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Liquid-phase noncatalytic butene oxidation with nitrous oxide

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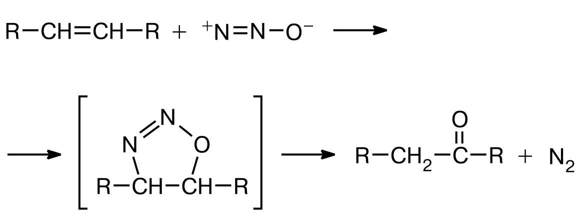
The kinetics and mechanism of noncatalytic liquid-phase oxidation of but-1-ene and but-2-ene with nitrous oxide in a benzene solution in the temperature range from 180 to 240 °C were studied. Oxidation proceeds *via* the 1,3-dipolar cycloaddition mechanism to form carbonyl compounds. Both of these reactions occur with close rates and activation energies and have the first orders with respect to the alkene and N_2O. A considerable fraction (39%) of but-1-ene involved in oxidation undergoes cleavage at the double bond yielding propanal and an equivalent amount of methylene, the latter producing ethylcyclopropane and cycloheptatriene. The oxidation of but-2-ene proceeds with a minimum bond cleavage and affords methyl ethyl ketone with 84% selectivity. Regularities of the oxidation of terminal and internal alkenes C_2—C_8 with nitrous oxide were analyzed using the previously published data.

Key words: oxidation, butenes, nitrous oxide, carbonyl compounds, methyl ethyl ketone, methylene, carbenes.

Nitrous oxide (N_2O) attracts attention as an oxidizing agent for the gas-phase catalytic oxidation. Reactions of this type are strikingly exemplified by the selective oxidation of benzene and other aromatic compounds to the corresponding phenols in the presence of iron-containing zeolites FeZSM-5. The works in this area are considered in several reviews.[1—6]

It has previously been shown that nitrous oxide can also be an efficient oxidizing agent in liquid-phase oxidation. These reactions are mainly alkene epoxidation and alcohol oxidation, occurring with ~100% selectivity in the presence of the Ru porphyrin complexes,[7,8] metal-containing polyoxometallates,[9,10] and some metal—oxide systems.[11] Meanwhile, the most remarkable feature of nitrous oxide is, probably, its capability for noncatalytic liquid-phase alkene oxidizing to form carbonyl compounds.[12—15] Cyclopentene and cyclohexene are oxidized with N_2O at 150—250 °C, transforming into the corresponding cyclic ketones with 96—99% selectivity.[14,15] The reaction proceeds *via* the nonradical 1,3-dipolar cycloaddition mechanism to form an intermediate 1,2,3-oxadiazoline complex (Scheme 1).

Scheme 1



R is hydrocarbon radical or hydrogen atom

The energy route of cyclohexene oxidation was completely described[16,17] by the quantum-chemical method. The results agree well with the experimental data.

The recent screening of substrates shows[18] that nitrous oxide can noncatalytically oxidize alkenes of different classes, including linear, cyclic, and heterocyclic alkenes and their derivatives. The rate and selectivity of the reaction depend strongly on the substrate composition and structure. In particular, those effects are especially pronounced for linear alkenes C_2—C_8, whose behavior differs considerably depending on the position of the double bond. However, it is difficult to compare quantitatively the results obtained for different alkenes, because even under strictly standardized experimental conditions (reactant concentration, reaction temperature, and pressure) the real conditions of alkene oxidation are different due to different boiling points of alkenes. For instance, for the reaction temperature 220 °C, the main amount of oct-1-ene (b.p. 121 °C) exists in solution, whereas a considerable portion of ethylene (b.p. −107 °C) goes to the gas phase and exists outside the reaction zone, thus resulting in a seemingly decreased activity in the reaction with N_2O.

To avoid these difficulties, in this work, we studied the oxidation of butene isomers with the terminal and internal double bonds. Since the physical properties of

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but-1-ene and but-2-ene are similar, this study should certainly answer the question about the influence of the alkene structure on the reaction mechanism and composition of the products. The reaction can also be of practical interest, because the main expected product is such a valuable substance as methyl ethyl ketone (**1**), whose methods for preparation are far from perfection.

In the final part of the present work, we consider the results in comparison with the earlier obtained data for linear alkenes[18] to reveal general regularities of oxidation with nitrous oxide.

Experimental

Experiments on butene oxidation were carried out in benzene solution using a stainless steel autoclave-type 100-cm^3 reactor (Parr). To decrease a possible condensation of components of the reaction mixture in cold parts of the reactor, the stirrer was removed and the solution was stirred with a glass-sealed metallic rod, which was rotated (300 rpm) with an alternating magnetic field providing the reaction to occur in the kinetic region.

The scheme of the setup is shown in Fig. 1. The reactor was loaded with benzene (50 cm^3) and tightly closed. Then, air was removed for 1 min from the reactor through shutoff valves *1* and *2*, and butene and N_2O were conveyed. Butene was supplied by portions from metallic cylinder *5* through intermediate 1-L bypass cylinder *6*. Upon loading the reactor, butene was absorbed with benzene, and the amount of the loaded alkene was determined from a pressure change in the vessel. If necessary, this procedure was repeated several times to provide the required initial amount of butene. In the most part of experiments, the butene load was $N^0_R = 0.08$ mol.

Nitrous oxide was supplied from a 0.5-L bypass cylinder *7*. The amount of loaded nitrous oxide usually was $N^0_{N_2O} = 0.12$ mol. Nitrous oxide is well dissolved in benzene, and the initial N_2O pressure in the reactor for this load is ~10 atm.

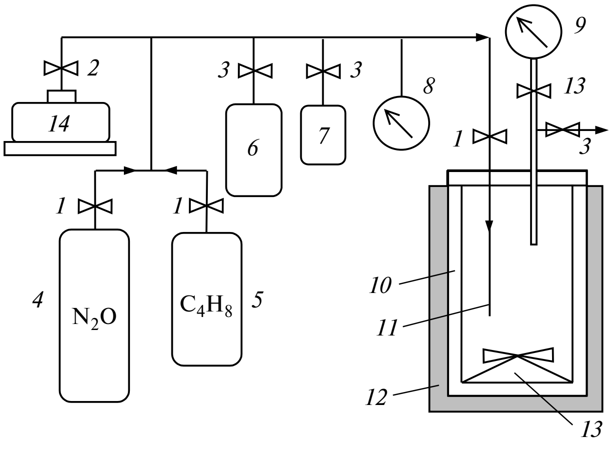


Fig. 1. Scheme of the experimental setup: *1—3*, shutoff valves; *4* and *5*, gas cylinders; *6* and *7*, bypass cylinders; *8*, reference pressure gauge; *9*, pressure gauge; *10*, reactor (autoclave); *11*, capillary for gas supply; *12*, oven; *13*, magnetic stirrer; and *14*, vacuum pump.

After the reactants were loaded, the reactor was heated with a rate of 6 °C min^{-1} to the experimental temperature (180—240 °C) at which the reactor was stored for a specified time. After the end of the experiment, the reactor was cooled to room temperature. The gas phase was analyzed by gas chromatography. Further, after the pressure was slowly discharged, the liquid phase was analyzed by GLC. The composition of the gas phase (N_2O, N_2, O_2, CO, CO_2) was analyzed on a Tsvet 500 M chromatograph at room temperature using a heat-conductivity detector and a column packed with Porapak Q. For a higher measurement accuracy of small amounts of CO and CO_2, they were prehydrogenated over a nickel catalyst and then analyzed as methane on a flame-ionization detector. Molecular nitrogen was the only gaseous reaction product, whose amount corresponded to that of the oxygen-containing compounds formed in the liquid phase. In all cases, the CO_x concentration did not exceed 0.01 mol.%.

Liquid reaction products were analyzed by chromatography on a Kristal 2000 instrument equipped with a capillary column (SE-50, 50 m×0.2 mm) and a flame-ionization detector. Calibrating solutions of authentic compounds were used to identify the products and determine their concentration. The products were additionally identified by ^{1}H and ^{13}C NMR spectroscopy (Bruker DPX-250, ^{1}H, 250.13 MHz; ^{13}C, 62.9 MHz; Bruker MSL-400, ^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz) and GC-MS (VG Analytical Ltd. 7070HS and Varian Saturn 2000).

The butene conversion (X_R) was calculated from the amount of the products taking with stoichiometric coefficients. The reaction rate was determined by the equation

$$W = N^0_R X_R/(100Vt), \qquad (1)$$

where N^0_R is the initial amount of butene, V is the solution volume, and t is the reaction duration.

But-1-ene and but-2-ene (99%, Aldrich) and medical 99.8% nitrous oxide (Azot Plant, Cherepovets, Russia), which is delivered in the fluidized state in metallic cylinders under ~50 atm, were used in experiments. Benzene (99%) was used as solvent.

Results and Discussion

But-1-ene oxidation. The results on but-1-ene oxidation in the 180—240 °C temperature region are presented in Table 1. The main reaction products are carbonyl compounds **1—3**, being ~75% in total, and two compounds containing no oxygen: ethylcyclopropane (**4**) and cycloheptatriene (**5**). A small amount of unidentified products (1.4—2.5 mol.%) is also present in the solution.

The duration of experiments at different temperatures was chosen in such a way that a relatively low conversion of but-1-ene ($\leq$25%) was provided. Entry *4* with a higher conversion (220 °C, 12 h) was carried out to compare but-1-ene with other linear alkenes, whose oxidation has previously been studied under these conditions.[18] The data in Table 1 show that the reaction rate increases by more than an order of magnitude with the temperature increase from 180 to 240 °C. The activation energy calculated from the Arrhenius plot (Fig. 2) is 21±1 kcal mol^{-1},

Table 1. Temperature effect on the parameters of but-1-ene oxidation*

Entry	T/°C	τ/h	Conversion of but-1-ene, X_R (%)	Composition of reaction products in liquid phase (mol.%)						W /μmol cm^{-3} h^{-1}
				1	Butanal (**2**)	Propanal (**3**)	Ethylcyclopropane (**4**)	Cycloheptatriene (**5**)	Other products	
1	180	12	6.9	34.7	11.1	30.5	16.3	6.0	1.4	9.2
2	200	12	19.8	35.3	11.6	26.4	12.4	12.4	2.0	26.4
3	220	3	11.9	34.1	12.7	30.6	12.7	7.4	2.5	63.5
4	220	12	37.9	33.3	13.4	29.4	12.6	9.5	1.8	50.5
5	240	2	17.6	32.7	14.2	30.0	12.3	8.7	2.1	140.8
Averaged concentrations:				33.8	12.8	29.5	13.1	9.0	1.8	

* Reaction conditions: $N^0_R = 0.08$ mol, $N^0_{N_2O} = 0.12$ mol, solvent benzene (50 mL).

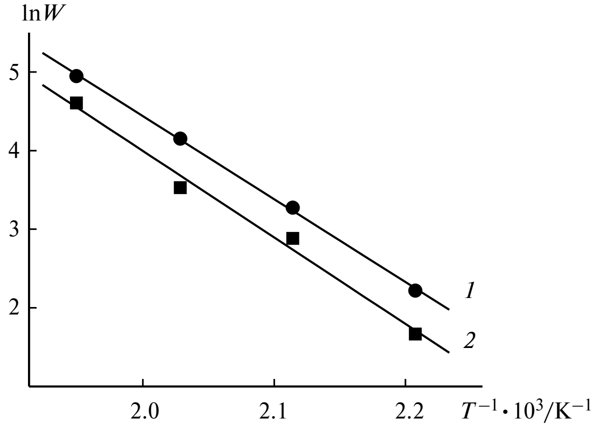


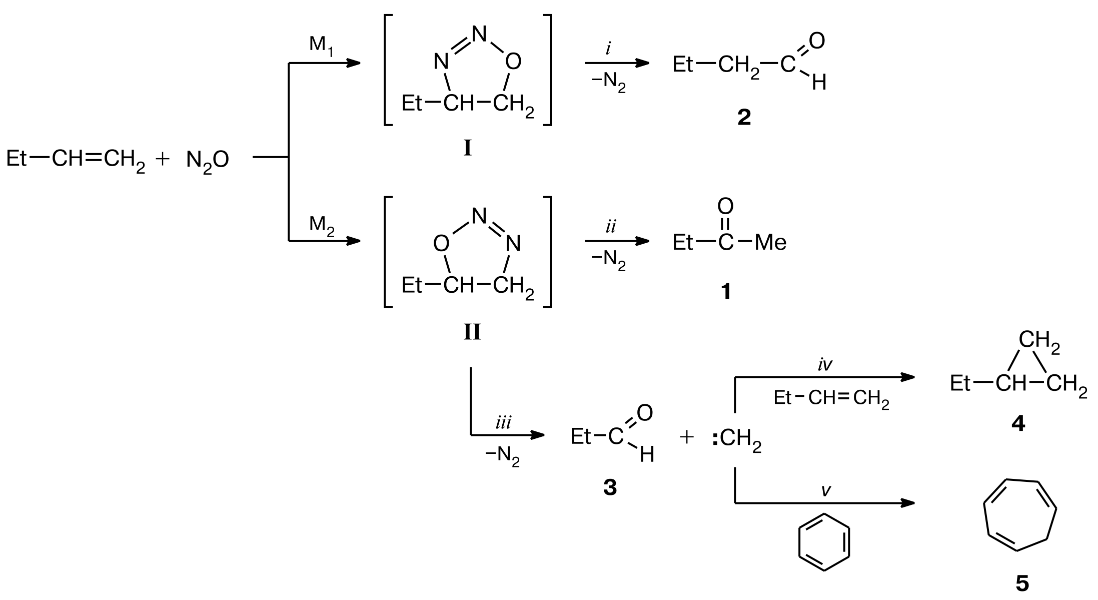
Fig. 2. Arrhenius plots for the oxidation of but-1-ene (*1*) and but-2-ene (*2*) by nitrous oxide (according to the data in Tables 1 and 3).

which slightly differs from a value of 24 kcal mol^{-1} calculated by the quantum-chemical study of this reaction.[17]

Reaction mechanism. The composition of the products of but-1-ene oxidation (see Table 1) agrees well with the mechanism of 1,3-dipolar cycloaddition of N_2O to the alkene double bond.[12,17] The general reaction mechanism is shown in Scheme 2.

As can be seen, two reaction routes (M_1 and M_2) are possible, depending on which the carbon atom (first or second) is bound to the oxygen atom of the N_2O molecule. According to this, the intermediate oxadiazoline complex can exist in two configurations: **I** and **II**. Correspondingly, this leads to the formation of compounds **2** (route *i*) and **1** (route *ii*). Complex **II** can also decompose through the carbon—carbon bond cleavage to form propanal (**3**) and an equivalent quantity of methylene (route *iii*). Methylene, being a highly reactive carbene

Scheme 2



species,[19,20] reacts rapidly either with but-1-ene to yield ethylcyclopropane (**4**, route *iv*), or with benzene affording cycloheptatriene (**5**, route *v*).

It cannot be excluded that the cleavage primarily produces not methylene but diazomethane[12] (CH_2N_2), which can rapidly decompose to methylene and nitrogen or reacts directly with but-1-ene and benzene. Since diazomethane should be very unstable under the reaction conditions and produces the same products as methylene does, it is difficult to establish the exact nature of a species formed by the cleavage. In this case, we can speak about the formation of methylene in the reaction.

Quantitative comparison of the composition of the reaction products with Scheme 2 makes it possible to determine (a) contribution of routes M_1 and M_2 to the overall oxidation rate, (b) fraction of the reaction leading to the cleavage of molecules at the double bond, and (c) reactivity of methylene toward but-1-ene and benzene.

The results presented in Table 1 indicate that the composition of the reaction products is almost independent of the temperature and duration of experiments within the experimental accuracy.

As can be seen from the data in Scheme 2, the contribution of route M_1 to the overall oxidation rate (F_{M_1}) can be expressed through the concentrations of the corresponding products:

$$F_{M_1} = M_1/(M_1 + M_2) = C_2/(C_1 + C_2 + C_3). \quad (2)$$

Calculation with the averaged data in Table 1 shows that F_{M_1} is 17%. Thus, the reaction mainly proceeds *via* route M_2 through intermediate complex **II**.

The fraction of the reaction leading to the cleavage of but-1-ene molecules at the double bond (F_{cleav}) can be found from the equation

$$F_{cleav} = C_3/(C_1 + C_2 + C_3), \quad (3)$$

which gives $F_{cleav} = 39\%$.

As already mentioned in earlier works,[12,18] the "cleavage" mechanism of terminal alkene oxidation affords a stoichiometric amount of methylene (or diazomethane) and aldehyde with a smaller number of carbon atoms. Methylene is grouped with highly reactive carbene intermediates that are used in organic synthesis. Several methods for methylene generation are known.[19,20] The simplest of them is based on the thermal, catalytic, or photodecomposition of diazomethane, which is a very expensive, toxic, and explosive substance. The generation of $:CH_2$ by alkene oxidation using N_2O is a simple method, which provides, in the case of but-1-ene, a considerable yield of this carbene (39%).

Knowing the contents of but-1-ene and benzene (with which methylene reacts), one can estimate the relative reactivity of methylene to these substrates. Based on Scheme 2, the ratio of the reaction rate constants of methylene with but-1-ene (k_{iv}) and benzene (k_v) can be presented as follows:

$$k_{iv}/k_v = C_4C_{C_6H_6}/(C_5C_{C_4H_8}). \quad (4)$$

Calculation by Eq. (4) gives the ratio $k_{iv} : k_v = 10$, which indicates a much higher reactivity of carbene toward alkene. The real difference in activities should be higher, because a considerable fraction of but-1-ene is in the gas phase, *i.e.*, outside the solution where the methylene-generating oxidation occurs, due to the low boiling point of but-1-ene (−6.3 °C).

Note that, according to Scheme 2, the yield of propanal should be equal to the sum of the yields of compounds **4** and **5** formed from methylene. However, the experimental yield of propanal (**3**) is somewhat higher (see Table 1). This can be related to the consumption of methylene in reactions with but-1-ene and benzene in other routes. We assumed that methylene can react with N_2O to form formaldehyde. However, detailed analysis using special chromatographic procedures and NMR found neither formaldehyde nor additional products of methylene conversion. Nevertheless, it cannot be excluded that formaldehyde is formed but polymerizes, under the reaction conditions, to produce an insoluble product, which is not detected by the above analyses.

The ratio between the competitive reactions of methylene can be controlled by the variation of the amounts of alkene and benzene in the reaction system. The results of experiments, where the amount of benzene was constant (50 cm^3) and the amount of but-1-ene was increased from 0.04 to 0.16 mol, are presented in Table 2. It is seen that an increase in the but-1-ene amount in the system results, in fact, in a proportional increase in the ratio of compounds **4** : **5** in the reaction products. The data presented in Table 2 also indicate that the reaction rate is proportional to the amount of introduced but-1-ene, *i.e.*, the reaction has the first order with respect to alkene.

It has previously been shown[12,14] that nitrous oxide is inert toward organic compounds containing no C=C bond (cyclohexane, benzene, acetonitrile, ethanol, and other). Therefore, alkenes can be oxidized by nitrous oxide only in the presence of different solvents usually used in organic synthesis. The solvent nature exerts no considerable effect on the alkene conversion and selectivity with respect to carbonyl compounds.[18] At the same time, a solvent can affect the character and ratio of the products of methylene conversion, if the latter forms. For instance, when toluene is used instead of benzene as a solvent, the conversion of but-1-ene and selectivity with respect to the main products remain virtually unchanged, but methylcycloheptatriene is formed instead of cycloheptatriene (**5**).

But-2-ene oxidation. The results of experiments on but-2-ene oxidation, which were carried out under the

Table 2. Influence of the initial amount of but-1-ene on the oxidation parameters*

Entry	N^0_R /mol	X_R (%)	Composition of the reaction products in solution (mol.%)						**4 : 5**	W /µmol cm^{-3} h^{-1}
			1	**2**	**3**	**4**	**5**	Other products		
1	0.04	11.1	31.9	13.0	28.0	12.3	11.7	3.1	1.1	29.6
2	0.08	11.9	34.1	12.7	30.6	12.7	7.4	2.5	1.7	63.5
3	0.16	10.8	33.9	12.5	31.7	14.8	4.6	2.5	3.2	115.2

* Reaction conditions: $N^0_{N_2O}$ = 0.12 mol, solvent benzene (50 mL), 220 °C, 3 h.

Table 3. Temperature effect on the parameters of but-2-ene oxidation

Entry	T /°C	τ/h	X_R (%)	Composition of reaction products in liquid phase (mol.%)						W /µmol cm^{-3} h^{-1}
				1	Isobutanal (**6**)	Acetaldehyde (**7**)	1,2,3-Trimethylcyclopropane (**8**)	7-Methylcyclohepta-1,3,5-triene (**9**)	Other products	
1	180	12	4.0	82.0	2.8	9.1	4.5	0.2	1.4	5.3
2	200	12	13.4	84.6	3.4	6.1	4.7	0.2	1.1	17.9
3	220	3	6.4	84.5	3.5	7.0	3.6	0.2	1.2	34.1
4	220	12	23.1	85.1	3.3	7.2	3.4	0.1	0.9	30.8
5	240	2	12.5	83.9	3.6	7.7	3.3	0.2	1.3	100.0
Averaged concentrations:				84.0	3.3	7.4	3.9	0.2	1.2	

* Reaction conditions: N^0_R = 0.08 mol, $N^0_{N_2O}$ = 0.12 mol, solvent benzene (50 mL).

conditions similar to those of but-1-ene oxidation, are presented in Table 3. In this case, the main products are also carbonyl compounds (methyl ethyl ketone (**1**), isobutanal (**6**), and acetaldehyde (**7**)), being >90% in total. In addition, 1,2,3-trimethylcyclopropane (**8**) and 7-methylcyclohepta-1,3,5-triene (**9**) are formed. As in the case of but-1-ene, the composition of the products of but-2-ene oxidation is virtually temperature-independent.

Noteworthy that the reaction is highly selective with respect to methyl ethyl ketone (**1**): the fraction of **1** in the reaction products is 84% on the average. Compound **1** is a valuable chemical product widely use as solvent in vanish-and-paint and petroleum processing industries. At present, this compound is mainly produced from a mixture of but-1-ene and but-2-ene through a complicated and poorly selective three-step process: sulfonation of butenes, hydrolysis of isobutyl sulfate, and dehydrogenation of the butan-2-ol that formed to yield **1**. Since nitrous oxide, which can be obtained by the selective oxidation of ammonia with oxygen,[21,22] is cheap, the results presented on the oxidation of but-2-ene with nitrous oxide are worth of attention as a new alternative method for methyl ethyl ketone (**1**) preparation.

The Arrhenius plot for the reaction rate of but-2-ene oxidation, which corresponds to an activation energy of 22±1 kcal mol^{-1}, is presented in Fig. 2. The theoretical activation energy value obtained by the quantum-chemical calculation is somewhat higher than the experimental value: 26 kcal mol^{-1}.[17]

The results of experiments on but-2-ene oxidation at different initial amounts of the reactants are listed in Table 4. The amount of N_2O was varied within 0.04—0.19 moles, and that of but-2-ene changed from 0.04 to 0.16 moles. Based on these data, we plotted the functions of the reaction rate *vs.* amounts of N_2O and but-2-ene (Fig. 3). The linear character of these plots indicates the first reaction order with respect to each reactant. Thus, the kinetic equation of butene oxidation can be presented as follows:

$$W = k_0\exp[-E/(RT)]C_{C_4H_8}C_{N_2O}, \qquad (5)$$

where k_0 is the pre-exponential factor, E is the activation energy, and $C_{C_4H_8}$ and C_{N_2O} are the concentrations of the reactants in solution. The exact concentrations of the dissolved reactants, under experimental conditions, are unknown but they are assumed to be proportional to the amounts of introduced substrates.

Reaction mechanism. The mechanism of but-2-ene oxidation is presented in Scheme 3. Unlike but-1-ene, the but-2-ene molecule is symmetrical relatively to the position of the C=C bond. Therefore, one can propose only one configuration of the intermediate oxadiazoline complex for which the oxygen atom is always bonded to the second carbon atom. As in the case of but-1-ene, this

Table 4. Influence of the initial amount of the reactants on the parameters of but-2-ene oxidation at 220 °C (solvent benzene, 50 mL)

Entry	N^0_R	$N^0_{N_2O}$	τ/h	X_R (%)	Composition of reaction products in liquid phase (mol.%)						W /μmol cm^{-3} h^{-1}
	mol				**1**	**6**	**7**	**8**	**9**	Other products	
1	0.08	0.04	12	8.6	81.6	3.2	8.3	4.0	0.3	2.7	11.5
2	0.08	0.06	6	7.0	82.1	4.0	6.7	4.3	0.5	2.4	18.7
3	0.08	0.12	6	13.5	84.0	3.4	7.6	3.5	0.1	1.4	36.0
4	0.08	0.19	6	23.6	84.0	2.9	7.8	2.6	0.2	2.5	62.9
5	0.04	0.06	12	15.3	81.2	3.3	9.8	2.4	0.3	3.1	10.2
6	0.04	0.12	6	15.6	79.2	3.8	9.7	2.6	0.6	4.1	20.8
7	0.16	0.12	6	15.2	84.7	3.3	7.1	2.6	0.4	2.1	81.1
Averaged concentrations:				82.4	3.4	8.1	3.1	0.3	2.6		

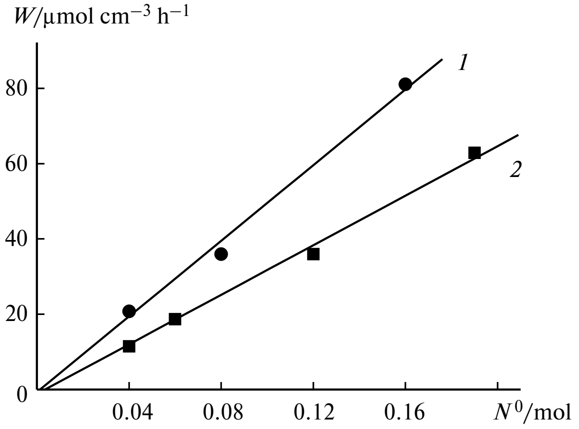


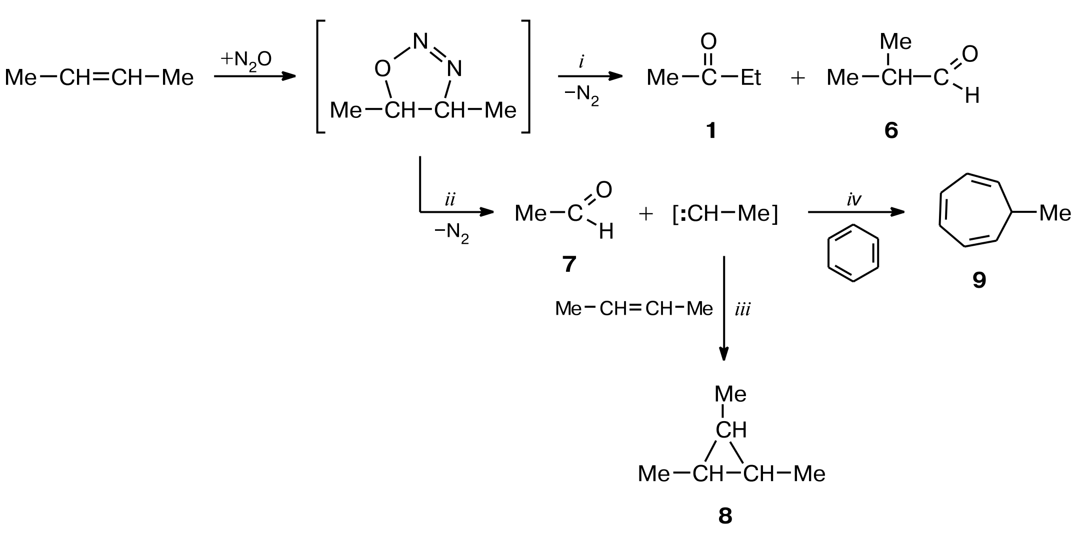
Fig. 3. Plots of the reaction rate (W) *vs.* initial amounts of but-2-ene (*1*) and N_2O (*2*) (according to the data in Table 4).

complex can decompose *via* two routes: without and with C—C bond cleavage in the complex. In the first case, methyl ethyl ketone (**1**) and isobutanal (**6**) are formed (route *i*); in the second case, acetaldehyde (**7**) and ethylidene :CH—Me are formed (route *ii*). The latter reacts subsequently with but-2-ene and benzene to afford 1,2,3-trimethylcyclopropane (**8**, route *iii*) and 7-methylcyclohepta-1,3,5-triene (**9**, route *iv*), respectively.

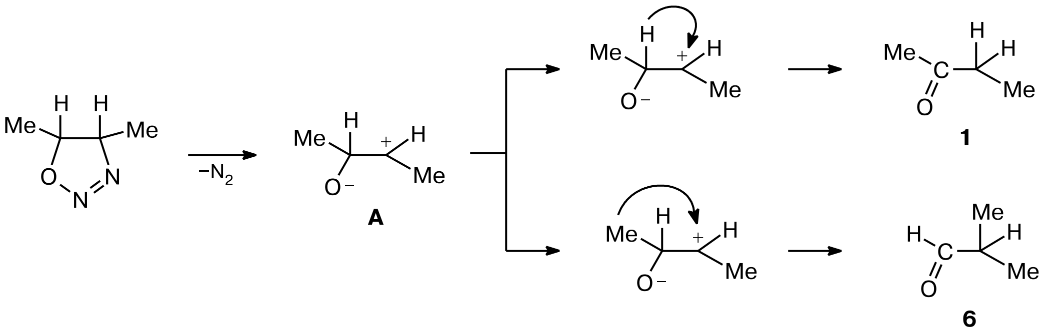
The formation of butanal **6** in step *i* can be understood by the detailed consideration of the mechanism of "non-cleavage" decomposition of the oxadiazoline complex shown in Scheme 4. It can be proposed that the elimination of an N_2 molecule in this complex affords a compound (**A**), whose further rearrangement proceeds as either hydride 1,2-shift to form **1**, or the 1,2-shift of the Me group to form isobutanal *via* the mechanism similar to the pinacoline rearrangement. The ratio of the amounts of these products (see Table 3) shows that hydrogen transfer is ~25-fold faster than the transfer of the Me group.

Although the rearrangement of compound **A** to alkene oxide (2,3-epoxybutane) cannot basically be excluded, this compound is not formed in the reaction. This fact agrees with the experimental data[12,14,15] and quantum-

Scheme 3



Scheme 4



chemical calculations,[16,17] which show that alkene oxides are neither intermediates, nor reaction products between alkenes and nitrous oxide.

It seems interesting to estimate the ratio of reaction rates *i* and *ii* (see Scheme 3), *i.e.*, the reactions with and without C—C bond cleavage in the oxadiazoline complex of but-2-ene. The fraction of step *ii*, which proceeds *via* the cleavage mechanism (F_{cleav}), can be expressed through the concentrations of the corresponding reaction products

$$F_{\text{cleav}} = C_7/(C_1 + C_6 + C_7). \qquad (6)$$

Calculation using the averaged data in Table 3 shows that the fraction of "cleavage" mechanism F_{cleav} for but-2-ene is only 8%, which is manifold lower than F_{cleav} for but-1-ene that is equal to 39%.

Ethylidene :CH—Me formed by the C—C bond cleavage is much less reactive than methylene :CH_2 and almost incapable of reacting with benzene. Estimation taking into account the amount of but-2-ene and benzene in the reaction system shows that the reactivity of this carbene toward benzene is at least two orders of magnitude lower than its reactivity toward alkene.

Regularities of the oxidation of linear alkenes. The data of the previous work[18] on the oxidation of linear alkenes were supplemented by the results on butene oxidation and are presented in Table 5. All the experiments were carried out at 220 °C for 12 h at similar initial amounts of alkenes and nitrous oxide. This set of substrates, including five terminal and two internal alkenes, makes it possible to analyze qualitatively the influence of the composition and structure of alkenes on the reaction course.

Reactivity of alkenes. Since the experiments were carried out under similar conditions, it seems reasonable to use the alkene conversion as a characteristic of the reactivity toward nitrous oxide. As can be seen from the data in Table 5, when the number of carbon atoms increases in the case of terminal alkenes, the conversion passes through a maximum and reaches the highest value for but-1-ene (38%). However, taking into account high differences in the physical properties of the alkenes under study, this estimation, most likely, is incorrect. We have already mentioned that the lower the boiling point of alkene, the greater its fraction occurrence in the gas phase, *i.e.*, outside the reaction zone, under the experimental conditions. The effect of unfavorable phase distribution should be especially pronounced for ethylene and weaken as the boiling point of the alkenes approaches that of the solvent (benzene, 80.1 °C). Taking into account this fact, we conclude that the data in Table 5 indicate a monotonic decrease in the reactivity of terminal alkenes with an increase in the number of carbon atoms in the series C_2—C_8. This conclusion is valid, probably, for internal alkenes.

The position of the double bond in an alkene molecule can also affect its reactivity. This question can be answered quite exactly by a comparison of two butene isomers. The results presented in Tables 1 and 3 and in Fig. 2 show that the reactivity of terminal but-1-ene is by ~1.5 times higher than that of internal but-2-ene.

Ratio of the reaction routes. As can be seen for but-1-ene (see Scheme 2), two reaction routes (M_1 and M_2) are possible. The probability of this or another route depends on the configuration of the intermediate oxadiazoline complex in which the oxygen atom is bonded to the first (complex **I**) or second (complex **II**) carbon atom. The contribution of each route can be estimated from the composition of the resulting products. The results of the estimation for the studied alkenes are given in Table 5 as a value of F_{M_1}, which is the fraction of route M_1 in the overall oxidation rate.

Naturally, in the case of ethylene when only complex **I** can form, F_{M_1} is 100%. When the formation of complex **II** becomes probable, the fraction of M_1 decreases sharply, being only 30% for propylene and 17% for but-1-ene. The F_{M_1} value remains approximately unchanged with the further elongation of the carbon chain. This implies that the formation of complex **II** is energetically more favorable than that of complex **I**, which agrees with the theoretical calculations.[17] This regularity can be due, probably, to the electrophilic nature of oxygen, due to which oxygen is preferentially bound to the carbon

Table 5. Oxidation of linear alkenes*

Entry	Alkene	B.p. /°C	X_R	F_{M_1}	F_{cleav}	Product	Yield (mol.%)
				%			
				Terminal alkenes			
1	Ethylene	−107.3	27	100	7	Acetaldehyde	91
						Cyclopropane	4
						Cycloheptatriene	3
2	Propylene	−47.8	26	30	29	Propanal	23
						Acetone	31
						Acetaldehyde	22
						Methylcyclopropane	4
						Cycloheptatriene	15
3	But-1-ene	−6.25	38	17	39	Butanal	13
						Methyl ethyl ketone	34
						Propanal	29
						Ethylcyclopropane	13
						Cycloheptatriene	9
4	Hex-1-ene	63.5	35	21	38	Hexanal	15
						Hexan-2-one	32
						Pentanal	27
						Butylcyclopropane	13
						Cycloheptatriene	10
5	Oct-1-ene**	121.3	30	19	39	Octanal	13
						Octan-2-one	28
						Heptanal	26
						Hexylcyclopropane	9
						Cycloheptatriene	18
				Internal alkenes			
1	But-2-ene	3.7	23	0	8	Methyl ethyl ketone	85
						Isobutanal	3
						Acetaldehyde	7
						Trimethylcyclopropane	3
2	Pent-2-ene	36.9	22	0	8	Pentan-2-one	41
						Pentan-3-one	47
						Acetaldehyde	5
						Propanal	3
						Cyclopropanes	1

* Reaction conditions: $N^0_R = 0.08$ mol, $N^0_{N_2O} = 0.12$ mol, solvent benzene (50 mL), 220 °C, and 12 h.

** The initial amount of oct-1-ene is 0.06 moles.

atom having an alkyl substituent and, hence, an enhanced electron-releasing ability.

Double bond cleavage. When studying butenes, we found that a molecule is cleaved at the double bond only if the reaction proceeds *via* route M_2, *i.e.*, through intermediate complex **II**. However, the data for ethylene (see Table 5) show that a small fraction of cleavage ($F_{cleav} = 7\%$) can also be observed for complex **I**, *i.e.*, for route M_1. The fact that this cleavage is not observed for the oxidation of other terminal alkenes can be related to its insignificant contribution to the overall reaction rate. In fact, if we accept that the fraction of cleavage for route M_1 is 7% in all cases, the contribution of this cleavage to the overall oxidation rate can be estimated for other alkenes. The estimation shows that it should be 2.1% for propylene and ~1.4% for other terminal alkenes, which virtually does not affect the composition of the reaction products.

As can be seen from the data in Table 5, for terminal alkenes, the contribution of the mechanism with C=C bond cleavage (F_{cleav}) to the overall oxidation rate increases sharply on going from ethylene (7%) to propylene (29%) and but-1-ene (39%) and further remains almost unchanged. Internal alkenes are much weaker prone to cleavage ($F_{cleav} = 8\%$). The reason for so high difference in the behavior of terminal and internal alkenes remains unclear. At first glance, this can be related to the dissipation of the energy that evolves upon the oxidative attack to the double bond, if assuming that the efficiency of this process is higher for the more remote position of the double bond from the "end" of the molecule. However, the fraction of cleavage for the "doubly" terminal ethylene is as low (7%) as that in the case of internal but-2-ene and pent-2-ene (8%). Therefore, this assumption is rather improbable.

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References

1. G. I. Panov, A. S. Kharitonov, and V. I. Sobolev, *Appl. Catal. A: General*, 1993, **98**, 1.
2. A. Reizman, M. Häfele, and G. Emig, *Trends Chem. Eng.*, 1996, **3**, 63.
3. G. Panov, A. Uriarte, M. Rodkin, and V. Sobolev, *Catal. Today*, 1998, **4**, 365.
4. G. Genti, S. Perathoner, and F. Vazzana, *CHEMTECH*, 1999, **48**.
5. G. Panov, *CATTECH*, 2000, **4**, 8.
6. A. V. Leont´ev, O. A. Fomicheva, M. V. Proskurina, and N. S. Zefirov, *Usp. Khim.*, 2001, **70**, 107 [*Russ. Chem. Rev.*, 2001, **70** (Engl. Transl.)].
7. T. Yamada, K. Hashimoto, Y. Kitaichi, K. Suzuki, and T. Ikeno, *Chem. Lett.*, 2001, 268.
8. K. Hashimoto, Y. Kitaichi, H. Tanaka, T. Ikeno, and T. Yamada, *Chem. Lett.*, 2001, 992.
9. K. Hashimoto, H. Tanaka, T. Ikeno, and T. Yamada, *Chem. Lett.*, 2002, 582.
10. R. Ben-Daniel, L. Weiner, and R. Neuman, *J. Am. Chem. Soc.*, 2002, **124**, 8788.
11. T. L. Stuchinskaya and I. V. Kozhevnikov, *Catal. Commun.*, 2003, **4**, 609.
12. F. S. Bridson-Jones, G. D. Buckley, L. H. Cross, and A. P. Driver, *J. Chem. Soc.*, 1951, 2999.
13. F. S. Bridson-Jones and G. D. Buckley, *J. Chem. Soc.*, 1951, 3009.
14. G. I. Panov, K. A. Dubkov, E. V. Starokon, and V. N. Parmon, *React. Kinet. Catal. Lett.*, 2002, **76**, 401.
15. K. A. Dubkov, G. I. Panov, E. V. Starokon, and V. N. Parmon, *React. Kinet. Catal. Lett.*, 2002, **77**, 197.
16. V. I. Avdeev, S. Ph. Ruzankin, and G. M. Zhidomirov, *Chem. Commun.*, 2003, 42.
17. V. I. Avdeev, S. F. Ruzankin, and G. M. Zhidomirov, *Kinet. Katal.*, 2005, **46**, No. 2, 191 [*Kinet. Catal.*, 2005, **46**, No. 2 (Engl. Transl.)].
18. E. V. Starokon, K. A. Dubkov, D. E. Babushkin, V. N. Parmon, and G. I. Panov, *Adv. Synth. Catal.*, 2004, **346**, 268.
19. W. Kirmse, *Carbene Chemistry*, Academic Press, New York, 1971.
20. O. M. Nefedov, A. I. Ioffe, and L. G. Menchikov, *Khimiya karbenov* [*The Chemistry of Carbenes*], Khimiya, Moscow, 1990, 304 pp. (in Russian).
21. A. K. Uriarte, *Stud. Surf. Sci. Catal.*, 2000, **130**, 743.
22. A. S. Noskov, I. A. Zolotarskii, S. A. Pokrovskaya, V. N. Korotkikh, E. M. Slavinskaya, V. V. Mokrinskii, and V. N. Kashkin, *Chem. Eng. J.*, 2003, **91**, 235.

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