4,5-dihydro-[1,2,3]-oxadiazole intermediate upon N_2O interaction with olefins.

Upon oxidation of 1-butene having the terminal monosubstituted 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 (:CH_2), 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 CH_3 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 N_2O 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 N_2 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 N_2O 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 CH_3 group to the adjacent C atom in the C–C bond (the 1,2-CH_3 shift or CH_3-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 CH_3-shift is quite a slow process. According to experimental data on the oxidation of 2-butene,[48] the rate of CH_3-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 CH_3-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 (:CH_2) 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

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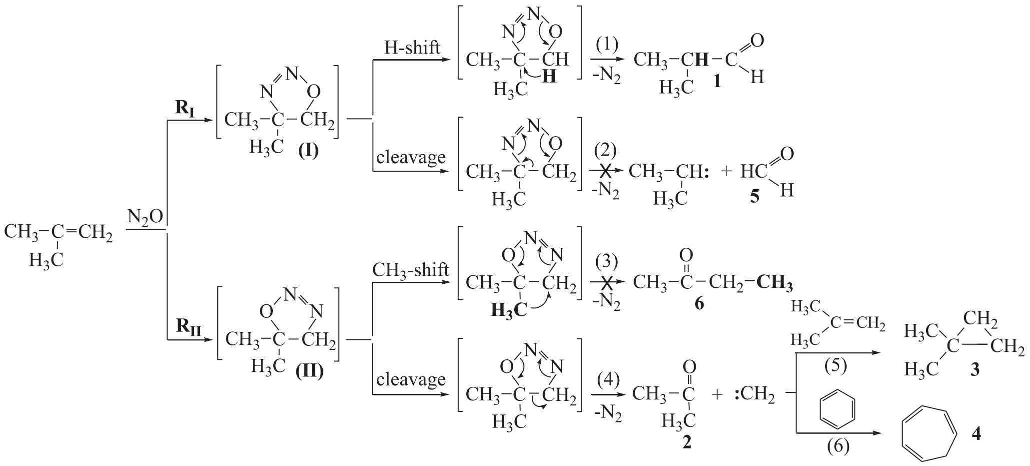
Table 1
Effect of reaction time and temperature on isobutene oxidation with N_2O.[a]

Run	*T, K*	t, h	Isobutene conversion, X_R, %	N_2O conversion, X_{N_2O}, %	Reaction rate, *r*, mmol/L·h	Distribution of products in the liquid phase, n_i, mol %				
						1	**2**	**3**	**4**	Other
1	453	12	1.5	1.0	2.0	3.8	47.3	30.1	16.4	2.4
2	473	12	7.3	4.8	9.7	5.0	50.8	28.5	14.2	1.5
3	493	3	5.6	3.7	31	5.4	49.2	27.0	16.8	1.6
4	493	6	11.8	7.9	32	5.1	50.5	25.2	16.7	2.5
5	493	12	22.6	15.1	30	5.1	52.0	23.1	17.1	2.7
6	513	2	10.6	7.3	85	5.9	51.6	23.0	16.3	3.2
Averaged concentrations						5.1	50.2	26.2	16.3	2.3

[a] Reaction conditions: 100 ml reactor, $N^0_R = 0.08$ mol, $N^0_{N_2O} = 0.12$ mol, 50 ml benzene.



Scheme 2. Mechanistic scheme for isobutene oxidation with N_2O.

the pathway with the cleavage leads to the primary formation of diazomethane (CH_2N_2) instead of methylene. A similar diazo-mechanism of the cleavage was proposed earlier for the oxidation of monosubstituted terminal olefins.[39,44] Since diazomethane is very unstable and should rapidly decompose into methylene and nitrogen under the reaction conditions,[44] it is difficult to identify experimentally an active fragment that is formed upon cleavage.

Note that, according to Scheme 2, the total fraction of products **3** and **4**, which are formed upon addition of methylene, should be equal to the fraction of acetone **2** among the reaction products (~50 mol %, Table 1). However, the experimental fraction of the addition products is somewhat lower (~42.5 mol. %). A similar discrepancy was observed earlier for the oxidation of 1-butene.[48] This can be related to additional consumption of methylene in side reactions, the products of which are not detected by the analysis.

Data of Table 1 allow a more detailed analysis of the reaction mechanism. Thus, the ratio of rate constants k_3 and k_4 for methylene interaction with isobutene and benzene (Scheme 2) can be estimated from the fractions of 1,1-dimethylcyclopropane **3** (n_3, Table 1) and cycloheptatriene **4** (n_4) among the products and from the initial amounts of olefin ($N^0_{\text{i-But}}$, mol) and benzene (N^0_B) using the following equation:

$$\frac{k_3}{k_4} = \frac{n_3 \cdot N^0_B}{n_4 \cdot N^0_{\text{i-But}}} \qquad (1)$$

Equation (1) gives the averaged ratio $k_3/k_4 \sim 11$. A close ratio (~10) was obtained earlier for the interaction of methylene with 1-butene and benzene.[48] This indicates a much higher activity of carbene toward olefin.

One can see from Scheme 2 that the contribution of route R_{II} ($F_{R_{II}}$), resulting in the formation of intermediate **II**, to the total oxidation rate can be calculated from the fractions of isobutanal **1** and acetone **2** formed by routes R_I and R_{II}, respectively:

$$F_{R_{II}} = \frac{n_2}{n_1 + n_2} \qquad (2)$$

The calculation using the averaged data of Table 1 gives $F_{R_{II}} = 91\%$. Upon oxidation of monosubstituted terminal olefins, quite a high contribution of a similar route is also observed. For propylene it is equal to 70%, while for 1-butene, 1-hexene and 1-octene, $F_{R_{II}}$ is 83, 79 and 81%, respectively.[48] Hence, the addition of N_2O oxygen to the second carbon atom in the double bond of terminal olefins is energetically more favorable. This agrees with the results of quantum-chemical simulation.[44,46] In particular, a theoretical contribution of route R_{II} for 1-hexene is 75%,[44] which is close to the experimental value.

Such regioselectivity of N_2O cycloaddition may be related to the orienting effect of electron-donor alkyl substituents at the double bond in terminal olefin, which should shift electron density to the first carbon atom.[44,52] So, the oxygen atom in N_2O molecule, on which the negative charge is mostly located,[36,44,46] should preferentially be added to position 2. For isobutene, which has two methyl substituents at the second carbon atom, such effect should be more pronounced as compared to monosubstituted olefins, which agrees with experimental data.

In the case of isobutene, route R_{II} yields intermediate **II**, which decomposes only with the cleavage of the C–C bond (cleavage pathway 4, Scheme 2). Therefore, the contribution of the cleavage

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route (F_{cleav}) i-C_4H_8 + N_2O → [**II**] → **2** +:CH_2 + N_2 to the total oxidation rate is equal to that of route R_{II} ($F_{R_{II}}$, Eq. (2)), i.e. is also 91%. This value is much higher than F_{cleav} for linear internal olefins and monosubstituted terminal olefins, where a similar intermediate can decompose both with and without the cleavage of the C–C bond. For example, the contribution of the cleavage route is 4.2% for cis-3-heptene,[49] 13.5% for trans-3-heptene,[49] 8% for 2-butene and 2-pentene (mixtures of cis/trans isomers),[48] and 38% for 1-butene.[48] In distinction to these olefins, in the oxidation of isobutene the major part of reacting molecules is cleaved. Evidently, this difference is also related with specific features of isobutene structure and reaction mechanism, namely, with the presence of the 1,1-disubstituted C=C bond in its composition and a hindered CH_3-shift.

A comparison of data on isobutene oxidation (Table 1) with the data reported in[48] shows that the structure of butene isomers also affects their reactivity toward N_2O. The reaction rate (r) under similar conditions and, accordingly, the reactivity decrease in the following order: 1-butene > 2-butene > isobutene. For example, at 473 K the oxidation rates for the listed isomers are, respectively, 26.4, 17.9 and 9.7 mmol/L•h.

The lower reactivity of isobutene may also be attributed to the presence of the 1,1-disubstituted double bond, namely to the electronic effects of two electron-donor methyl substituents at the double bond on the N_2O cycloaddition. The apparent activation energy for isobutene oxidation (28 kcal/mol) calculated from the Arrhenius plot (Fig. 1) is substantially higher than that for 1-butene and 2-butene (21 and 22 kcal/mol, respectively).[48]

For the synthesis of carbonyl compounds, the route with the cleavage during the oxidation of olefins with N_2O is an undesirable process that decreases the reaction selectivity. Nevertheless, in the case of isobutene, where this process is most intensive, it can be of special interest for methylene generation. Methylene, similar to other highly active carbenes, is employed in organic synthesis.[50,51,53] In particular, the addition of carbenes to the double bonds of olefins is widely used for obtaining cyclopropane derivatives. The most used and simple method for methylene generation is based on thermal, photo- or catalytic decomposition of explosive and toxic diazomethane (CH_2N_2). However, depending on conditions, its decomposition can yield triplet or singlet methylene. At the same time, exactly the singlet methylene is the most suitable species for cyclopropanation due to stereospecificity of its addition to the double bond.

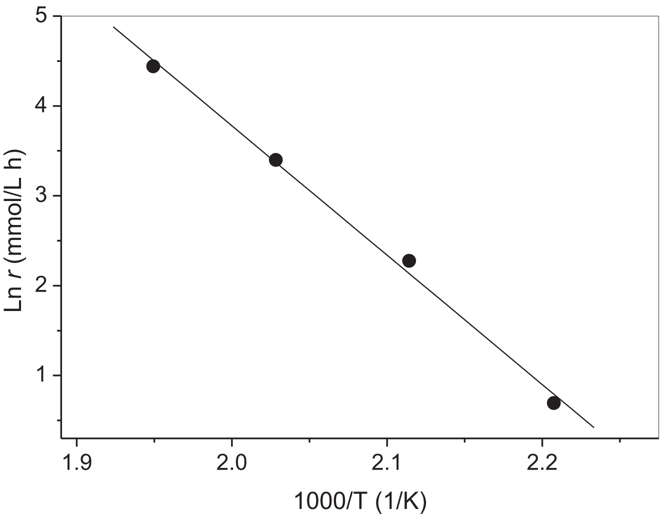

Fig. 1. The Arrhenius plot for isobutene oxidation with N_2O (according to data of Table 1).

As the ground state of olefins and N_2O is singlet, methylene that is formed upon oxidation of terminal olefins with the cleavage is likely to be in the singlet state, too. Thus, these reactions may be of interest for *in situ* generation of singlet methylene from simple and stable compounds. In the case of isobutene oxidation, this method gives an especially high yield of the active carbene.

Evidently, the use of the indicated method for methylene generation has some limitations. Organic compounds suitable for the addition of methylene generated by this method should be thermally stable under the reaction conditions and inert to N_2O. Such substrates can be represented, for example, by alkanes and compounds with aromatic rings. If olefins are used for the addition, they should preferably have a lower reactivity toward N_2O in comparison with isobutene.

Nevertheless, we believe that in some applications the isobutene oxidation by N_2O can be used as a source of methylene. In this case, selectivity for the addition products will depend on the concentration ratio of organic substrate and isobutene and also on their reactivity toward methylene. Thus, to increase selectivity for such products, the oxidation of isobutene with N_2O should be carried out in a solution of organic substrate used for methylene addition.

To check the applicability of this method for the insertion of methylene into C–H bonds of alkanes, we performed an additional experiment on the oxidation of isobutene with N_2O in a solution of n-hexadecane at 523 K for 24 h. Under these conditions, the isobutene conversion was 95%. The liquid phase products were acetone and isobutanal obtained in a ratio of 10:1 (the isobutene oxidation products), and also the products of methylene reactions with isobutene (1,1-dimethylcyclopropane) and n-hexadecane (methylhexadecanes and n-heptadecane).

Selectivity of methylene addition to n-hexadecane and isobutene was ~60 and ~40%, respectively. After distillation of volatile products, n-hexadecane contained ~20 mol % of methylhexadecanes and ~4 mol % of n-heptadecane (See the Supplementary file). Such mixture of isomers can be used as a retention time standard for chromatography.

In order to rationalize the experimental results and elucidate details of the reaction mechanism, quantum-chemical calculations of the reaction routes for isobutene interaction with N_2O were performed. The obtained results are presented in the next section.

2.2. Quantum-chemical study of the reaction mechanism

The elementary steps of the N_2O reaction with isobutene were simulated using the CBS-QB3 method. This method was successfully applied for studying the N_2O interactions with cis- and trans-isomers of 3-heptene and other olefins reported in our previous paper.[49] It was shown that the distribution of products observed experimentally for the gas phase oxidation of cyclohexene with nitrous oxide at 598–723 K quantitatively agrees with theoretical calculation. For the liquid phase reactions, a good qualitative agreement was observed between theory and experiment.

The theoretical method applied here also assumes that all the reactions occurred in the gas phase. This strongly simplifies the simulation while retaining good agreement with experimental data. The E_a and ΔH_r values (Table 2) were calculated at 298.15 K and pressure 1 atm. Quantum-chemical simulation revealed that, similar to other olefins,[44–46] in the first step of the reaction 4,5-dihydro-[1,2,3]-oxadiazole (OD) is formed *via* 1,3-dipolar cycloaddition of N_2O to the isobutene double bond. Two ways of cycloaddition and, respectively, two reaction paths are possible. The oxygen atom of N_2O can add either to the first carbon atom in the double bond of isobutene (path I) or to the second one (path II)

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Table 2
Calculated activation energies and enthalpies for the gas phase oxidation of isobutene with N_2O (T = 298.15 K, pressure 1 atm; **1, 2, 5–8** – the reaction products, see Scheme 2, Fig. 2, and the text).

Path number	Reaction	E_a, kcal/mol	ΔH_r, kcal/mol
(I)	$i\text{-}C_4H_8 + N_2O \rightarrow$ OD-I	27.1	−7.7
(II)	$i\text{-}C_4H_8 + N_2O \rightarrow$ OD-II	25.8	−9.1
(1)	OD-I → **1** + N_2	17.5	−58.3
(2)	OD-I → **5** + **7**	22.9	+17.1
(3)	OD-II → **2** + **8**	22.8	+5.9
(4)	OD-II → **6** + N_2	27.7	−62.8

giving, respectively, OD-I or OD-II intermediates (see Fig. 2). In the second step the oxadiazoles decompose, yielding the reaction products.

A comparison of the calculated activation energies for two ways of N_2O cycloaddition (27.1 and 25.8 kcal/mol, Table 2) shows that path II is preferential. Assuming that the ratio of paths I and II is determined by the reaction kinetics, i.e. by the probability of passing the activation barrier, the calculation predicts the following ratio of OD-I and OD-II concentrations under standard conditions:

$$\mathrm{OD{-}I/OD{-}II} = k_{\mathrm{I}}/k_{\mathrm{II}} = \exp(-\Delta E_a/\mathrm{RT}) \approx 0.1 \qquad (3)$$

In addition, the OD-II intermediate is thermodynamically more stable than OD-I isomer: the difference between enthalpies of formation for these isomers is 1.4 kcal/mol. Hence, main products of the reaction observed in experiment should be formed *via* further transformations of exactly the OD-II intermediate.

The main decomposition path for OD-I intermediate (Fig. 2) involves a hydrogen shift and gives isobutanal **1** and nitrogen (path 1, $Ea = 17.5$ kcal/mol). Decomposition of OD-I intermediate with the cleavage of the C—C bond leading to formaldehyde **5** and 2-diazopropane **7** (path 2) is also possible. However, the contribution of such reaction should be very small due to a higher activation barrier ($E_a = 22.9$ kcal/mol). The theoretical fraction of formaldehyde **5** among all carbonyl products does not exceed 0.001%, which agrees with the experimentally observed absence of this product.

Owing to the structural features of OD-II intermediate, it cannot be involved in decomposition *via* the 1,2-hydrogen shift. Accordingly, this intermediate can decompose only *via* the cleavage of C—C bond yielding acetone **2** and diazomethane **8** (path 3, $E_a = 22.8$ kcal/mol) or *via* the transfer of methyl group over the C—C bond yielding methyl ethyl ketone **6** and nitrogen (path 4, $E_a = 27.7$ kcal/mol). However, the reaction with the 1,2-alkyl shift is also hindered by a higher activation barrier. As a result, a theoretical ratio of the fractions of products **6** and **2** (n_6: n_2) is only 0.03.

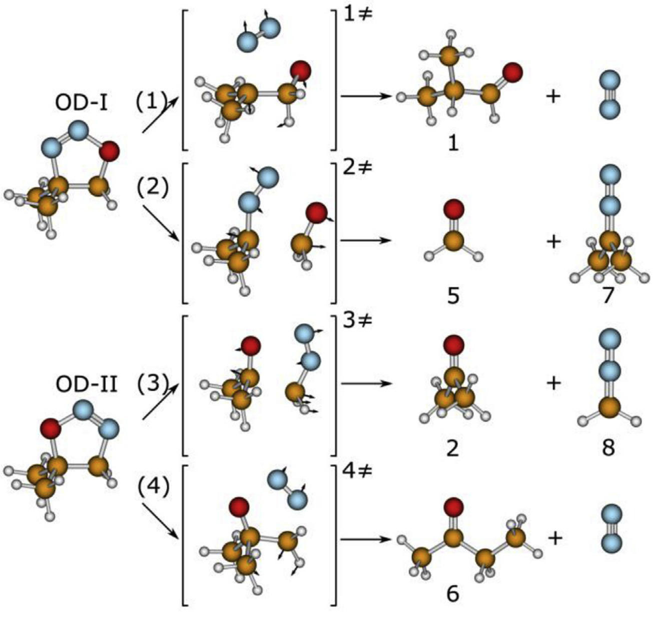

Fig. 2. Possible routes of isobutene oxidation with N_2O. The structures of activated complexes are shown in square brackets.

Thus, theory predicts the most favorable reaction route to be the formation of OD-II intermediate and its decomposition with the cleavage of the C—C bond. A theoretical contribution of this route, which is determined primarily by the OD-I/OD-II ratio, is ~90%, as in experiment. This provides a clear explanation of the products distribution found experimentally.

According to calculations, the cleavage should liberate a very unstable diazomethane **8**. The preferable pathway of its further transformation includes decomposition under the reaction conditions with the formation of singlet methylene and nitrogen.

Data of Table 2 indicate that exactly the first reaction step, the formation of 1,2,3-oxadiazole intermediate, should be the rate-limiting one due to its higher activation barrier. This agrees with the quantum-chemical simulation of N_2O reactions with other olefins.[45,46] Thus, for the main route of isobutene oxidation ($i\text{-}C_4H_8 + N_2O \rightarrow$ [OD-II] → **2** + **8**), the activation energy of the first step is 25.8 kcal/mol, which is higher as compared to the second step (22.8 kcal/mol). Note that the activation energy of this route (25.8 kcal/mol) calculated for the gas phase reaction cannot be compared directly with the experimental value for the liquid phase reaction (28 kcal/mol). Nevertheless, in this case the indicated values are quite close.

3. Conclusions

Isobutene is a valuable component of the C_4 fraction, which is formed as a by-product of oil refining *via* cracking or pyrolysis. A detailed experimental and quantum-chemical study of isobutene reaction with nitrous oxide, which was performed for the first time in this work, extends knowledge on the mechanism of 1,3-dipolar cycloaddition of N_2O to olefins and possible routes of their oxidative transformation by this promising alternative oxidant.

The experimental study on the liquid phase oxidation of isobutene with N_2O at 453–513 K revealed that the main route of the reaction involves the addition of N_2O oxygen to the second carbon atom in the double bond with the formation of 4,5-dihydro-[1,2,3]-oxadiazole intermediate, which decomposes with the cleavage of the C—C bond in the oxadiazole cycle. The obtained results along with earlier published experimental data on the oxidation of 1-butene and 2-butene were used to elucidate the effect of substitution degree of the double bond in butene isomers on their reactivity toward N_2O, the contribution of different reaction routes and the composition of products. In distinction to 2-butene and 1-butene, where contribution of the cleavage route is 8 and 39%, respectively, the main part of isobutene molecules (~90%) undergoes the cleavage. Therewith, the reactivity decreases in the following order: 1-butene > 2-butene > isobutene. It was found that these pronounced distinctions are related to the presence of the 1,1-disubstituted double bond in isobutene. It has been shown that electron-donor alkyl substituents at the double bond in terminal olefins exert an orienting effect on the regioselectivity of N_2O cycloaddition. As a result, the N_2O oxygen is preferentially added to the second carbon atom.

The quantum-chemical simulation (the CBS-QB3 method) revealed that the reaction actually proceeds *via* the 1,3-dipolar cycloaddition mechanism and confirmed a very high contribution of the cleavage route for isobutene. In particular, detailed

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information on the structure of 1,2,3-oxadiazole intermediates, the way the C=C bond is cleaved, and the products distribution was obtained. A good quantitative agreement between theory and experiment was achieved.

The oxidation of isobutene with the cleavage yields acetone and the highly reactive singlet methylene, which can readily react with the C–H bonds of alkanes or unsaturated bonds of aromatic compounds and olefins to form cyclopropane derivatives in the latter case. The reaction of isobutene with N_2O is an unusual example of *in situ* generation of methylene with a high yield *via* the oxidation of a simple and accessible compound.

4. Experimental section

4.1. Chemicals

Isobutene (99%) and benzene (99.9%) were purchased from Sigma-Aldrich. Medical grade nitrous oxide (99.8%) was obtained from Cherepovets Azot Plant.

4.2. Typical procedure for isobutene oxidation

The liquid phase oxidation of isobutene with nitrous oxide was carried out in a benzene solution using a 100 ml Parr reactor equipped with a stirrer. In a typical experiment, benzene (50 ml) was loaded to the reactor. To remove air, the reactor was purged with helium and then filled with 0.12 mol isobutene and 0.08 mol N_2O by the method described elsewhere.[48] The reactor was heated at a 6 K/min ramp to the required reaction temperature (453–513 K) and kept for 2–12 h under stirring (300 r.p.m.). An additional experiment on the oxidation of isobutene (0.05 mol) with N_2O (0.3 mol) in a solution of n-hexadecane (20 ml) was performed using similar procedure at 523 K for 24 h.

After termination of the reaction, the reactor was cooled to room temperature. The composition of the gas phase (N_2O, N_2, O_2, CO, CO_2) was analyzed by gas chromatography (GC) using a TCD and a column packed with Porapak Q. N_2 was the only gaseous product, whose amount corresponded to that of the carbonyl products formed in the liquid phase. The N_2O conversion was calculated by the equation:

$$X_{N_2O} = \frac{N_{N_2}}{N^0_{N_2O}} \cdot 100\ (\%) \tag{4}$$

where N_{N_2} is the amount of nitrogen formed (mol); $N^0_{N_2O}$ is the initial amount of N_2O (mol).

Then, the pressure was slowly released and the liquid phase was analyzed by the ^1H and ^{13}C NMR methods. ^1H and ^{13}C NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, with a Bruker Avance spectrometer. Quantitative ^{13}C NMR relative intensity measurements were made with inverse gated proton decoupling and long relaxation delays (30–60 s). Spectral data for isobutene and the reaction products were as follows:

Isobutene: ^1H (ppm): 1.56 (6H, t 1.2 Hz), 4.60 (2H, septet 1.2 Hz); ^{13}C (ppm): 24.02 (2C, CH_3), 110.96 (1C, CH_2), 141.94 (1C, C).

Isobutanal (**1**): ^1H (ppm): 0.82 (6H, d), 1.99 (1H, m), 9.32 (1H, d 1.1 Hz); ^{13}C (ppm): 15.37 (2C, CH_3), 41.10 (1C, CH), 203.05 (1C, -CHO).

Acetone (**2**): ^1H (ppm): 1.55 (6H, s); ^{13}C (ppm): 30.14 (2C, CH_3), 204.4 (1C, CO).

1,1′-Dimethylcyclopropane (**3**): ^1H (ppm): 0.14 (4H, s), 0.93 (6H, s); ^{13}C (ppm): 11.54 (1C, C), 14.08 (2C, CH_2), 25.55 (2C, CH_3).

Cycloheptatriene (**4**): ^1H (ppm): 2.11 (2H, t), 4.76 (2H, br.s), 6.08 (2H, dt), 6.47 (2H, t); ^{13}C (ppm): 28.29 (1C, CH_2), 120.75 (2C, CH), 126.96 (2C, CH), 131.28 (2C, CH).

The isobutene conversion (X_R) was calculated from the amount of the reaction products in the liquid phase that formed from isobutene. The liquid phase obtained after the oxidation of isobutene with N_2O in n-hexadecane solution was additionally analyzed by GC using a capillary column (SE-52, 50 m, 0.2 mm) and FID. Other details of experiments were given earlier.[48]

4.3. Quantum-chemical methods

The exploration of possible reaction pathways of isobutene oxidation with nitrous oxide were carried out assuming gas-phase conditions. Reactions rates were estimated using Transition State theory. Potential Energy Surfaces (PESs) of relevant reaction steps were constructed at the Density Functional Theory (DFT) level using the B3LYP functional.[54] Kinetic control of the reaction means that activation energy of the preferred path is lowest. These gas-phase activation energies were calculated using CBS-QB3 quantum chemical model[55] that was applied in our previous work.[49] Detailed discussion of the accuracy of this model with respect to the reactions similar to ones considered here is given elsewhere.[44,49] All calculations were performed with the Gaussian 09 software.[56] Calculations were performed at the Siberian Supercomputer Centre SB RAS. Visualization of the results was performed using the MOLDEN program.[57]

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.05.022.

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