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PII: S0040-4020(16)30226-5

DOI: [10.1016/j.tet.2016.03.084](https://doi.org/10.1016/j.tet.2016.03.084)

Reference: TET 27624

To appear in: *Tetrahedron*

Received Date: 28 January 2016

Revised Date: 11 March 2016

Accepted Date: 24 March 2016

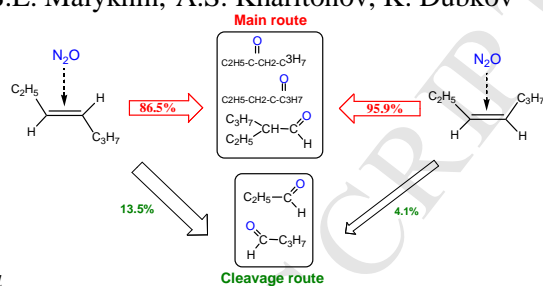
Please cite this article as: Ivanov D, Babushkin D, Semikolenov S, Malykhin S, Kharitonov A, Dubkov K, Effect of *cis/trans* isomerism on selective oxidation of olefins with nitrous oxide, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.03.084.

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Graphical Abstract

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ARTICLE INFO

Article history:

Received

Received in revised form

Accepted

Available online

Keywords:

Olefins

Cycloaddition

Isomers

Nitrous oxide

Oxidation

ABSTRACT

Liquid phase oxidation of olefins with nitrous oxide is a promising synthetic route to ketones. The effect of *cis/trans* isomerism on the reactivity of olefins towards N₂O and on the reaction mechanism was studied for the first time using 3-heptene oxidation as an example. Our experimental study revealed that *cis*- and *trans*- isomers of 3-heptene have similar reactivity and yield the same set of products. However, the *cis/trans* isomerism of the olefin has a pronounced effect on the reaction route involving the cleavage of the initial C=C bond and, accordingly, on the products ratio. The yield of ketones is lower for the *trans*-isomer due to higher contribution of the cleavage route.

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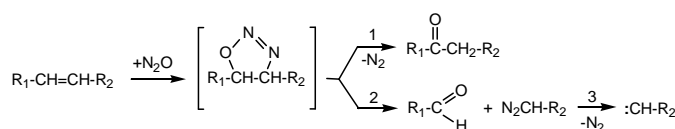
1. Introduction

The development of more efficient and environmentally acceptable methods for producing ketones and aldehydes remains an important task of modern chemistry. In the last decades, nitrous oxide (N₂O) has attracted growing attention as a selective oxygen donor for both catalytic¹ and non-catalytic^{2,3} partial oxidation of various hydrocarbons into valuable oxygenated products.

In particular, recently it was shown that the thermal liquid phase oxidation of various olefins with nitrous oxide (the so-called ketonization reaction) proceeds with selective formation of ketones and aldehydes.³ The reaction selectivity often exceeds 90% and depends on the olefin structure. This opens a new way to synthesise a wide variety of valuable carbonyl compounds. Some of these reactions are currently commercialized, BASF uses this novel method for the large scale production of cyclododecanone and cyclopentanone.⁴

Another very promising approach is the use of ketonization reaction for functionalization of various polydienes by converting their double bonds into C=O groups.⁵ This allows for obtaining new perspective materials – unsaturated polyketones.

Quantum-chemical studies on the interaction of N₂O with different types of olefins predicted that the first reaction step is the 1,3-dipolar cycloaddition of N₂O to the C=C bond (See Scheme 1) leading to a 4,5-dihydro-[1,2,3]-oxadiazole intermediate.^{3d,6}



Scheme 1. Main pathways for the N₂O reaction with linear olefins (R₂ is an alkyl group or an H atom).

Subsequent decomposition of the intermediate mainly proceeds via a H-shift, yielding a corresponding carbonyl product (route 1). Another possible decomposition pathway (route 2) involves diazo cleavage of C-C bond in the intermediate and leads to a shorter aldehyde and diazoalkane.^[3d] Diazoalkane can eliminate N₂ forming carbene, which undergoes further transformations.

It has been previously reported that the diazo channel is negligible for internal (non-terminal) olefins.^{3d} However, our experimental data show that ketonization of such olefins (for example, 2-butene *cis/trans* mixture)^{3c,7} and polydienes⁵ at 453–513 K also proceeds with the cleavage. Besides, it remains unclear whether the *cis/trans* configuration of the olefin has an effect on the reaction kinetics and mechanism, especially on the contribution of the cleavage route. Accounting for such influence is particularly important for N₂O ketonization of *cis*- or *trans*-1,4-butadiene units in polydienes, since the molecular weight of the resulting unsaturated polyketones depends on the contribution

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of the cleavage route.⁵ The goal of the present work is to clarify the NMR data, the reaction mechanism for 3-heptene can be represented as follows (See Scheme 2).

It is known that the cycloaddition of 1,3-dipoles to the C=C bond usually proceeds as a stereospecific *syn* addition with respect to olefin, i.e., the *configuration of the olefin* is retained in the cycloaddition product.^{8]} However, in the case of the N₂O reaction with olefins, cyclic 1,2,3-oxadiazole is a very unstable intermediate. For this reason, its structure cannot be determined by direct experimental methods. Nevertheless, it is possible to clarify the effect of *cis/trans* isomerism on the olefin reactivity towards N₂O and on the products distribution. Here, this effect was studied for the first time using an example of N₂O reaction with individual *cis*- and *trans*- isomers of 3-heptene.

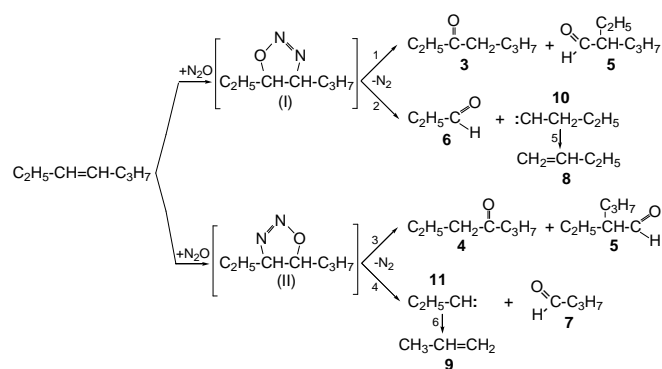
2. Results and Discussion

2.1. Liquid phase oxidation of *cis*- and *trans*- 3-heptenes with N₂O

Table 1 presents the results for the liquid phase oxidation of *cis*-3-heptene (**1**) and *trans*-3-heptene (**2**) with nitrous oxide in the temperature range of 473-513 K. Special experiments showed that under the used conditions the *cis/trans* isomerization does not occur. The reaction time was chosen to provide moderate conversion (ca. 20%) of the isomers. In this case, the olefin conversion depends linearly on time, which allows calculating the reaction rate (*r*).

It can be seen from Table 1 that the reaction rates for both isomers under identical conditions are very close to each other. For example, at 513 K and 6 h the rates were 23 and 24.8 mmol/L·h, respectively. This indicates that the *cis*- and *trans*- isomers have approximately the same reactivity with respect to N₂O. The activation energies determined from the temperature dependence of the reaction rate are 20.1 kcal/mol for the *cis*- isomer and 19.8 kcal/mol for the *trans*- one. These values are close to the activation energy for the liquid phase ketonization of other olefins.^{3b,7}

According to ¹³C NMR analysis, the main products of 3-heptene oxidation are the corresponding isomeric ketones: 3-heptanone (**3**) and 4-heptanone (**4**). The reaction also leads to the formation of three aldehydes: 2-ethylpentanal (**5**), propanal (**6**), and butanal (**7**). Furthermore, the olefins with fewer carbon atoms (1-butene (**8**) and propene (**9**)) are also present among the reaction products. The obtained results suggest that, similar to the earlier studied olefins, the mechanism of 3-heptene oxidation with nitrous oxide most likely implies the 1,3-dipolar cycloaddition of the N₂O molecule to the C=C bond. Based on



Scheme 2. Mechanistic scheme for 3-heptene oxidation with N₂O.

Since the 3-heptene molecule is asymmetric, in this case the 1,2,3-oxadiazole intermediate may have two configurations (I or II) depending on the carbon atom in the double bond to which the oxygen atom of N₂O is attached. According to the NMR data, these intermediates are mostly decomposed without cleavage of the C-C bond in the oxadiazole cycle (reactions 1 and 3), i.e., without breaking the initial C=C bond. The decomposition is accompanied mainly by the H atom transfer to the adjacent C atom in the C-C bond (1,2-hydrogen shift) and yields ketones **3** and **4**. In addition, the decomposition of intermediates (I) and (II) with the transfer of C₂H₅ or C₃H₇ groups, respectively, over the C-C bond (1,2-alkyl shift) leads to the formation of small amounts of aldehyde **5**. Such 1,2-alkyl shift is similar to the transfer of a methyl group observed by us earlier for the N₂O oxidation of 2-butene into iso-butanal.⁷

Note that the ratio of the fraction of aldehyde **5** (formed via the 1,2-alkyl shift) to the total fraction of ketones **3** and **4** (formed via the 1,2-hydrogen shift) is different for the two isomers. For example, at 473 K this ratio is ca. 1:60 for the *cis*- isomer, and ca. 1:20 for the *trans*- one. Consequently, the contribution of 1,2-alkyl shift over the C-C bond is more sterically hindered in the case of *cis*-isomer oxidation due to the location of C₂H₅ and C₃H₇ substituents on one side of the 1,2,3-oxadiazole ring.

The reaction may also proceed with the cleavage of the initial C=C bond. According to the theoretical calculations (see section 3.2.3), the cleavage leads to the formation of diazoalkane.

Table 1. Effect of reaction time and temperature on ketonization of *cis*- and *trans*- 3-heptene with nitrous oxide.^a

Run	Isomer	T, K	t, h	3-Heptene conversion, X_R %	Reaction rate, r mmol/L h	Distribution of carbonyl products, mol %				F_{cleav} , % ^c
						3	4	6+7	5	
1	<i>cis</i> -	473	24	15.9	4.6	48.5	45.7	4.3 (3.9) ^b	1.5	3.9
2	<i>trans</i> -	473	24	17.5	5.1	43.1	40.6	12.1	4.2	12.1
3	<i>cis</i> -	493	12	18.8	10.9	48.3	45.4	4.7 (4.2) ¹	1.6	4.2
4	<i>trans</i> -	493	12	19.3	11.2	42.1	39.7	13.4	4.8	13.4
5	<i>cis</i> -	513	6	19.9	23.0	48.0	45.2	4.9 (4.3) ^b	1.9	4.3
6	<i>trans</i> -	513	6	21.4	24.8	41.1	38.8	15.4	4.7	15.4

^a Reaction conditions: 0.005 mol 3-heptene; 0.08 mol N₂O; 0.067 mol cyclohexane.

^b The calculation took into account that the *cis*-isomer contained 5.3 mol % of *trans*-isomer according to NMR.

^c Fraction of cleavage route.

We assume here that it rapidly decomposes under the reaction conditions to give the corresponding alkylcarbene and nitrogen. Upon decomposition of intermediate (I) with the cleavage (Scheme 2, reaction 2), aldehyde **6** and C4-alkylcarbene (**10**) are formed. Decomposition of intermediate (II) with the cleavage (reaction 4) gives aldehyde **7** and C3-alkylcarbene (**11**). Alkylcarbenes **10** and **11** further isomerize into corresponding terminal olefins **8** and **9** (reactions 5 and 6).

The data of Table 1 show that the oxidation of *cis*-3-heptene or *trans*-3-heptene with nitrous oxide yields the same set of products. However, depending on the isomer type, these products are formed in different ratios indicating different contributions of the cleavage route for the two isomers. For example, after the reaction at 513 K for 6 h, the total fraction of ketones **3** and **4** among carbonyl products for the *trans*-isomer is 79.9 mol %, that of aldehyde **5** – 4.7 mol %, and aldehydes **6** and **7** – 15.4 mol %. The fractions of the corresponding carbonyl products for the *cis*-isomer are 93.2, 1.9 and 4.9 mol %, respectively.

Contribution of the cleavage route (F_{cleav}) to the total oxidation rate for each isomer can be calculated using the fractions of carbonyl products (n_i) according to the following definition:

$$F_{\text{cleav}} = \frac{n_6 + n_7}{n_3 + n_4 + n_5 + n_6 + n_7} \cdot 100 \quad (\text{1})$$

For *trans*-3-heptene, the value of F_{cleav} averaged over all runs (Table 1) is ca. 13.5%, which is about three times higher than that for *cis*-3-heptene ($F_{\text{cleav}} \approx 4.1\%$). Consequently, the *trans*-isomer has a greater tendency to cleave during the interaction with N_2O as compared to the *cis*-isomer.

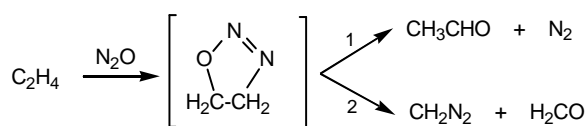
It should be noted that the fraction of the cleavage route for different isomers is in good agreement with the results of our previous studies. Thus, in the case of N_2O oxidation of 2-butene or 2-pentene, representing a mixture of *cis*- and *trans*- isomers, an intermediate value of $F_{\text{cleav}} \approx 8\%$ was observed.⁷ In addition, the contribution of the cleavage route for *cis*-3-heptene ($F_{\text{cleav}} \approx 4.1\%$) is close to $F_{\text{cleav}} \approx 5\%$ observed at ketonization of stereoregular *cis*-1,4-polybutadiene rubber with nitrous oxide.^[5a] In turn, the F_{cleav} value for *trans*-3-heptene agrees quite well with $F_{\text{cleav}} \approx 15\%$ for ketonization of C=C bonds of nitrile-butadiene rubber,^[5b] which contains predominantly *trans*-1,4-butadiene units.⁹

Based on the obtained results one can suggest that, similar to cycloaddition of other 1,3-dipoles to C=C bond, the N_2O reaction with olefins proceeds stereospecifically. If this is the case, geometrical isomerism of olefin will determine the structure of 1,2,3-oxadiazole intermediate. In turn, the contribution of the cleavage route is expected to depend on the structure of the intermediate. In order to verify these assumptions, quantum-chemical calculations were carried out.

2.2. Quantum-chemical study of the reaction mechanism

2.2.1. Ethylene oxidation

The gas phase ethylene oxidation with N_2O is the simplest example of reactions considered here. It was selected for validation of theoretical methods used in this study. The following possible reaction routes were considered (See Scheme 3).



Scheme 3. Mechanism of ethylene oxidation with N_2O .

At the first stage of the reaction 4,5-dihydro-1,2,3-oxadiazole (OD) is formed via 1,3-dipolar cycloaddition. After that, oxadiazole decomposes via a hydrogen shift yielding CH_3CHO (acetaldehyde, AA) and N_2 (path 1) or via a hydrogen shift yielding CH_2N_2 (diazomethane, DM) and formaldehyde (FA) (path 2). In contrast to CBS-QB3 method, DFT predicts that the formation of DM is more preferable in comparison with AA due to a lower value ΔG^\ddagger in the first case (see Table 2). The explanation of the particular DFT inconsistency with CBS-QB3 is probably related to the overestimation of N_2O and DM stability. For example, B3LYP/6-311G(2d,d,p) calculation gives ΔH_f for N_2O 17.2 instead of the experimental value 19.6 kcal/mol.¹⁰

Table 2. Calculated Gibbs activation energies for the ethylene gas phase oxidation by N_2O using the DFT and CBS-QB3 methods (T = 298.15 K, pressure 1 atm).

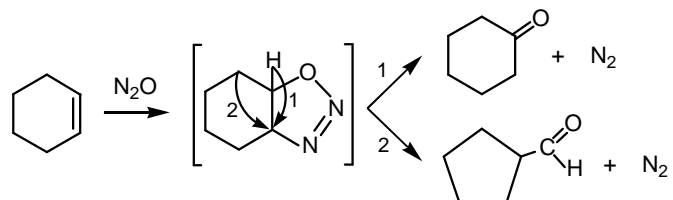
Reaction	ΔG^\ddagger , kcal/mol	
	DFT	CBS-QB3
$\text{C}_2\text{H}_4 + \text{N}_2\text{O} \rightarrow \text{OD}$	37.7	37.1
$\text{OD} \rightarrow \text{AA} + \text{N}_2$	19.8	21.7
$\text{OD} \rightarrow \text{DM} + \text{FA}$	18.3	22.1

The CBS-QB3 method predicts that acetaldehyde formation dominates, which is consistent with the experimental data. Meanwhile, the liquid phase oxidation of ethylene by N_2O at 493 K proceeds with the predominant formation (91%) of acetaldehyde.^{3c}

2.2.2. Cyclohexene oxidation.

Taking into account the above results, it is interesting to apply CBS-QB3 method for more complex reaction, namely the oxidation of cyclohexene by nitrous oxide. Kinetic studies for this reaction were performed by us earlier both in the liquid phase^{3b} and in the gas phase.¹¹ The liquid phase oxidation of cyclohexene in the temperature range 423-503 K provides cyclohexanone (CHN) with high selectivity 96–98.5%. In the case of the gas phase reaction, cyclopentanecarbaldehyde (CPC) was obtained as an additional product.

Quantum-chemical CBS-QB3 simulation performed here reveals that the reaction can proceed via 1,2-H shift (path 1) and via 1,2-alkyl shift (path 2), see Scheme 4.



Scheme 4. Mechanism of cyclohexene oxidation with N_2O .

The cyclohexene oxidation was first simulated using DFT by Avdeev et al.⁶ They found that the activation energy is mostly determined by the first step of the reaction, i.e. oxadiazole formation. The predicted energy barrier was 26.7 kcal/mol which agrees well with our experimental value 26 ± 1 kcal/mol for the gas phase reaction.¹¹ However, the CPC formation route involving 1,2-alkyl shift was not theoretically studied. Hermans et al.^{3d} first considered a similar alkyl shift for the 1-methyl-1-

cyclohexene oxidation by N₂O leading to cyclopentyl methyl ketone.

DFT overestimates the contribution of the cleavage route and predicts the C-C bond cleavage in oxadiazole to be a main reaction channel for the cyclohexene oxidation. In this case the cleavage should lead to 6-diazohexanal (DHA), which in turn gives 5-hexenal. However, this expected final product of the cleavage was not detected in the experiment, since it probably forms in very small amounts.

The CBS-QB3 ΔH^\ddagger and ΔS^\ddagger values (Table 3) were calculated at 660.65 K (the middle point of the experimental temperature range 598-723 K for the gas phase reaction¹¹) and pressure 10 atm. The temperature dependence of CHN and CPC selectivities was obtained assuming that distribution of the products is controlled by passing the activation energy barrier, i.e.

$$n_1/n_2 = k_1/k_2 = \exp(-\Delta\Delta G^\ddagger/RT) \quad (2)$$

where n_i – product molar fraction and k_i – corresponding rate constant. Table 4 shows that the obtained results agree well with available experimental data.

Table 3. Calculated activation enthalpies and entropies for the cyclohexene gas phase oxidation by N₂O (T = 660.65 K, pressure 10 atm).

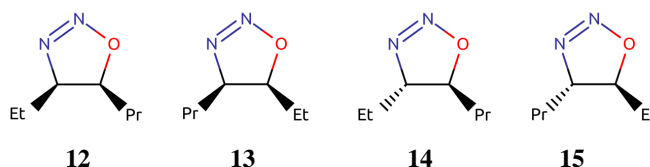
Reaction	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , cal/mol·K
C ₆ H ₁₀ + N ₂ O → OD	27.0	-42.4
OD → CHN + N ₂	17.2	+4.0
OD → CPC + N ₂	20.5	+4.4
OD → DHA	22.2	+3.8

Table 4. Theoretical and experimental selectivities of products for the gas phase oxidation of cyclohexene by N₂O. (Experimental conditions: reactor 5 cm³; reaction mixture: 20 mol. % C₆H₁₀, 20 mol. % N₂O, 60 mol. % He; flow rate 25 cm³/min (NTP); pressure 10 atm).¹¹

T, K	Product selectivity, %			
	CHN		CPC	
	Theory	Experiment ¹¹	Theory	Experiment ¹¹
598	92	93	7.0	7.0
623	91	93	7.7	7.0
648	90	92	8.4	8.0
673	89	92	9.2	7.5
698	88	89	9.9	10.5
723	87	85	10.7	11.0

2.2.3. Cis- and trans- 3-heptenes oxidation.

An initial cycloaddition of N₂O to 3-heptene can produce four isomers of 4,5-dihydro-1,2,3-oxadiazole:



The first two isomers belong to *cis*-3-heptene oxidation, the other ones – to *trans*-3-heptene. According to the CBS-QB3 calculation, the enthalpy differences between **12** and **13** isomers or between **14** and **15** isomers are negligible – 0.03 kcal/mol. However, the enthalpy difference between isomers for *cis*-3-heptene (**12** and **13**) and *trans*-3-heptene (**14** and **15**) is higher – 1.2 kcal/mol. The isomers corresponding to *trans*-3-heptene oxidation are more stable. The activation barriers for N₂O cycloaddition to *cis*- and *trans*- isomers of 3-heptene are 24.3 and 25.5 kcal/mol, respectively, see Table 5. The difference between activation barriers are the same as the difference between enthalpies of formation for the *cis*- or *trans*- isomers, which is predicted to be 1.4 kcal/mol in accordance with the experimental value (1.1±0.2 kcal/mol).¹² Note that these activation energies cannot be directly compared with the experimental values for *cis*- and *trans*- isomers (20.1 and 19.8 kcal/mol, respectively), which were determined for the liquid phase reaction.

The step of N₂O cycloaddition to *cis*-3-heptene and subsequent decomposition of corresponding oxadiazole species are shown in Fig 1. In agreement with the experimental data, the most favorable reaction path is 3-heptanone (**3**) and 4-heptanone (**4**) formation (path 2#), see Table 5.

Table 5. Calculated activation enthalpies and entropies for the gas phase oxidation of *cis*- and *trans*- 3-heptenes by N₂O (T = 298.15 K, pressure 1 atm). (**3-9** – the reaction products, see Scheme 2).

Reaction	ΔH^\ddagger [kcal/mol]		ΔS^\ddagger [cal/mol·K]	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
C ₇ H ₁₄ + N ₂ O → OD	24.3	25.5	-41.0	-39.4
OD → (3+4) + N ₂	19.0	19.9	+3.4	+1.0
OD → (6+7) + (8+9)	22.5	22.2	+4.3	+3.4
OD → 5 + N ₂	22.3	23.5	+4.0	+1.9

The effect of temperature on the distribution of carbonyl byproducts is shown in Table 6. The experimental dependence of the reaction product distribution on *cis*- and *trans*- isomerism of 3-heptene observed in the liquid phase oxidation by N₂O should also hold for the gas phase reaction at the same temperatures

The following rationale behind the *cis*- *trans*- dependence of the reaction products distribution can be suggested. The 3-heptene configuration is retained during the N₂O cycloaddition reaction. The *trans*- isomer derived oxadiazole is more stable than the *cis*- one. Subsequent rearrangements of the *trans*- isomer require more energy. However, the steric hindrance has less effect on the C-C cleavage transition state for both isomers, because of longer distance between ethyl- and propyl- radicals, see Fig. 1, transition state 3#. Therefore, the energy gap between the C-C cleavage and 1,2-H shift energy barriers is smaller for the *trans*- isomer derived oxadiazole, than for the *cis*- one. The difference between *cis*- and *trans*- $\Delta\Delta G^\ddagger$ that controls

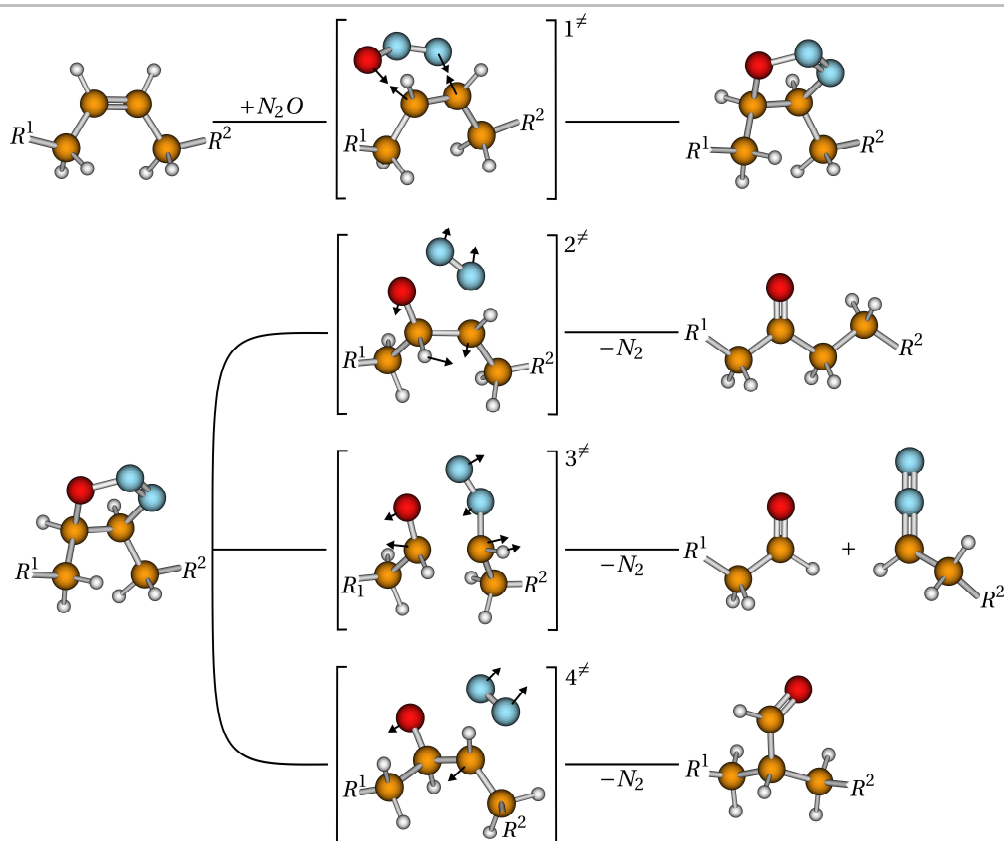


Fig.1. Mechanism of *cis*-3-heptene oxidation with N_2O . The structures of activated complexes are shown in square brackets

Table 6. Theoretical and experimental distribution of carbonyl byproducts for the oxidation of 3-heptene by N_2O . (5-7 – the reaction products, see Scheme 2).

Isomer	T, K	Distribution of carbonyl byproducts, mol. %			
		Aldehydes (6+7)		2-ethylpentanal (5)	
		Theory	Experiment	Theory	Experiment
<i>cis</i> -	473	3.6	3.9	3.8	1.5
<i>trans</i> -	473	22.8	12.1	2.5	4.2
<i>cis</i> -	493	4.2	4.2	4.3	1.6
<i>trans</i> -	493	24.5	13.4	2.9	4.8
<i>cis</i> -	513	4.7	4.3	4.9	1.9
<i>trans</i> -	513	26.1	15.4	3.2	4.7

the distribution of products is 1.2 kcal/mol. It is exactly the difference between oxadiazoles enthalpies.

The calculations show that the fraction of aldehydes **6** and **7** among the carbonyl products (i.e. the contribution of the cleavage route) is higher for the *trans*- isomer than for the *cis*- one, which is qualitatively consistent with experiment. However, an agreement between the theoretical and experimental distributions of carbonyl products is not complete, in contrast to the gas phase cyclohexene oxidation considered above. The calculations predict $F_{\text{cleav}} = 24.5\%$ on average for *trans*-3-heptene and $F_{\text{cleav}} = 4.2\%$ for *cis*-3-heptene. Besides, a theoretical yield of 2-ethylpentanal forming via the alkyl shift is higher for the *cis*- isomer than for

the *trans*-one, contrary to the experimental findings. The reason is obvious: the quantum-chemical method used here can be applied only to the gas phase reactions and cannot consider the effect of reactants environment in the liquid phase on the reaction.

3. Conclusions

We have studied for the first time the effect of the *cis/trans* isomerism on the kinetics and mechanism of liquid phase selective oxidation of olefins with nitrous oxide into carbonyl compounds (the so-called ketonization reaction). The experimental study has revealed that *cis*- and *trans*- isomers of 3-heptene have similar reactivities towards N_2O in the temperature range of 473-513 K. Their oxidation yields the same set of ketones and aldehydes, but the ratio of these products is different. For the *trans*-isomer, the fraction of ketones among the carbonyl products (79.9-83.7 mol %) is lower compared to the *cis*-isomer (93.2-94.2 mol %). This is due to higher contribution of the cleavage route (F_{cleav}) for *trans*-3-heptene (~13.5%) than for *cis*-3-heptene (~4.1%).

The CBS-QB3 quantum-chemical method was applied to reveal the mechanism of olefins oxidation with N_2O . The calculation provides an understanding of the *cis/trans* isomerism effect on the distribution of products formed during the liquid phase oxidation of 3-heptene and confirms higher F_{cleav} value for *trans*- isomer. In particular, it gives detailed information on the way the C=C bond is cleaved and which products are formed. Theory predicts that cleavage leads to shorter aldehydes and diazo- compounds. The latter decompose to terminal olefins. Also, an alkyl shift as one of side reactions is predicted in accordance with the experiment. The distribution of oxidation products was calculated according to Transition State Theory assuming that only chemical kinetics controls the product ratios.

A quantitative agreement between theory and experiment was achieved for the gas-phase cyclohexene oxidation with N₂O.

The observed difference in the contribution of the cleavage route for *cis*- and *trans*- isomers of olefins is responsible for different behavior of the polydienes containing *cis*- or *trans*- 1,4-butadiene units with respect to the cleavage during their ketonization with nitrous oxide.

4. Experimental Section

4.1. Chemicals

Cis-3-heptene (96%), *trans*-3-heptene (99%), and cyclohexane (99.9%) were purchased from Sigma-Aldrich. Medical grade nitrous oxide (99.8%) was purchased from Cherepovets Azot Plant.

4.2. Typical procedure for oxidation reaction

The liquid phase oxidation of *cis*-3-heptene or *trans*-3-heptene with nitrous oxide was carried out using a 25 ml Parr reactor equipped with a stirrer. In a typical experiment, a solution containing 0.005 mol of 3-heptene and 0.067 mol of cyclohexane (a solvent) was loaded to the reactor. To remove air, the reactor was purged with helium and then filled with 0.08 mol N₂O by the method described elsewhere.⁷ The reactor was heated at a 6 K/min ramp to the required reaction temperature and kept for 6–24 h. After termination of the reaction, the reactor was cooled to room temperature and the pressure was slowly released. The reaction products were analyzed by the ¹³C NMR method. The spectra were recorded at 100.61 MHz with a Bruker Avance spectrometer. ¹³C NMR spectral data for *cis*-3-heptene, *trans*-3-heptene and the reaction products were as follows:

cis-3-Heptene (1): 131.43, 128.72, 29.27, 23.04, 20.58, 14.04, 13.40

trans-3-Heptene (2): 132.00, 128.96, 34.90, 25.79, 22.90, 13.75, 13.28

3-Heptanone (3): 206.14 (C=O, C3), 41.64 (CH₂, C4), 35.38 (CH₂, C2), 26.01 (CH₂, C5), 22.55 (CH₂, C6), 13.56 (CH₃, C7), 7.34 (CH₃, C1).

4-Heptanone (4): 205.70 (1C, C=O, C4), 44.34 (2C, CH₂, C3 and C5), 17.15 (2C, CH₂, C2 and C6), 13.44 (2C, CH₃, C1 and C7).

2-Ethylpentanal (5): 200.70 (CHO, C1), 53.22 (CH, C2), 30.90 (CH₂, C3), 22.00 (CH₂, Et), 20.41 (CH₂, C4), 11.07 (CH₃, Et).

Propanal (6): 197.55 (CHO, C1), 37.14 (CH₂, C2), 5.58 (CH₃, C3).

Butanal (7): 197.43 (CHO, C1), 45.80 (CH₂, C2), 15.65 (CH₂, C3).

1-Butene (8): 139.81 (=CH-, C2), 112.85 (=CH₂, C1).

Propene (9): 132.81 (=CH-, C2), 115.28 (=CH₂, C1).

4.3. Quantum-chemical methods

In order to rationalize 1,2-alkyl shift and the C-C cleavage dependence on the *cis/trans*-substrate isomer observed experimentally in this study, Density Functional Theory (DFT) calculations were carried out. Potential Energy Surfaces (PESs) of relevant reaction steps were constructed at the DFT level using the B3LYP functional.¹³ Optimal geometry search and subsequent vibrational and intrinsic reaction coordinate (IRC) analysis were performed using B3LYP/6-311G(2d,d,p).

Geometry optimization and vibrational analysis at the selected B3LYP/6-311G(2d,d,p) level are actually the first steps of composite method applied here: CBS-QB3.¹⁴ This is a Complete Basis Set (CBS) method developed by George Peterson and coworkers. It extrapolates several single-point energies in order to get the best estimate of the total energy, which is hard to

compute due to incomplete electron correlation energy account and finite size of the basis set.

All calculations were performed with the Gaussian 09 software.¹⁵ Visualization of the results was performed using the MOLDEN program.¹⁶

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Grant No. 14-03-31052 mol_a) and by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.3).

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