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Nitrous oxide as a selective oxidant for ketonization of C=C double bonds in organic compounds

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The oxidation chemistry of nitrous oxide (N_2O) includes a wide range of both catalytic and non-catalytic selective oxidation reactions. This review summarizes the results of modern experimental and theoretical studies devoted to non-catalytic oxidation reactions of N_2O with carbon – carbon double bonds of alkenes and polymers. It is shown that these reactions open up a promising way for the synthesis of diverse carbonyl compounds (ketones and aldehydes) as well as a new type of functionalized oligomers — unsaturated polyketones. Possible applications of unsaturated polyketones, as well as economic aspects of N_2O production and use as a selective oxidant are discussed.
The bibliography includes 109 references.

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I. Introduction

Selective oxidation of organic compounds with molecular oxygen forms the basis for a variety of industrial catalytic processes for the production of valuable oxygenates.[1–5] However, this approach is not always efficient. Often, the use of O_2 leads to low reaction selectivity because of intense formation of complete oxidation products. New opportunities for such reactions are offered by alternative oxidants, among which nitrogen oxide(I) (nitrous oxide) has drawn especially high attention in recent years.

The properties of N_2O as a selective oxidant were first discovered in the gas-phase[6–8] and later liquid-phase catalytic oxidation of various hydrocarbons.[9–11] Numerous publications on this subject are surveyed in a number of reviews.[12–21] A vivid example of the selective action of N_2O is direct oxidation of benzene to phenol. Many-year researchers' efforts to conduct this reaction in one stage by using O_2 have not met with success. The application of N_2O fundamentally changed the situation. In this case, the reaction catalyzed by FeZSM-5 zeolite provides ~100% selectivity to phenol.[16]

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Apparently, the most remarkable feature of nitrous oxide as an oxidant is the unique ability to selectively oxidize organic compounds at C=C double bonds without a catalyst. The key goal of the present review is to consider recent studies in this area carried out in the last 15 years with emphasis put on the mechanisms of this type of reactions. Our early studies along this line have been briefly covered in review articles.[18,19]

The non-catalytic reactions of N_2O were discovered in 1951 by a research team from the ICI British company.[22,23] The idea of the authors was to switch from the known high-temperature combustion of hydrocarbons in an N_2O atmosphere to their partial oxidation by conducting the reaction at reduced temperatures. To maintain a reasonable process rate, the decrease in the temperature was counterbalanced by very high pressure. Under typical experimental conditions (300 °C, 45 – 50 MPa), the reactants existed, most often, in the gas phase or in the supercritical state. Generally, the idea of the researchers cited[22,23] has proved itself. Indeed, the oxidation of alkenes was found to afford considerable amounts of carbonyl compounds — ketones and aldehydes. However, the selectivity of these reactions was moderate and did not exceed 65% even in the best cases (*e.g.*, in cyclohexene oxidation). Low selectivity and difficulty of conducting these experiments were the reason for the absence of any known attempts to reproduce these results in the subsequent 50 years.

The new interest in alkene oxidation with nitrous oxide arouse in the very beginning of the 21st century when the researchers from the Boreskov Institute of Catalysis, Siberian Branch of the RAS, discovered the possibility of conducting this reaction in the liquid phase under markedly milder conditions.[24–26] This resulted in a dramatic increase in the selectivity to carbonyl compounds, which in some cases approached 100%. This rather broad class of reactions involving various types of alkenes (aliphatic, cyclic, heterocyclic and so on) was initially called carboxidation.[18] However, since ketones are often formed as the major products, these reactions are also called ketonization.[19,27]

Basing on the works performed at the Boreskov Institute of Catalysis, BASF developed[28–32] and commissioned in 2009 two new industrial processes[33] for the production of cyclopentanone and cyclododecanone by ketonization of cycloalkenes. This was the first example of commercial use of N_2O as a selective oxidant.

It is known that, apart from alkenes, many natural and synthetic polymers also contain unsaturated C=C bonds. It turned out that in this case, too, N_2O can selectively perform ketonization reaction, which is suitable for both modification of polymers and production of oligomeric materials of a new type.[34–36]

Currently, the oxidation chemistry of nitrous oxide, which is rather cheap, readily accessible and convenient for handling, is far from being completely investigated. Presumably, many new reactions involving this molecule are still to be discovered. Indeed, recently it was found that N_2O can act not only as the oxygen atom donor, but also as the diazo group donor, which opens up a new synthetic path to diazo compounds. The possibility of carbene generation in the reactions with N_2O also deserves attention. All this calls for a closer acquaintance with the works in this area and stimulates further research along this promising line.

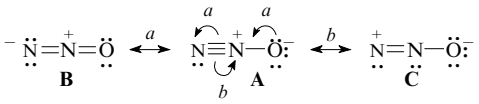
The list of the main abbreviations used in the review is presented below.

AA — acetaldehyde;
BA — butanal;
BBF — butane – butene fraction;
BNR — butadiene nitrile rubber;
HHP — 3a-hydroxyhexahydropntalen-1-one;
1,4-DK — cyclooctane-1,4-dione (1,4-diketone);
1,5-DK — cyclooctane-1,5-dione (1,5-diketone);
DMCP — 1,1-dimethylcyclopropane;
iBA — isobutanal;
MCHT — 7-methylcyclohepta-1,3,5-triene;
MEK — methyl ethyl ketone;
USK — cyclooct-4-enone (unsaturated ketone);
PA — propanal;
SBR — synthetic butadiene rubber;
SIR — synthetic isoprene rubber;
THP — 3,4,5,6-tetrahydro-2*H*-pentalen-1-one;
TMCP — 1,2,3-trimethylcyclopropane;
CHT — cyclohepta-1,3,5-triene;
COD — cycloocta-1,5-diene;
CPC — cyclopentanecarbaldehyde;
ECP — ethylcyclopropane.

II. Structure and physicochemical properties of nitrous oxide

The structure of the N_2O molecule is usually depicted by two zwitterion resonance structures **A** and **B**[17,37,38] and structure **C**,[17,39,40] which is a 1,3-dipole (Scheme 1).

Scheme 1



It is presumed that the major contribution to the structure description of the N_2O molecule is made by structure **A**. The effective charges (q) on the atoms calculated by Houk *et al.*[37] are as follows: $q(N) = -0.14$, $q[N(O)] = 0.47$, $q(O) = -0.33$, while according to Olah *et al.*,[41] the charges are $q(N) = -0.07$, $q[N(O)] = 0.62$, $q(O) = -0.55$. This charge distribution accounts for a rather low dipole moment of N_2O: 0.161 D.[42] The N–N and N–O bond lengths in the N_2O molecule are 1.128 and 1.184 Å, which corresponds to 2.73 and 1.61 bond orders.[17]

The N_2O molecule is a representative of a broad class of compounds capable of participating in 1,3-dipolar cycloaddition ([3 + 2]-cycloaddition) with dipolarophiles.[37–40,43] Particularly these reactions involving N_2O are considered below.

The key properties of nitrous oxide are summarized in Table 1.[17,19,44,45] Although the N_2O molecule is thermodynamically unstable ($\Delta_fG^\circ_{298} = 24.6$ kcal mol^{-1}), it is fairly kinetically stable. In the absence of a catalyst, its thermal decomposition to N_2 and O_2 has an activation barrier of ~59 kcal mol^{-1} and becomes noticeable only at temperatures above 600 °C.[17,46]

The release of the O atom from N_2O is energetically more favourable than that from the O_2 molecule.[47]

$$N_2O \longrightarrow N_2 + O \qquad (1)$$

($\Delta_rH^\circ_{298} = 40.0$ kcal mol^{-1}; $\Delta_rG^\circ_{298} = 30.5$ kcal mol^{-1})

Table 1. Properties of nitrous oxide.[17, 19, 44, 45]

Parameter	Value
Boiling point /°C	−88.48
Melting point /°C	−90.86
Critical temperature /°C	36.5
Critical pressure /MPa	7.17
Critical density /kg litre^{-1}	0.452
Water solubility at 20 °C /cm^3 of N_2O in 1 cm^3 of H_2O	0.67
Enthalpy of formation ($\Delta_f H^\circ_{298}$) /kcal mol^{-1}	19.6
Entropy of formation ($S^\circ_{f\,298}$) /cal K^{-1} mol^{-1}	52.52
Gibbs energy of formation ($\Delta_f G^\circ_{298}$) /kcal mol^{-1}	24.6
Heat capacity (C°_p) /cal K^{-1} mol^{-1}	9.19

$$\frac{1}{2}O_2 \longrightarrow O \qquad (2)$$

($\Delta_r H^\circ_{298}$ = 59.6 kcal mol^{-1}; $\Delta_r G^\circ_{298}$ = 55.3 kcal mol^{-1})

Nitrous oxide is rather readily soluble in organic solvents. For example, at 24 – 25 °C and a pressure of 0.1 MPa, the following amounts of N_2O can be dissolved in 1 cm^3 of solvents: 5.5 cm^3 in acetone, 5.74 cm^3 in methyl acetate, 4.93 cm^3 in amyl acetate, 4.55 cm^3 in acetic acid, 5.26 cm^3 in chloroform, 3.92 cm^3 in tetrachloromethane, 3.38 cm^3 in benzene, 3.0 cm^3 in benzaldehyde, 3.23 cm^3 in methanol and 2.85 cm^3 in ethanol.[45]

Nitrous oxide can form ignitable mixtures with organic compounds. This should be taken into account to provide safe conditions for using N_2O as an oxidant. Data on the flammability limits for hydrocarbons in mixtures with N_2O are scarce and have mainly been obtained at room temperature and atmospheric pressure (Table 2).[19, 48 – 51] The flammability limits for mixtures with N_2O are somewhat wider than those with air, but narrower than those with O_2. Mixtures with N_2O become non-flammable at any component ratio upon the addition of 75% – 78% of an inert diluent gas (He, Ar, N_2 and so on).[48, 49]

In relation to methane, cyclohexene and benzene mixtures with N_2O, the upper flammability limits have been shown[49] to depend little on temperature in the 20 – 200 °C range (see Table 2). However, with increasing initial pressure, the flammability range is extended. For example, as the pressure increases from 0.1 to 0.8 MPa, the upper limit for cyclohexene mixtures with N_2O at 200 °C increases from 19.4 vol.% to 26.7 vol.%.[49]

Table 2. Flammable limits of organic compounds in mixtures with N_2O at an initial pressure of 0.1 MPa.

Compound	Initial temperature /°C	Concentration limits (vol.%)		Ref.
		lower	upper	
Methane	20	3.9	40.0	50
	22	–	46.5	49
	200	–	49.0	49
Propane	20	2.1	24.8	50
n-Butane	20	1.8	21.0	50
		0.17	21.5	48
Ethylene	20	1.9	40.0	51
Propene	20	1.8	26.8	50
		1.45	29.0	51
Cyclopropane	20	1.6	30.3	51
Cyclohexane	20	0.33	16.5	48
Diethyl ether	20	1.5	24.2	51
Cyclohexene	50	–	19.6	49
	100	–	18.6	49
	200	–	19.4	49
Benzene	100	1.6	26.0	49
	150	1.25	26.5	49
	200	0.75	23.0	49
p-Xylene	20	0.19	13.0	48
Phenol	220	1.75	29.5	49

The equilibrium pressure above liquid N_2O at room temperature is ~5 MPa. Nitrous oxide is stored and transported in the liquefied state in steel cylinders or cooled tanks.

Below we consider the results of state-of-the-art studies devoted to non-catalytic reactions of N_2O with alkenes and polymers.

III. Liquid-phase non-catalytic oxidation of alkenes with nitrous oxide

III.1. Cycloalkenes

The liquid-phase non-catalytic oxidation of cyclohexene and cyclopentene with nitrous oxide has been studied in detail.[24, 25, 52, 53] The reactions were carried out under static conditions in a 100 cm^3 high-pressure reactor (Parr Instrument) at 140 – 280 °C and N_2O initial pressure ($P^0_{N_2O}$) of 1 – 2.5 MPa. It can be seen from Tables 3 and 4 that the

Table 3. Oxidation of cyclohexene to cyclohexanone with nitrous oxide.[24, 52, 53]

Entry No.	Reaction conditions			Reaction performance			W_R /mmol litre^{-1} h^{-1}
	T/°C	P_Σ /MPa	time /h	conversion of cyclo-C_6H_{10} (%)	conversion of N_2O (%)	selectivity to $C_6H_{10}O$ (mol.%)	
1	150	5.3	23	1.2	1.5	–	5.4
2	200	6	12	7.5	9.3	98	69
3	220	6.5	12	16.8	20.5	98	140
4	240	9	2	7.7	9.4	97	480
5	250	10	5	26.5	32	97	650
6	250	10	15	62	75	96	–
7	280	12	3	46	56	96.5	2100

Note. 100 cm^3 reactor, $P^0_{N_2O}$ = 2.5 MPa, 25 cm^3 cyclo-C_6H_{10}; W_R is the reaction rate.

Table 4. Oxidation of cyclopentene to cyclopentanone with nitrous oxide.[25, 52, 53]

Entry No.	Reaction conditions				Reaction performance			W_R /mmol litre^{-1} h^{-1}
	T / °C	$P^0_{N_2O}$ /MPa	P_Σ /MPa	time /h	conversion of cyclo-C_5H_8 (%)	conversion of N_2O (%)	selectivity to C_5H_8O (mol.%)	
1	140	1	3.2	24	1.5	4.9	98.5	7.5
2	170	1	3.8	15	4.9	15.9	98.0	40
3	200	1	4.6	5	7.7	24.8	98.5	200
4	200	1	4.6	12	15.6	51	98.5	170
5	230	1	6.1	3	13.0	42	98.3	610
6	200	2.5	–	2	9.7	12.3	99.0	630
7	200	2.5	–	20	67	85	98.5	–
8 [a]	200	2.5	–	+20 (+N_2O)	94		97.8	–

Note. 100 cm^3 reactor, 33 cm^3 of cyclo-C_5H_8. [a] See text.

oxidation proceeds especially actively starting from the temperature of 200 °C.

The selectivity to the corresponding ketones (cyclohexanone and cyclopentanone) depends little on the temperature and conversion, being equal to 96% – 98.5%. A similar selectivity of the same reactions (97% – 99%) at 180 °C and cycloalkene conversion of 5% – 10% was obtained by Hermans *et al.*[27] This high selectivity is due to the fact that the resulting ketones are not further oxidized with nitrous oxide. Therefore, for example, the conversion of cyclopentene can be brought to 94%, with the selectivity to cyclopentanone being maintained at 97.8% (see Table 4, entry 8). In this case, after entry 7, the reactor was cooled to room temperature, the gas phase was replaced by a fresh portion of N_2O (2.5 MPa), and additional oxidation was carried out at 200 °C for 20 h.

The activation energies for the oxidation of cyclopentene and cyclohexene found from the Arrhenius plots (Fig. 1) are equal and amount to 21 kcal mol^{-1}. Comparison of the reaction rates for cyclohexene (69 mmol litre^{-1} h^{-1}, see Table 3, entry 2) and cyclopentene (630 mmol litre^{-1} h^{-1}, see Table 4, entry 6) under similar conditions indicates that the reactivity of cyclopentene towards N_2O is approximately an order of magnitude higher.

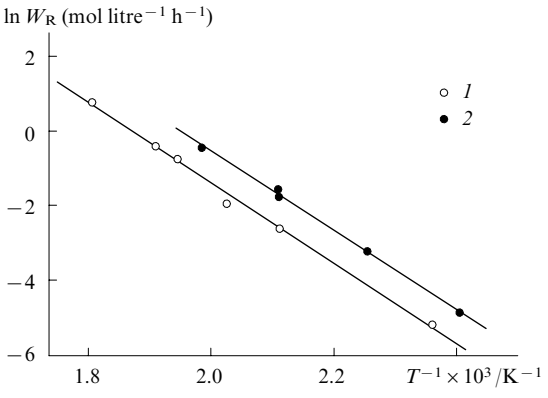


Figure 1. Arrhenius plots for the oxidation rates of cyclohexene (*1*) and cyclopentene (*2*).[52]

Under the conditions used, arenes, alkanes, alcohols, nitriles and other organic compounds containing no C=C double bonds (for example, cyclohexane, toluene, acetonitrile, isobutyl alcohol) do not react with N_2O.[24, 25] They have no significant effect on the characteristics of alkene oxidation and, therefore, they can be used as solvents for the reaction.

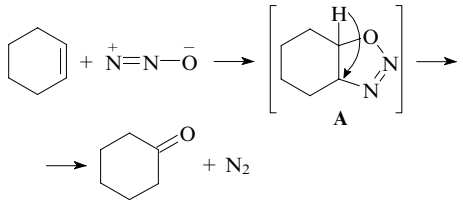
The orders of the reaction with respect to the alkene and N_2O found for the cyclohexene oxidation are close to one.[52, 53] Hence, the reaction is overall second order.

It was found[24, 25] that the oxidation of alkenes under these conditions occurs mainly in the liquid phase. For estimation of the contribution of the gas-phase oxidation, Panov *et al.*[24] conducted the experiment at 250 °C (100 cm^3 reactor, $P^0_{N_2O}$ = 2.5 MPa, 12 h) with a minor amount of cyclohexene (2.5 cm^3), which fully evaporated to the gas phase at the reaction temperature. In this case, the alkene conversion was only 0.5%. This is approximately two orders of magnitude lower than that in the oxidation of 25 cm^3 of cyclohexene (62%, see Table 3, entry 6), which is mainly in the liquid state at the reaction temperature. In addition, calculations of the phase diagrams for a number of reaction mixtures containing N_2O and various alkenes indicate that the system does not reach critical or near-critical state under these conditions.[53]

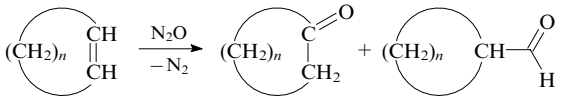
The high selectivity of cyclohexene and cyclopentene oxidation, relatively high activation energy and the lack of influence of hydroquinone added as a radical reaction inhibitor[24, 25] means that the oxidation evidently does not involve the formation of free radicals. Furthermore, N_2O oxidizes only the alkene double bonds and is inert towards other types of bonds (C–H, C–C, C=O, *etc.*).

The reaction mechanism includes, most likely, the 1,3-dipolar cycloaddition of N_2O to the C=C bond of alkene. This mechanism, which was first proposed by Bridson-Jones *et al.*,[22] is in good agreement with both experimental data[22 – 27] and results of quantum chemical modelling of the reactions between N_2O and a number of alkenes.[27, 40, 54 – 57] It has been shown in theoretical works[27, 56, 57] that the oxidation of cyclohexene to cyclohexanone should actually proceed *via* the intermediate formation of 4,5-dihydro[1,2,3]oxadiazole derivative (**A**, Scheme 2). Decomposition of the intermediate in the second step, which includes H atom transfer to the neighbouring carbon atom (1,2-hydride shift) and release of an N_2 molecule, yields ketone.

Scheme 2



Scheme 3



The calculated activation energy (27.8 kcal mol^{-1} according to Ref. 27 and 26.7 kcal mol^{-1} according to Refs 56 and 57) for the first step, which is the rate-limiting one, is close to the experimental value of 21 kcal mol^{-1}. The minor deviation from the experiment is obviously attributable to the fact that the calculations were performed for the gas-phase reaction without considering solvation effects. According to Hermans *et al.*,[27] the theoretical activation energy for the reaction of cyclopentene with N_2O is 24.3 kcal mol^{-1}, which is also close to the experimental value.

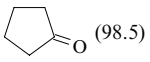
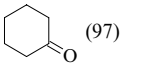
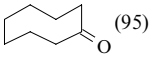
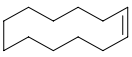
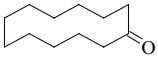
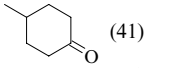
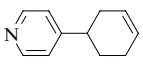
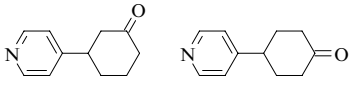
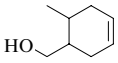
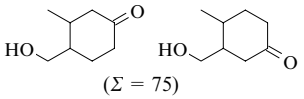
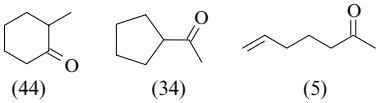
Table 5 summarizes the results of the liquid-phase oxidation of monocyclic alkenes with nitrous oxide.[19, 26] Owing to the symmetrical positions of the endocyclic 1,2-disubstituted C=C bond in cyclooctene and cyclododecene (see Table 5, entries 3, 4), they are also oxidized to give the corresponding ketones with a high selectivity (94% – 95%). The slight decrease in the selectivity to the ketone in the series of C_6 – C_{12} cycloalkenes is largely related to increasing contribution of the reaction that leads to the ring size decreasing by one carbon atom and gives cyclic aldehyde (Scheme 3).

Also, the linear unsaturated aldehyde (the product of oxidation with the initial C=C bond cleavage and ring opening) and the products of aldol crotonic condensation of the ketone are also formed in a low concentration. For example, in the oxidation of cyclohexene, cyclopentanecarbaldehyde predominates among the by-products, while in the case of cyclopentene, the linear aldehyde (pent-4-enal) is the main by-product, which is evidently due to instability of the saturated four-membered ring.

When the ring contains a substituent remote from the double bond, the reaction is most often also highly selective. For instance, the oxidation of 4-methylcyclohexene (see Table 5, entry 5) and 4-(cyclohexen-4-yl)pyridine (entry 6) affords two expected ketone isomers with a total selectivity of 95% and 97%, respectively. In the case of 6-methylcyclohex-3-enylmethanol (see Table 5, entry 7), the selectivity decreases, mainly due to the side dehydration involving the CH_2OH group.

The oxidation of 1-methylcyclohexene (see Table 5, entry 8) containing a trisubstituted double bond follows a different pathway. The reaction gives three major products: the expected cyclic ketone, 2-methylcyclohexanone (with 44% selectivity); a ketone with a smaller ring, methyl cyclopentyl ketone (34%); and hept-6-en-2-one resulting from ring cleavage at the initial C=C bond (5%).[26] A similar product ratio was obtained by Hermans *et al.*[27] The

Table 5. Oxidation of monocyclic alkenes with nitrous oxide.[19, 26]

Entry No.	Alkene	T/°C	Time /h	Alkene conversion (X_R) (%)	Major products [selectivity (mol.%)]
1		200	20	67	 (98.5)
2		250	5	26.5	 (97)
3		220	12	56	 (95)
4		250	3	22	 (94)
5		220	5	10	 (41) (54)
6		250	5	15	 (45) (52)
7		250	5	16	 (Σ = 75)
8		250	12	33	 (44) (34) (5)

Note. 100 cm^3 reactor, $P^0_{N_2O}$ = 2.5 MPa, 25 cm^3 of alkene.

composition of products suggests that in this case, the N_2O oxygen atom adds to both positions of the unsymmetrical double bond. This was confirmed by quantum chemical calculations,[27] which state that in the formation of the oxadiazoline intermediate, the selectivity of addition of the N_2O oxygen atom to position 1 is ~65% and that to position 2 is ~35%. The reactivity of 1-methylcyclohexene proves approximately twice lower than that of cyclohexene.[27, 53]

III.2. Bicyclic alkenes

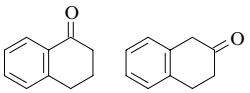
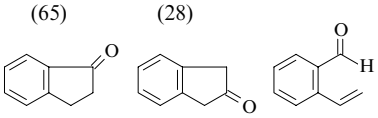
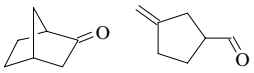
1,2-Dihydronaphthalene is oxidized (Table 6, entry 1) to give α- and β-tetralones with high selectivity (93% – 95%).[26] The oxygen atom adds predominantly to the α-position. In the case of indene (see Table 6, entry 2), the major products are also the corresponding ketones — α- and β-indanones (77%). However, the contribution of the C=C bond cleavage reaction to give 2-vinylbenzaldehyde becomes noticeable (10%).

In the case of norbornene (see Table 6, entry 3), which has a double bond in the strained ring, the contribution of the ring cleavage reaction is even higher. Therefore, the unsaturated aldehyde (3-methylenecyclopentanecarbaldehyde, 29%) is formed in approximately the same amount as the ketone (norcamphor, 28%).

III.3. Heterocyclic alkenes

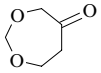
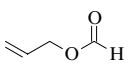
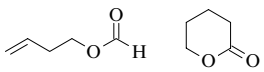
The oxidation of heterocyclic alkenes with the endocyclic C=C bond is affected most appreciably by two factors: the nature of the heteroatom and position of the double bond. The effect of the heteroatom nature has been evaluated [26] in relation to five-membered unsaturated heterocycles that have similar structures, but contain an oxygen (2,5-dihydrofuran), nitrogen (3-pyrroline) or sulfur atom (3-sulfolene). Among these compounds, only 2,5-dihydrofuran is

Table 6. Oxidation of bicyclic alkenes with nitrous oxide.[18, 19, 26]

Entry No.	Alkene (concentration, solvent)	T/°C	Time /h	Alkene conversion (X_R) (%)	Major products [selectivity (mol.%)]
1					
	(5 cm³ in 20 cm³ of benzene)	220	5	17	(65) (30)
		250	5	46	(65) (28)
2					
	(5 cm³ in 20 cm³ of benzene)	250	5	35	(63) (14) (10)
3					
	(5 g in 45 cm³ of cyclohexane)	180	4	42	(28) (29)

Note. 100 cm³ reactor, $P^0_{N_2O}$ = 2.5 MPa.

Table 7. Oxidation of heterocyclic alkenes with nitrous oxide.[18, 19, 26]

Entry No.	Compound (concentration, solvent)	$P^0_{N_2O}$ /MPa	T/°C	Time /h	Alkene conversion (X_R) (%)	Major products [selectivity (mol.%)]
1						
	(0.13 mol in 50 cm³ of benzene)	1	220	12	16	(94)
2						
	(0.1 mol in 15 cm³ of benzene)	2.5	220	5	16	(94)
3						
	(0.13 mol in 60 cm³ of cyclohexane)	1	200	5	34	(71)
4						
	(0.11 mol in 50 cm³ of benzene)	2.5	240	5	20	(48) (31)

Note. 100 cm³ reactor.

selectively oxidized. 3-Pyrroline and 3-sulfolene undergo intensive side reactions to give a lot of unidentified products.

The effect of the double bond position on the reaction can be followed in the series of O-heterocycles (Table 7).[18, 19, 26] 2,5-Dihydrofuran (entry 1) and 4,7-dihydro-1,3-dioxepine (entry 2) in which the C=C bond is remote from oxygen are oxidized to the expected ketones with high selectivity (94%). In the case of 2,3-dihydrofuran and 3,4-dihydro-2*H*-pyran (entries 3 and 4) with closer oxygen and double bond positions, the bond cleavage and ring opening reaction route predominates, resulting in the formation of allyl formate and but-3-enyl formate, respectively. 2,3-Dihydrofuran is oxidized with the bond cleavage only, while the oxidation of 3,4-dihydro-2*H*-pyran with a less strained six-membered ring follows also the route without bond cleavage to give δ-valerolactone.

III.4. Cyclodienes

Cyclodienes contain two double bonds, which can successively react with N_2O yielding first unsaturated ketone and then diketone. Ivanov *et al.*[58] reported a detailed study of the liquid-phase oxidation of cycloocta-1,5-diene (COD) containing isolated double bonds. The reaction was carried out in benzene at 200–280 °C. From the obtained data (Table 8), it can be seen that the expected unsaturated ketone, cycloocta-4-enone (USK), and two isomeric diketones, cyclooctane-1,4- and -1,5-diones (1,4-DK and 1,5-DK) are the major reaction products when the COD conversion is below 30%. At higher conversion, two more products are formed: 3a-hydroxyhexahydropentalen-1-one (HHP) and 3,4,5,6-tetrahydro-2*H*-pentalen-1-one (THP). The total yield of oxygenates upon complete conversion of COD is >90%.

The pattern of variation of the concentration of unsaturated ketone with time during the reaction at 250 °C (Fig. 2) clearly attests to a consecutive mechanism of oxidation with the unsaturated ketone being formed as an intermediate product.

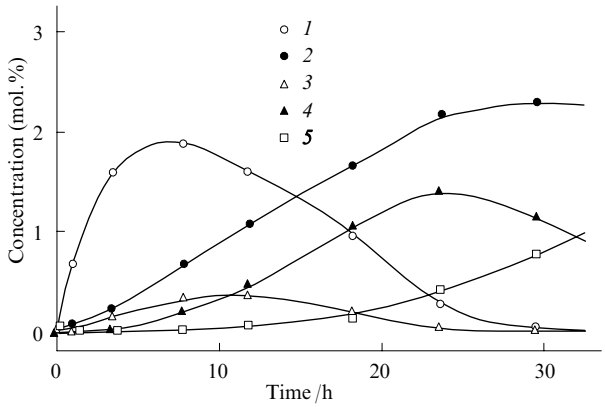


Figure 2. Concentrations of the products of cycloocta-1,5-diene oxidation at 250 °C *vs.* reaction time.[58]
(*1*) Cyclooct-4-enone, (*2*) cyclooctane-1,5-dione, (*3*) cycloctane-1,4-dione, (*4*) 3a-hydroxyhexahydropentalen-1-one, (*5*) 3,4,5,6-tetrahydro-2*H*-pentalen-1-one.

Similarly to oxidation of other alkenes, the COD oxidation proceeds, most likely, as the 1,3-dipolar cycloaddition of N_2O to the C=C bond. The reaction at the first double bond leads to the formation of unsaturated ketone (USK, Scheme 4). The oxidation of the second bond can follow two routes depending on the position of the oxygen atom. Route *a* leads to 1,5-diketone and route *b* affords unstable 1,4-diketone, which undergoes intramolecular aldol crotonic condensation to give HHP and then THP. This conclusion is confirmed by the fact that the ratio of the products formed according to route *a* (1,5-DK) and route *b* (1,4-DK + HHP + THP) remains approximately constant (~0.55 : 0.45), irrespective of the reaction conditions.

Scheme 4

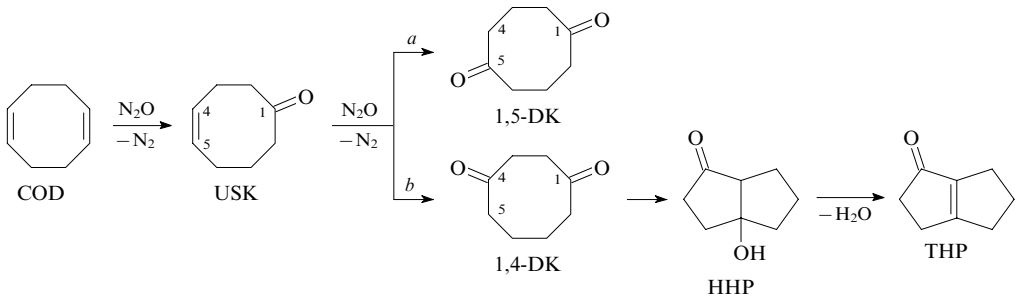


Table 8. Effect of temperature on the oxidation of cycloocta-1,5-diene.[58]

Entry No.	*T*/°C	Conversion (%)			Selectivity (mol.%)					
		N_2O	COD	C=C	USK	1,5-DK	1,4-DK	HHP	THP	other products
1	200	2.1	11.7	6.2	92.9	2.6	1.9	0	0	2.6
2	220	6.0	30.7	17.7	84.9	7.1	5.7	0	0	2.3
3	250	22.7	84.5	67.3	40.8	28.5	10.5	11.7	1.4	7.1
4	280	31.3	100	92.7	4.3	48.9	0	22.9	15.6	8.3

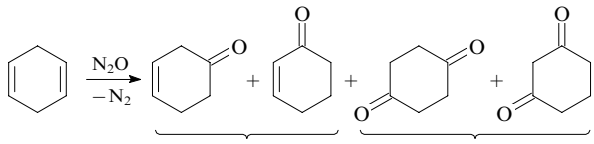
Note. 100 cm^3 reactor, 0.096 mol of N_2O, 0.0162 mol of COD, 30 cm^3 of benzene, 12 h.

The reaction rate and the ratio between routes *a* and *b* depend little on the type of the solvent (benzene, cyclohexane, acetonitrile, THF, 1,4-dioxane). The activation energy for the COD oxidation is 27 kcal mol^{-1}. As in the case of other alkenes, the reaction has an overall second order.

An important specific feature of the reactions of N_2O with dienes is the distribution of products of consecutive oxidation of two double bonds. In the COD oxidation, the relative fraction of the unsaturated ketone in the final reaction mixture and the total fraction of all transformation products (1,5-DK, 1,4-DK, HHP and THP) are close to statistical values. This attests to equal reactivity of the C=C bonds in COD and USK with respect to N_2O.

Unlike cycloocta-1,5-diene, in the case of cyclohexa-1,4-diene oxidation with closer positions of double bonds, the formation of the first C=O group, which has strong electron-withdrawing effect, markedly decreases the reactivity of the remaining C=C bond.[26] When the diene conversion is 37%, the fraction of diketones in the products is 3% instead of 9% expected statistically (Scheme 5).

Scheme 5



X_R = 37% (250 °C, 5 h): 90% (1 : 0.7) 3% (1 : 0.1)
[100 cm^3 reactor, 10 cm^3 of cyclo-C_6H_8, 20 cm^3 of benzene (solvent), $P^0_{N_2O}$ = 2.5 MPa]

Therefore, the major reaction products are unsaturated ketones — cyclohex-3- and cyclohex-2-enones, which are formed with high selectivity (90%). The formation of cyclohex-2-enone is obviously related to C=C bond migration under the reaction conditions to a position conjugated with the C=O group.

The oxidation of cyclohexa-1,3-diene, which has conjugated double bonds, is complicated by a substantial contribution of the side Diels – Alder reaction.[26] Therefore, for the total conversion of 80% (10 cm^3 of cyclo-C_6H_8, 50 cm^3 of cyclohexane, $P^0_{N_2O}$ = 1 MPa, 220 °C, 3 h), only 25% of the diene is oxidized to cyclic ketones.

III.5. Aliphatic alkenes

The liquid-phase nitrous oxide oxidation of three butene isomers differing in the position and degree of substitution of the double bond has been studied in a number of papers.[53, 59, 60] Owing to similar physical properties, they can be oxidized under the same conditions, which makes it possible to elucidate the effect of the alkene structure on the reaction mechanism. Table 9 summarizes the results of oxidation of but-2-ene with the 1,2-disubstituted internal C=C bond (a mixture of *trans*- and *cis*-isomers in 3 : 1 ratio) in benzene at 180 – 240 °C.[59] The major products of this reaction are carbonyl compounds: methyl ethyl ketone (MEK, ~84%), isobutyraldehyde (iBA, ~3.3%) and acetaldehyde (AA, ~7.4%), which in total account for ~95% of the products. Also, minor amounts of oxygen-free products are present: 1,2,3-trimethylcyclopropane (TMCP, ~3.9%) and 7-methylcyclohepta-1,3,5-triene (MCHT, ~0.2%). The product ratio depends little on the reaction conditions.

Table 9. Oxidation of but-2-ene with nitrous oxide.[59]

Entry No.	T/°C	Time /h	Conversion of but-2-ene (%)	Composition of products [C_i (mol.%)]						W_R /mmol litre^{-1} h^{-1}
				MEK	iBA	AA	TMCP	MCHT	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	18
3	220	3	6.4	84.5	3.5	7.0	3.6	0.2	1.2	34
4	220	12	23.1	85.1	3.3	7.2	3.4	0.1	0.9	31
5	240	2	12.5	83.9	3.6	7.7	3.3	0.2	1.3	100
Averaged concentrations:				84.0	3.3	7.4	3.9	0.2	1.2	

Note. 100 cm^3 reactor, 0.12 mol of N_2O, 0.08 mol of the alkene, 50 cm^3 of benzene.

Table 10. Oxidation of but-1-ene with nitrous oxide.[59]

Entry No.	T/°C	Time /h	Conversion of but-2-ene (%)	Composition of products [C_i (mol.%)]						W_R /mmol litre^{-1} h^{-1}
				MEK	BA	PA	ECP	CHT	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	12.3	2.0	26
3	220	3	11.9	34.1	12.7	30.6	12.7	7.4	2.5	64
4	220	12	37.9	33.3	13.4	29.4	12.6	9.5	1.8	51
5	240	2	17.6	32.7	14.2	30.0	12.3	8.7	2.1	140
Averaged concentrations:				33.8	12.8	29.5	13.1	9.0	1.8	

Note. 100 cm^3 reactor, 0.12 mol of N_2O, 0.08 mol of the alkene, 50 cm^3 of benzene.

Table 11. Oxidation of isobutene with nitrous oxide.[53]

Entry No.	T/°C	Time /h	Conversion of isobutene (%)	Composition of products [C_i (mol.%)]					W_R /mmol litre^{-1} h^{-1}
				acetone	iBA	DMCP	CHT	other products	
1	180	12	1.5	47.3	3.8	30.1	16.4	2.4	2.0
2	200	12	7.3	50.8	5.0	28.5	14.2	1.5	9.7
3	220	3	5.6	49.2	5.4	27.0	16.8	1.6	30
4	220	6	11.8	50.5	5.1	25.2	16.7	2.5	32
5	220	12	22.6	52.0	5.1	23.1	17.1	2.7	30
6	240	2	10.6	51.6	5.9	23.0	16.3	3.2	85
Averaged concentrations:				50.2	5.1	26.2	16.3	2.3	

Note. 100 cm^3 reactor, 0.12 mol of N_2O, 0.08 mol of the alkene, 50 cm^3 of benzene.

In the case of but-1-ene with the terminal monosubstituted C=C bond, the product composition and ratio crucially change (Table 10).[59] The oxidation under similar conditions affords MEK (~33.8%), butanal (BA, ~12.8%), propanal (PA, ~30%), ethylcyclopropane (ECP, ~13,1%) and cyclohepta-1,3,5-triene (CHT, ~9%). The total fraction of carbonyl products is ~76%.

The oxidation of isobutene (Table 11)[53] containing the terminal, but 1,1-disibstituted C=C bond affords only two carbonyl compounds: acetone (~50%) and isobutyraldehyde (~5.1%), with their total fraction being ~55%. The fraction of oxygen-free products — 1,1-dimethylcyclopropane (DMCP) and CHT — reaches 42.5%.

The activation energies for but-1-ene and but-2-ene oxidation determined from the Arrhenius plots (Fig. 3) are 21 and 22 kcal mol^{-1}, respectively;[59] they are close to theoretical values of 22–24 kcal mol^{-1} (but-1-ene) and 25.8 kcal mol^{-1} (but-2-ene).[57] For isobutene, the activation energy is somewhat higher (28 kcal mol^{-1}).[53] The reaction orders with respect to but-2-ene and N_2O found from the logarithmic dependences for the reaction rate at 220 °C on the initial amounts of reactants (Fig. 4), like those for the oxidation of other alkenes with nitrous oxide, are close to one.[53, 59] A comparison of the oxidation rates for butene isomers under identical conditions (see Tables 9–11) shows that the but-1-ene reactivity at 200–240 °C is approximately 1.5 times higher than that of but-2-ene and 2–2.5 times higher than that of isobutene.

The composition of products formed upon oxidation of butene isomers (see Table 9–11) is in good agreement with the mechanism of 1,3-dipolar cycloaddition of N_2O at the alkene double bond. Because of the symmetrical position of the C=C bond, the oxidation of but-2-ene can give only one isomer of the oxadiazoline intermediate (Scheme 6).[59] It can decompose without C=C bond cleavage (reaction *1*) with either H atom transfer along the C–C bond (1,2-hydride shift) to give MEK or methyl group transfer (1,2-alkyl shift) to give isobutyraldehyde. The ratio of these products demonstrates that the H atom transfer is ~25 times faster. According to quantum chemical calculations,[27, 61] the 1,2-hydride and 1,2-alkyl shifts occur simultaneously with N_2 molecule evolution by a concerted mechanism.

Decomposition of the intermediate with C–C bond cleavage (reaction *2*) affords acetaldehyde and ethylidene (:CHMe), which then reacts with the initial but-2-ene and benzene (reactions *3* and *4*) to give TMCP and MCHT, respectively.

In the case of oxidation of unsymmetrical but-1-ene (Scheme 7), two isomeric intermediates (**I** and **II**) and, hence, two reaction routes (*a* and *b*) are possible.[59] The addition of the oxygen atom to the first carbon atom of the

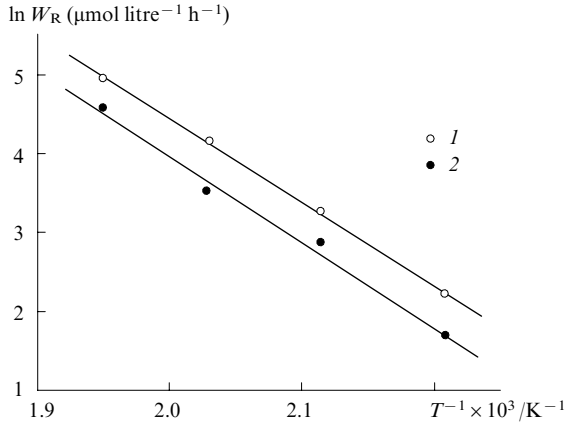


Figure 3. Arrhenius plots for the oxidation rates of but-1-ene (*1*) and but-2-ene (*2*).[59]

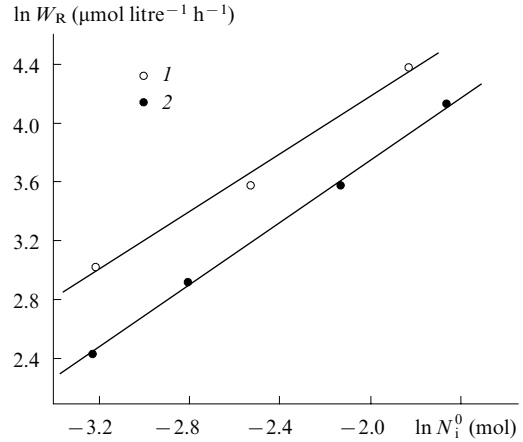
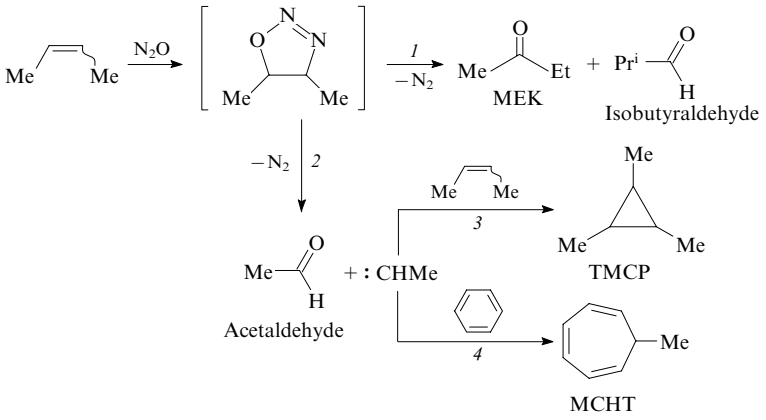
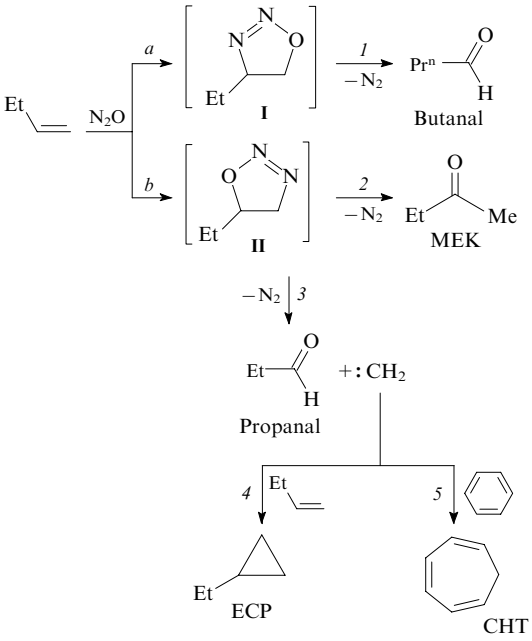


Figure 4. Oxidation rates at 220 °C *vs.* initial amounts (N_i) of but-2-ene (*1*) and N_2O (*2*).[53]

Scheme 6



Scheme 7



double bond leads to butanal (reaction *1*) and the addition to the second carbon atom yields MEK (reaction *2*).

Intermediate **II** can also decompose with C−C bond cleavage (reaction *3*) to give propanal and methylene, which reacts with but-1-ene or benzene (reactions *4* and *5*) to give ECP and CHT.

Possibly, bond cleavage may first give diazomethane (CH_2N_2), as has been suggested.[22,27] Since diazomethane is extremely unstable and is expected to rapidly decompose under the reaction conditions to methylene and nitrogen,[27] it is difficult to ascertain which active fragment is formed upon bond cleavage.

Similarly to other terminal alkenes[22,26,27] but-1-ene does not give formaldehyde upon oxidation, which could have been expected upon C−C bond cleavage in intermediate **I**. According to quantum chemical modelling of the reaction between hex-1-ene with N_2O, the theoretical contribution of this route to the overall reaction rate is indeed very low (~0.25%).[27]

The oxidation of isobutene (Scheme 8) can also follow two routes (*a* and *b*) involving intermediates **I** or **II**.[53] Intermediate **I** decomposes only without C=C bond cleavage to furnish isobutyraldehyde (reaction *1*). Upon decomposition of intermediate **II**, the C=O group can be formed only as a result of CH_3 group transfer or C−C bond cleavage. As has been shown above, this transfer is rather slow; therefore, intermediate **II** mainly decomposes with bond cleavage, giving rise to acetone and methylene (reaction *2*). Methylene then reacts with isobutene or benzene to give DMCP and CHT (reactions *3* and *4*).

The contributions of particular routes to the overall rates of oxidation for various alkenes can be calculated *via* the concentrations of the carbonyl products (C_i, see Tables 9 – 11). For example, in the case of but-1-ene (see Scheme 7), the contributions of the cleavage route (F_{cleav}) and route *a* (F_a) can be found from the following equations:

$$F_{cleav} = \frac{C_{PA}}{C_{BA} + C_{MEK} + C_{PA}} \times 100\ (\%) \qquad (3)$$

$$F_a = \frac{C_{BA}}{C_{BA} + C_{MEK} + C_{PA}} \times 100\ (\%) \qquad (4)$$

Scheme 8

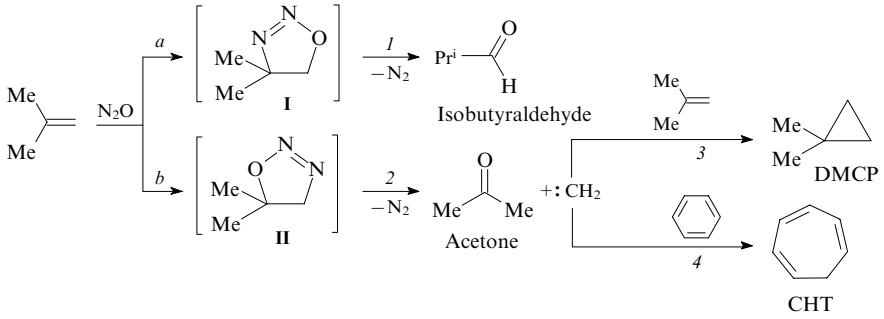


Table 12 presents a comparison of the oxidation of a number of terminal and internal C_2-C_8 aliphatic alkenes under similar conditions.[19, 26, 53, 59, 60] The contributions of the reaction routes were calculated using equations similar to Eqn (3) and (4) and data on the product ratios (see Table 12). Using these results, it is possible to analyze the key patterns of the oxidation of aliphatic alkenes with nitrous oxide.

The oxidation of linear terminal alkenes is similar to the oxidation of but-1-ene (see Scheme 7). It can be seen from Table 12 that in the case of symmetrical ethylene where only one intermediate is possible, the contribution of route *a* (F_a) is 100%. For propene, this value decreases to 30% and then to 17% – 21%. Thus implies that the addition of the N_2O oxygen atom to the second carbon atom in terminal alkenes (route *b*, see Scheme 7) is energetically more favourable.

This regioselectivity of N_2O cycloaddition can be attributed to the directing influence of the electron-donating alkyl substituents at the C=C bond in the terminal alkene, which shifts the electron density towards the first carbon atom.[27, 62] Therefore, the N_2O oxygen, which bears the major negative charge,[27, 37, 41, 57] should add predominantly to position 2, as is actually observed in experiments. This is also in line with the results of quantum chemical modelling.[27, 57] In particular, the theoretical contribution of route *a* for hex-1-ene is 25%,[27] which does not differ much from the experimental value of 21% (see Table 12, entry 4). For isobutene, which has two CH_3 groups at the second carbon atom, this influence should evidently be more pronounced, which is consistent with the very low fraction of route *a* (9%) for this alkene (see Table 12, entry 6).

For linear terminal alkenes, the contribution of the bond cleavage route sharply increases from ethylene (7%) to propene (29%) and but-1-ene (38%) and after that remains almost invariable (see Table 12). The relatively low contribution of the bond cleavage route in the case of ethylene is attributable to the fact that this route, giving rise to formaldehyde and methylene, has a higher activation barrier than the route in which the bond remains intact and acetaldehyde is formed.[61] In the oxidation of isobutene with the 1,1-disubstituted C=C bond, the contribution of the bond cleavage route can be as high as 91% (see Table 2, entry 6). This route becomes predominant and, hence, energetically the most favourable. In this case, a greater part of the reacting molecules are cleaved.

Considering the synthesis of carbonyl compounds, bond cleavage is an undesirable reaction route decreasing the selectivity. However, in the oxidation of terminal alkenes for which this reaction is most pronounced, it can be of separate interest for the generation of methylene ($:CH_2$). Methylene thus formed can be used for many synthetic reactions, in particular, to prepare cyclopropane derivatives. The simplest way of generating methylene is based on the thermal, photo or catalytic decomposition of diazomethane CH_2N_2,[63, 64] which is fairly toxic and explosive. The methylene formation *via* oxidation of alkenes with N_2O is an alternative method, which gives this carbene in especially high yield in the case of isobutene.

For the internal alkenes with the 1,2-disubstituted C=C bond (but-2-ene and pent-2-ene, which are equilibrium mixtures of *cis*- and *trans*-isomers), the contribution of the cleavage route is much lower (~8%) than for terminal alkenes and the formation of ketones is hence more selective (see Table 12, entries 7 and 8). The oxidation of symmetrical but-2-ene furnishes methyl ethyl ketone (85%) as the major product, while in the case of pent-2-ene, the major products are pentan-2- and -3-ones (88%).

In order to clarify the issue about the influence of spatial isomerism on the reactions of aliphatic alkenes with N_2O, Ivanov *et al.*[61] studied the liquid-phase oxidation of single *cis*- and *trans*-isomers of hept-3-ene under identical conditions. The reactions were carried out in a 25 cm^3 reactor at 200 – 240 °C for 6 – 12 h, the initial mixture contained 0.005 mol of alkene, 0.065 mol of cyclohexane (solvent)

Table 12. Oxidation of C_2-C_8 aliphatic alkenes with nitrous oxide.[19, 26, 53, 59, 60]

Entry No.	Alkene	Alkene conversion (%)	F_a (%)	F_{cleav} (%)	Products [content (mol.%)]
			Terminal alkenes		
1	Ethylene	27	100	7	Acetaldehyde (91), cyclopropane (4), cycloheptatriene (3)
2	Propene	26	30	29	Propanal (23), acetone (31), acetaldehyde (22), methylcyclopropane (4) cycloheptatriene (15)
3	But-1-ene	38	17	38	Butanal (13), methyl ethyl ketone (34), propanal (29), ethylcyclopropane (13), cycloheptatriene (9)
4	Hex-1-ene	35	21	37	Hexanal (15), hexan-2-one (29), pentanal (27), butylcyclopropane (14), cycloheptatriene (12)
5	Oct-1-ene [a]	30	19	39	Octanal (13), octan-2-one (28), heptanal (26), hexylcyclopropane (9), cycloheptatriene (18)
6	Isobutene	23	9	91	Acetone (52), isobutyraldehyde (5), dimethylcyclopropane (23), cycloheptatriene (17)
			Internal alkenes		
7	But-2-ene (*cis*/*trans*)	23	–	8	Methyl ethyl ketone (85), isobutyraldehyde (3), acetaldehyde (7), trimethylcyclopropane (3)
8	Pent-2-ene (*cis*/*trans*)	22	–	8	Pentan-2-one (41), pentan-3-one (47), acetaldehyde (5), propanal (3), cyclopropanes (1)

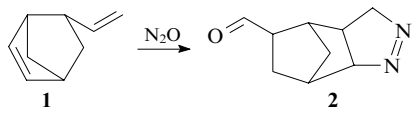
Note. 100 cm^3 reactor, 0.12 mol of N_2O, 0.08 mol of the alkene, 50 cm^3 of benzene, 220 °C, 12 h. [a] 0.06 mol of the alkene.

and 0.08 mol of N_2O. It turned out that *cis*- and *trans*-isomers have similar reactivities towards N_2O. For example, the rates of their oxidation at 240 °C are 23 and 24.8 mmol litre^{-1} h^{-1}, respectively. The activation energies are 20.1 and 19.8 kcal mol^{-1}, respectively, which are close to the theoretical values (24.3 and 25.5 kcal mol^{-1}). However, in the case of the *cis*-isomer, the averaged contribution of the cleavage route is only 4.2%, which is much lower than that for the *trans*-isomer (~13.5%). As a result, the fraction of ketones (heptan-3- and -4-ones) among the carbonyl products is higher for the *cis*-isomer (~94%) than for the *trans*-isomer (~82%).

III.6. Nitrous oxide as a diazo group donor

In a recent study dealing with the reaction of nitrous oxide with 5-vinyl-2-norbornene (**1**) (Scheme 9), which contains endocyclic and vinyl double bonds, the ability of N_2O to react with alkenes as a donor of not only an oxygen atom, but also a diazo group was found for the first time.[65,66] Unlike the reactions with other alkenes with simpler structures, in this case the liquid-phase reaction at 105 – 180 °C is not accompanied by nitrogen evolution and results in the formation of stable 1-pyrazoline derivative (4,5-dihydro-3*H*-pyrazole) **2** comprising both the aldehyde and diazo groups.

Scheme 9

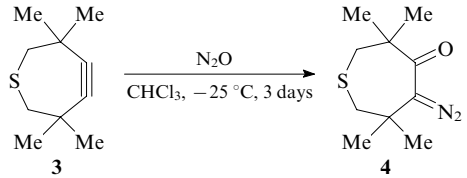


1 **2**

The selectivity to product **2** reaches 40%. It was isolated and identified by ^{1}H, ^{13}C and ^{15}N NMR spectroscopy. This product is formed most likely by a stepwise mechanism that includes cycloaddition of N_2O to the more reactive endocyclic double bond to afford the 1,2,3-oxadiazoline intermediate, the subsequent C – C bond cleavage in the intermediate giving a diazo compound containing CHN_2 and CHO groups, and then intramolecular 1,3-cycloaddition of the CHN_2 group to the vinyl C=C bond. Thus, the formation of product **2** incorporating all of the three atoms of the N_2O molecule can be regarded as the first piece of experimental evidence that nitrous oxide reacts with alkenes *via* the 1,2,3-oxadiazoline intermediate.

It is noteworthy that previously the addition of all atoms of the N_2O molecule during a thermal reaction with unsaturated compounds had been observed only in the reaction with a cyclic alkyne, 3,3,6,6-tetramethyl-1-thiacycloheptyne (**3**), at negative temperatures (Scheme 10).[67] In this case, the reaction leads to the formation of α-diazo ketone **4**, which is unstable at room temperature.

Scheme 10



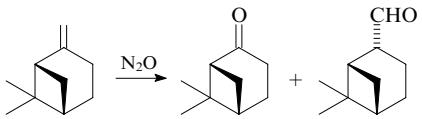
3 **4**

To summarize this Section, we can conclude that the liquid-phase oxidation with nitrous oxide can be accomplished for various types of alkenes: aliphatic, cyclic, bicyclic, heterocyclic compounds and their derivatives and also dienes. The oxidation occurs as a thermal reaction in the temperature range of 140 – 280 °C and affords ketones and aldehydes as the major products. The reaction route and selectivity depend significantly on the alkene structure. Nevertheless, in many cases, the oxidation occurs with a high selectivity exceeding 90%. This opens up a new synthetic route to a variety of carbonyl compounds.

Hermans *et al.*[68] successfully used this approach for ketonization of more complex compounds — fatty acid methyl esters and triglycerols. The selectivities to the corresponding ketones were as high as 95% – 99% at 220 – 240 °C, which is much superior to the characteristics of the traditional Wacker process.

Romanenko *et al.*[69] showed the possibility of preparing diverse carbonyl products by the liquid-phase nitrous oxide oxidation of monoterpenes (benzene as the solvent, 250 °C, 12 h). Under these conditions, the conversion of, for example, β-pinene (**5**) (Scheme 11) was 19%, with the major products being nopinone (**6**) (82.7%) and *cis*-dihydromyrtenal (**7**) (5.8%).

Scheme 11



5 **6** **7**

Newman *et al.*[70] investigated the nitrous oxide oxidation of a mixture of dodecene isomers containing an internal double bond in positions 2 – 6. The process was conducted at 300 – 375 °C and 6.2 – 10.3 MPa in a flow type reactor, which was supplied with 6.1 μl min^{-1} of dodecene and 12.1 μl min^{-1} of liquid N_2O. The reaction proceeded in both the liquid and gas phases. The dodecene conversion was up to 77% and the yield of ketones was up to 49%.

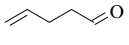
IV. Gas-phase oxidation of alkenes with nitrous oxide

Starokon *et al.*[71,72] demonstrated that cyclopentene and cyclohexene react with nitrous oxide in a gas phase under flow conditions in a temperature range of 300 – 450 °C and a pressure of up to 2 MPa. Like in the case of liquid-phase oxidation, these reactions yield cyclopentanone and cyclohexanone as the major products, while pent-4-enal and cyclopentacarbaldehyde (CPC), respectively, predominate among the by-products (Tables 13 and 14).

In both cases, the total selectivity to the carbonyl products barely depends on the temperature and is not less than 96%. However, on temperature rise, the selectivity to the ketone decreases as a result of increasing contribution of the reaction giving rise to aldehyde.

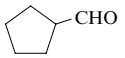
Similarly to the liquid-phase reactions, the gas-phase oxidation of cyclopentene and cyclohexene occurs, most probably, as the 1,3-dipolar cycloaddition of N_2O to the double bond. The formation of both ketone and aldehyde is evidently a consequence of two different routes existing for decomposition of the 1,2,3-oxadiazoline intermediate.[71,72] In the case of cyclopentene (Scheme 12),[71] decomposition of intermediate **B** without C – C bond cleavage (route *a*) is accompanied by 1,2-hydride shift and produces cyclopentanone. Bond cleavage (route *b*) gives rise to unstable carbene, which then isomerizes to linear unsatu-

Table 13. Gas-phase oxidation of cyclopentene with nitrous oxide.[53, 71]

Entry No.	T/°C	P/MPa	Conversion (%)		Selectivity (mol.%)		Contribution of route b (F_b) (%)	W_R /mmol litre^{-1} h^{-1}
			cyclo-C_5H_8	N_2O				
1	300	1	0.35	0.4	95	2.5	2.6	0.009
2	325	1	0.9	1.1	94	4.0	4.1	0.024
3	350	1	1.8	2.3	92	6.5	6.6	0.049
4	375	0.27	0.4	0.5	92	6.5	6.6	0.011
5	375	0.52	1.3	1.4	90	7.3	7.5	0.035
6	375	1	3.6	4.4	89	9.0	9.2	0.097
7	375	2	14.5	13.5	84	12.7	13.1	0.39
8	400	1	9.5	10.3	78	18	18.8	0.25
9	425	1	16.5	19.5	73	23	24.0	0.43

Note. 5 cm^3 reactor, 20 mol.% cyclo-C_5H_8, 20 mol.% N_2O, 60 mol.% He, flow rate 25 cm^3 min^{-1} (at 0 °C, 0.1 MPa).

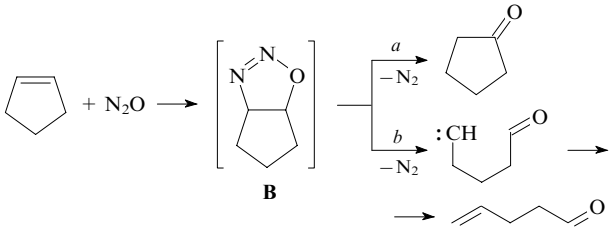
Table 14. Gas-phase oxidation of cyclohexene with nitrous oxide.[53, 72]

Entry No.	T/°C	Conversion (%)		Selectivity (mol.%)		Contribution of route b (F_b) (%)	W_R /mol litre^{-1} h^{-1}
		cyclo-C_6H_{10}	N_2O				
1	325	0.2	0.2	93	7.0	7.0	0.005
2	350	0.4	0.45	93	7.0	7.0	0.010
3	375	1.1	1.2	92	8.0	8.0	0.027
4	400	2.3	2.4	92.5	7.2	7.2	0.060
5	425	4.0	4.7	89	10.5	10.6	0.10
6	450	8.1	10.7	85	11.0	11.5	0.21

Note. 5 cm^3 reactor, 20 mol.% cyclo-C_6H_{10}, 20 mol.% N_2O, 60 mol.% He, flow rate 25 cm^3 min^{-1} (at 0 °C, 0.1 MPa), pressure 1 MPa.

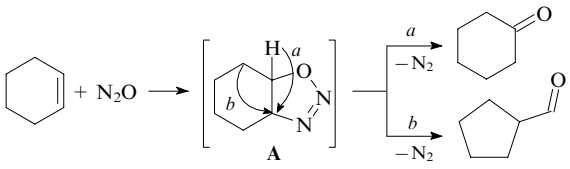
rated aldehyde (pent-4-enal). According to quantum chemical calculations,[27] this cleavage may result in the intermediate formation of 5-diazopentenal, which splits subsequently to give carbene and N_2.

Scheme 12



In the cyclohexene oxidation (Scheme 13), the major route *a*, which comprises decomposition of intermediate **A** with 1,2-hydride shift, also generates a ketone.[72] This route is similar to that considered above for the liquid-phase reaction (see Scheme 2). Starokon *et al.*[72] have suggested that cyclopentanecarbaldehyde is formed, similarly to pent-4-enal, upon bond cleavage decomposition of intermediate **A** followed by carbene cyclization. However, a different mechanism is also possible, namely, decomposition of the intermediate accompanied by 1,2-alkyl shift (route *b*, see Scheme 13),[53, 61] which occurs *via* formation of a bond

Scheme 13



between the 6th and 2nd carbon atoms in the ring to give cyclopentanecarbaldehyde. As noted in Section III.1, in the case of cyclopentene, the cyclic aldehyde is not formed obviously because of instability of the four-membered ring.

The contribution of route *b* (F_b) to the overall rates of cyclopentene and cyclohexene oxidation found from the product concentration ratio is close to the selectivity to the corresponding aldehyde (see Tables 13 and 14).

The Arrhenius plots for the overall rates of cyclopentene oxidation and pent-4-enal formation calculated from the contribution of route *b* (see Scheme 12) are shown in Fig. 5. The activation energy for route *a* leading to cyclopentanone is close to the activation energy of the overall reaction, which amounts to 24 kcal mol^{-1} (Ref. 71). This value is consistent with the theoretical value of 24.3 kcal mol^{-1} (Ref. 27). The activation energy for route *b* is higher,

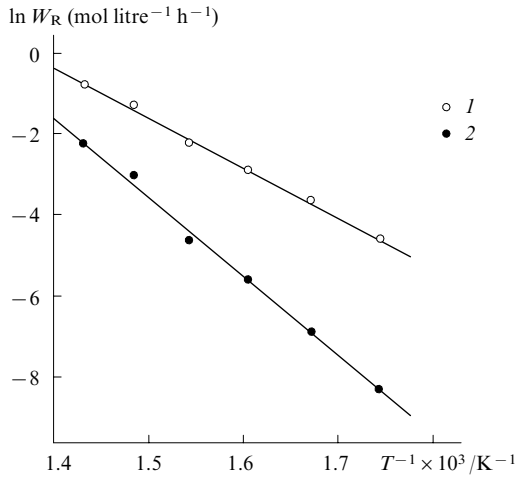


Figure 5. Arrhenius plots for the cyclopentene oxidation rate in the gas phase at a pressure of 0.1 MPa.[53, 71]
(*1*) Overall reaction rate, (*2*) pent-4-enal formation rate.

38 kcal mol^{-1}. Therefore, contribution of route *b* substantially decreases with decreasing temperature and becomes low for the liquid-phase oxidation of cyclopentene at 140 – 230 °C. This accounts for the formation of only a minor amount of pent-4-enal in the liquid-phase reaction (see Section III.1).

The activation energy for cyclohexene oxidation to cyclohexanone (route *a*, see Scheme 13) is 26 kcal mol^{-1} (Ref. 53), which is close to the theoretical values of 26.7 kcal mol^{-1} (Refs 56 and 57) and 27.8 kcal mol^{-1} (Ref. 27). The activation energy for route *b*, which leads to CPC, is only slightly higher (29 kcal mol^{-1}).[53] Therefore, although the contribution of route *b* does decrease with lowering the temperature, liquid-phase oxidation of cyclohexene at 200 – 280 °C (see Section III.1) still generates considerable amounts of CPC (2% – 3%). The overall order of the gas-phase oxidation of cyclopentene and cyclohexene under the action of N_2O is close to 2, like that of the liquid-phase oxidation.[53, 72]

These reactions could be of practical value for the synthesis of the corresponding cyclic ketones. The relatively low oxidation rates can be increased by either using higher reactant concentrations or increasing the pressure. For example, extrapolation of the results for cyclohexene (see Table 14) to a pressure of 4 MPa taking account of the second reaction order gives rather high cyclohexanone output: ~0.16 kg litre^{-1} h^{-1} at 425 °C and ~0.3 kg litre^{-1} h^{-1} at 450 °C.[72]

It has been shown in a patent[73] that the gas-phase nitrous oxide oxidation of butenes as a part of the butane – butene fraction (BBF) in the temperature range of 400 – 500 °C and at a pressure of up to 2 MPa provides C_2-C_4 carbonyl compounds with an overall selectivity up to 90%. For example, the oxidation of BBF containing 32.9 vol.% but-1-ene, 39.4 vol.% but-2-ene and 15.1 vol.% isobutene affords methyl ethyl ketone as the major product formed with a selectivity of up to 50%. At a temperature of 450 °C, a pressure of 1 MPa, a BBF : N_2O volume ratio of 7 : 3 and a residence time of 60 s, the conversions of N_2O and butenes are 78% and 40%, respectively.

V. Reactions of nitrous oxide with polymers

The chemical modification of polymers containing olefinic double bonds is among the key methods for the preparation of functionalized polymers.[74, 75] The high selectivity of alkene oxidation to carbonyl compounds with nitrous oxide indicates that a similar approach could be useful for the generation of carbonyl functional groups in polydienes. Basing on this idea, Dubkov and co-workers[34 – 36] investigated the reactions of N_2O with various types of rubber. Regarding these reactions, the term ketonization appears more appropriate than oxidation, as the latter is usually related to the undesirable non-selective oxidative destruction of polymers.

V.1. Ketonization of butadiene rubber

Dubkov *et al.*[34] studied the reaction of N_2O with *cis*-1,4-butadiene rubber (synthetic butadiene rubber, SBR) containing 250 C=C bonds per 1000 carbon atoms. The reaction was conducted in a benzene solution at 160 – 230 °C for 5 – 12 h (Table 15). The designation of polymeric products includes the reaction temperature (°C) and time (h). Like the oxidation of aliphatic alkenes, this reaction proceeds most actively at temperatures above 200 °C. According to the data of ^{1}H and ^{13}C NMR analysis of the initial rubber and polymeric products, N_2O is consumed only for the oxidation of double bonds in the rubber. Furthermore, the decrease in the concentration of C=C bonds is accompanied by the equivalent increase in the concentration of the C=O groups within the polymer. Among them, the fraction of ketone groups is, on average, 92% and that of aldehyde groups is only 8%.

According to gel permeation chromatography (GPC), the reaction is accompanied by a decrease in the polymer molecular weight (see Table 15), while narrow molecular weight distribution is retained ($M_w/M_n \approx 2.0$). The introduction of a small amount of oxygen affects little the molecular weight and, therefore, it can be used for chemical modification of rubber. The formation of a large number of C=O groups decreases the molecular weight by a large factor. For the most oxygenated SBR-230-12 sample (sample 6 in Table 15), which contains 9.8 mass % oxygen, M_n decreases ~50-fold — from 128 000 to 2700. In this case, the conversion of double bonds in the reaction with N_2O is 34%.

The decrease in the molecular weight is accompanied by a change in the product physical state. With increasing degree of ketonization, the products become less viscous, and upon the introduction of $\geqslant$5 wt.% oxygen, they become viscous liquids (see Table 15).

Table 15 also presents the average number of cleavage (N_{cleav}) in the initial rubber macromolecule. This value increases with increasing conversion of the C=C bonds to reach $N_{rupt} = 51$ for the SBR-230-12 sample, which is a liquid oligomer. In this case, the initial macromolecule containing, on average, 2370 monomer units splits into 52 oligomer fragments, each consisting, on average, of 45 units (see Table 15). Among them, 16 units contain C=O groups and 29 units contain C=C bonds.

By analogy with oxidation of internal aliphatic alkenes (see Section III.5) and considering the NMR and GPC data, the mechanism of ketonization of butadiene rubber can be presented by a scheme based on 1,3-dipolar cycloaddition of nitrous oxide. The rubber mainly contains internal C=C

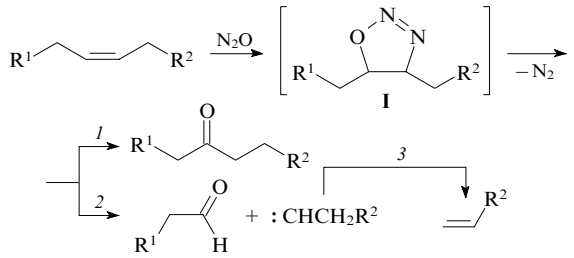
Table 15. Ketonization of butadiene rubber.[34, 53, 60]

Entry No.	Sample	Conversion of N_2O (%)	Reaction rate (W_{N_2O}) /mmol h^{-1}	Conversion of C=C (%)	Amount of introduced O (wt.%)	$M_n \times 10^{-3}$	M_w/M_n	N_{cleav}	Averaged composition of the macromolecule		Product physical state
									number of units	number of C=O groups	
1	SBR (init.)	0	0	0	0	128	2.2	0	2370	0	Rubber
2	SBR-160-12	0.4	0.06	0.7	0.2	92	1.9	0.4	1700	12	Rubber-like
3	SBR-200-5	1.2	0.45	2.6	0.8	38	2.0	2.4	698	18	The same
4	SBR-200-10	2.7	0.5	5.5	1.6	23	2.1	4.7	419	23	Flowable polymer
5	SBR-230-6	8.2	2.5	18	5.0	6.3	2.2	20	111	20	Viscous liquid
6	SBR-230-12	16.8	2.6	34	9.2	2.7	2.0	51	45	16	The same

Note. 100 cm^3 reactor, 0.186 mol of N_2O, 5 g of the rubber (0.093 mol of C=C bonds), 60 cm^3 of benzene.

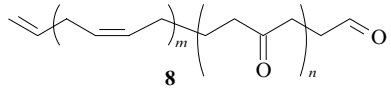
bonds in the 1,4-units, their fraction being 96.5%. These bonds react with N_2O to give intermediate **I** (Scheme 14), which mainly decomposes without cleavage of the initial C=C bond (reaction *1*) to give ketone groups statistically distributed along the polymer chain and does not induce a decrease in the molecular weight. Decomposition accompanied by bond cleavage (reaction *2*) gives fragments with lower molecular weight: aldehyde R^1CH_2CHO and alkylcarbene $R^2CH_2\ddot{C}H$, which then rearranges to the $R^2CH{=}CH_2$ molecule with a terminal vinyl group (reaction *3*). These groups are also detected in the reaction products by NMR spectroscopy.

Scheme 14



The calculations based on ^{13}C NMR spectroscopy and GPC indicate that the contribution of the major route is 95%, while that of the C=C bond cleavage route is only ~5%. However, in the case of polymers, even this minor contribution of bond cleavage may considerably decrease the molecular weight. The averaged composition of the products can be depicted as structure **8**.

Structure 8



These products are materials of a new type: unsaturated polyketones that differ from known polymers, such as polyketones synthesized by copolymerization of CO with alkenes, in the chemical composition.[76–79] By varying reaction conditions, one can control the content of the C=O groups in the unsaturated polyketones and their molecular weight.

V.2. Ketonization of butadiene nitrile rubber

Table 16 summarizes the results of ketonization of butadiene nitrile rubber (BNR) of the BNKS-18AMN trademark under similar conditions.[35] According to ^{13}C NMR spectroscopy, this rubber contains 65.4 mol.% 1,4-units, 13.3 mol.% 1,2-units and 21.3 mol.% acrylonitrile units. In this case, too, the molecular weight decreases with increasing conversion of the double bonds and the amount of introduced oxygen. For the most oxygenated BNR-230-12 sample (sample 6, $X_{C=C} = 22.4\%$), which contains 5 wt.% oxygen, the initial $M_n = 58\,000$ decreases ~30-fold to $M_n = 2000$. The products have a narrower molecular weight distribution ($M_w/M_n = 2.3–3.6$) than the initial rubber ($M_w/M_n = 6.9$) and are plastic oligomers.

Analysis of the products by ^{13}C NMR spectroscopy indicates that the double bonds of butadiene nitrile rubber also react with N_2O to selectively give C=O groups, comprising ketone (~81%) and aldehyde ones (~19%). The content of CN groups in the products remains the same as that in the initial rubber (~21 mol.%). Thus, the reaction gives bifunctional rubbers containing both nitrile and carbonyl groups.

The mechanism of ketonization of the butadiene nitrile rubber mainly containing internal double bonds in 1,4-butadiene units (83%) is similar to that shown above in Scheme 14 for polybutadiene. However, in this case, the contribution of the double bond cleavage route is higher, ~15%. Most likely, this is attributable to the fact that the butadiene nitrile rubber, unlike *cis*-1,4-butadiene rubber, contains mainly *trans*-1,4-units.[80, 81] Indeed, the contributions of the cleavage route for these rubbers are close to F_{cleav} values for *trans*-hept-3-ene (~13.5%) and *cis*-hept-3-ene (~4.2%).[61]

The butadiene nitrile rubber also has double bonds in 1,2-units (>CHCH=CH_2), their fraction being 17% of all C=C bonds. The oxidation of these bonds is similar to the oxidation of double bonds of terminal alkenes (see Section III.5) to give additionally the ketone groups >CH(C=O)Me and aldehyde groups >$CHCH_2CHO$ and

Table 16. Ketonization of butadiene nitrile rubber.[35, 53]

Entry No.	Sample	Conversion of N_2O (%)	Reaction rate (W_{N_2O}) /mmol h^{-1}	Conversion of C=C (%)	Amount of introduced O (wt.%)	$M_n \times 10^{-3}$	M_w/M_n	N_{cleav}	Averaged composition of the macromolecule		
									number of units	number of CN groups	number of C=O groups
1	BNR (init.)	0	0	0	0	58	6.9	0	1078	230	0
2	BNR-180-12	0.8	0.12	1.8	0.4	14	3.6	3.2	260	55	3.7
3	BNR-200-12	1.7	0.26	4.4	1.1	6.9	2.6	7.5	127	27	4.4
4	BNR-215-12	4.5	0.7	11.1	2.5	3.5	2.3	16	63	13	5.5
5	BNR-230-6	5.1	1.6	13.3	3.1	3.0	2.3	19	54	11	5.7
6	BNR-230-12	9.5	1.5	22.4	5.0	2.0	2.3	30	35	7.5	6.2

Note. 100 cm^3 reactor, 0.186 mol of N_2O, 5 g of the rubber (0.073 mol of C=C bonds), 60 cm^3 of benzene.

>CHCHO. These reactions are not accompanied by cleavage of the backbone.

V.3. Ketonization of the isoprene rubber

Ketonization of the *cis*-1,4-isoprene rubber (SIR) of the SKI-3 trademark with nitrous oxide has been studied by Dubkov *et al.*[36] A distinctive feature of the reaction in this case is a very fast decrease in the molecular weight with increasing conversion of the double bonds (Table 17). Even at a minor conversion (sample 2, $X_{C=C} = 1.2\%$), the M_n value decreases by more than an order of magnitude. For the most oxygenated SIR-230-12 sample (sample 6, $X_{C=C} = 17.3\%$), it decreases ~300-fold to $M_n = 1000$. The macromolecules of this oligomer comprise, on average, 14 monomer units, of which 2.4 units contain C=O groups and 11.6 units contain C=C bonds. All products obtained from polyisoprene have a narrower molecular weight distribution ($M_w/M_n = 1.6 - 1.9$) than the initial rubber ($M_w/M_n = 2.8$) and represent liquid oligomers.

According to analysis of the products by NMR spectroscopy, the reaction of polyisoprene with N_2O also involves the double bonds to give mainly keto groups. The fraction of keto groups among the carbonyl groups is >95%.

The isoprene rubber contains predominantly the internal C=C bonds in the 1,4-units (99.6%). These bonds are trisubstituted, which determines the features of the reaction mechanism. In this case, two isomers of the oxadiazoline intermediate can be formed (Scheme 15). Intermediate **I** completely decomposes only without C–C bond cleavage (reaction *1*) to give ketone groups in the polymeric chain.

In intermediate **II**, the oxygen atom is linked to the carbon atom bearing the additional CH_3 group. This intermediate can also decompose without bond cleavage and with methyl group transfer along the C–C bond to give analogous ketone groups. However, this transfer is rather slow (see Section III.5). Therefore, decomposition of this intermediate involves a substantial contribution of the bond cleavage route (reaction *2*) giving shorter fragments, methyl

Scheme 15

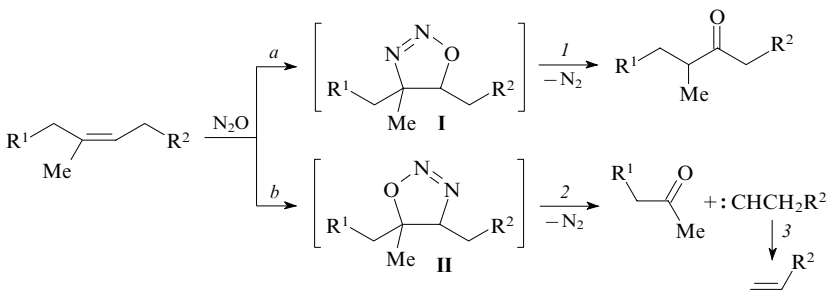


Table 17. Ketonization of the isoprene rubber of the SKI-3 brand.[36, 53]

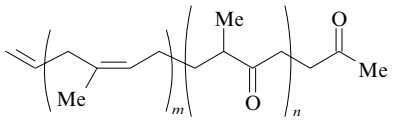
Entry No.	Sample	Conversion of N_2O (%)	Reaction rate (W_{N_2O}) /mmol h^{-1}	Conversion of C=C (%)	Amount of introduced O (wt.%)	$M_n \times 10^{-3}$	M_w/M_n	N_{cleav}	Averaged composition of the macromolecule	
									number of units	number of C=O groups
1	SIR (init.)	0	0	0	0	320	2.8	0	4706	0
2	SIR-180-12	0.5	0.08	1.2	0.3	19	1.8	16	279	3.3
3	SIR-200-12	1.3	0.20	3.3	0.8	5.8	1.7	55	85	2.8
4	SIR-215-12	2.3	0.36	6.2	1.4	3.4	1.7	94	49	3.1
5	SIR-230-6	2.8	0.87	7.4	1.7	2.8	1.6	115	41	3.0
6	SIR-230-12	7.3	1.13	17.3	3.9	1.0	1.9	332	14	2.4

Note. 100 cm^3 reactor, 0.186 mol of N_2O, 5 g of the rubber (0.074 mol of C=C bonds), 60 cm^3 of benzene.

ketone $R^1CH_2(C{=}O)Me$ and alkylcarbene $R^2CH_2\ddot{C}H$. The latter predominantly isomerizes to the $R^2CH{=}CH_2$ molecule with a vinyl group (reaction *3*). The presence of these groups in the oligomeric reaction products is confirmed by NMR spectroscopy data.

The averaged contribution of the cleavage route calculated from ^{13}C NMR and GPC is approximately 35%, which is substantially higher than that for butadiene and butadiene nitrile rubbers. This is attributable, most likely, to the presence of a trisubstituted double bond in the 1,4-unit of polyisoprene. The reaction products formed in this case are liquid unsaturated polyketones containing ketone groups and isoprene units (structure **9**).

Structure 9



9

Dubkov *et al.*[36] demonstrated also the possibility of obtaining similar products by ketonization of natural rubber.

The results covered in this Section indicate that, similarly to the oxidation of alkenes, the reactions of rubbers with nitrous oxide proceed, most likely, by a common 1,3-dipolar cycloaddition mechanism. The reaction leads to selective formation of mainly ketone groups in the polymer chain, without affecting other types of bonds. The cleavage of some of the reacting double bonds results in a decrease in the molecular weight. The activation energy for rubber ketonization is 23 – 24 kcal mol^{-1} (Refs 34 – 36), which is close to the activation energy for the alkene oxidation.[25, 52, 53, 59, 60]

The structure of the monomer units of the polymer has a pronounced influence on the course of the reaction. In the series of considered rubbers (*cis*-1,4-butadiene, butadiene nitrile and *cis*-1,4-isoprene rubbers), the rate of the reaction under the same conditions decreases (see Tables 15 – 17), but the contribution of the cleavage route increases.

The rubber ketonization with nitrous oxide opens up the way for the preparation of a broad spectrum of unsaturated polyketones with different compositions of monomer units, a specified content of carbonyl groups and controlled molecular weight. The presence of the C=O groups and the C=C bonds in the polymers provides additional opportunities for modification and application of these new materials.

In particular, oligomeric unsaturated polyketones obtained by ketonization of butadiene rubber can serve as a modifying component of rubber mixtures.[82, 83] This provides for the manufacture of compounded rubbers with greater relative elongation and enhancement of characteristics such as rupture strength, abrasion resistance, tear resistance and stability against thermooxidative ageing. Owing to the enhanced adhesion to metals caused by the presence of polar functional groups, unsaturated polyketones can be employed as the adhesion component for increasing the binding strength between the rubber and reinforcing material.[84]

Zolotarev *et al.*[85, 86] demonstrated the applicability of unsaturated polyketones as modifying agents in the synthesis of the neodymium *cis*-1,4-butadiene rubber. The addition of <1 g of unsaturated polyketone per kg of butadiene into the polymerized product provides the formation of a modified branched rubber with lowered cold flow and plasticity, close in the properties to the best samples of butadiene rubbers.

Due to the presence of reactive C=O groups, unsaturated polyketones are also of interest for the synthesis of oligomers containing functional groups of other types. For example, the reduction of unsaturated polyketone based on butadiene rubber with sodium borohydride affords unsaturated polyalcohol.[87] The reaction with hydroxylamine or its salts gives rise to unsaturated polyoximes.[87 – 89] Kazaryan and co-workers[87, 90] investigated the mechanism of the sorption interaction of CO_2 with these oligomers at high pressure and established the formation of specific noncovalent CO_2 complexes with the C=O, OH and =NOH functional groups.

The application of ketonization reaction to high-molecular-weight compounds is not limited to the synthesis of unsaturated polyketones. Yakovleva and co-workers[91, 92] utilized this approach to prepare a modified stationary phase for capillary gas chromatography. The modified phase based on poly(1-trimethylsilylprop-1-yne) functionalized by carbonyl groups *via* oxidative treatment with nitrous oxide at 220 °C ensured a high selectivity of separation of mixtures of organic compounds. It has been shown[93 – 96] that the reaction with N_2O can be used for thermooxidative destruction of carbons of various types and modification of their chemical composition.

The reaction with nitrous oxide has been shown to be applicable[97 – 99] for the controlled destruction of vulcanized rubbers, which can be utilized for the processing of waste tyre rubber (rubber crumb or large fragments of spent tyres) to plastic polymeric products. The oxidative treatment of rubbers with nitrous oxide is carried out in an organic solvent at a temperature of 180 – 230 °C and a pressure of 2 – 5 MPa. Under these conditions, vulcanized rubbers react with N_2O at the double bonds, like usual polydienes, to give mainly ketone groups. Cleavage of some of the reacting C=C bonds results in the destruction of polymer chains and, hence, the rubber vulcanization network. The degree of destruction of vulcanized rubber increases with increase in the conversion of double bonds in the reaction with N_2O and is easily controlled by the process conditions.

VI. Sources of nitrous oxide

The prospects of using nitrous oxide as a selective oxidant largely depend on its accessibility and cost. Currently, nitrous oxide is mainly used for medical purposes, and the world's output of N_2O is apparently limited to several tens of thousand tonnes per year. The traditional method for the preparation of N_2O is thermal decomposition of ammonium nitrate at 220 – 250 °C (see pp. 362 – 369 in the Encyclopaedia[100]).

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O \quad (5)$$

In the late 1990s, Mitsui Toatsu Chemicals produced ~450 tonnes of N_2O per year by catalytic oxidation of ammonia with air oxygen.[101]

$$2NH_3 + 2O_2 \longrightarrow N_2O + 3H_2O \quad (6)$$

The process was carried out in a fixed-bed reactor with a Mn-based catalyst. However, this reaction is highly exothermic; this precluded the use of higher-capacity reactors due to considerable problems with heat withdrawal from the catalyst bed. The selectivity to N_2O did not exceed 84%.[18]

In 2002, the Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, and the Solutia company developed an improved version of this process, which was carried out at 340 – 370 °C in a fluidized bed of the Bi-Mn oxide catalyst.[18, 102 – 104] The key advantage of this process is the possibility to construct high-capacity units owing to effective mass and heat transfer. According to pilot tests, the process provides a selectivity to N_2O not less than 86% with almost complete conversion of NH_3.

With this process at hand, the major contribution to the cost of N_2O (~70%) is made by the cost of the initial ammonia.[18] According to an estimate,[19] the cost of N_2O manufactured by this process should be several-fold lower than that of hydrogen peroxide, which is a widely used oxidant. Therefore, the use of N_2O for the oxidation reactions aimed at the synthesis of relatively expensive products may be economically sound.

An alternative source of N_2O is the exhaust gas formed in the nitric acid production and in the processes where HNO_3 is used as the oxidant (productions of adipic acid, caprolactam, glyoxal, acrylonitrile and so on).[46, 105, 106] Especially large emission — ~700 thousand tonnes of N_2O per year with concentration of 30% – 40% — is produced by cyclohexanone and cyclohexanol oxidation to adipic acid where N_2O is formed as a by-product in a stoichiometric amount.[101, 105]

In recent decades, in relation to the discovery of N_2O contribution to ozone layer destruction and greenhouse effect,[17, 18, 46, 101, 105] considerable attention has been paid to the catalytic methods for neutralizing N_2O emission.[46, 105, 106] However, the most attractive method is to recover N_2O from the exhaust gas for the subsequent use as a valuable oxidant. Modern processes for N_2O recovery and purification for such purposes have been developed by Solutia and BASF.[101, 107, 108]

VII. Conclusion

This review addresses an unusual type of oxidation reactions involving nitrous oxide. These are reactions of alkene oxidation to carbonyl compounds, which have been called ketonization (carboxidation) reactions. A specific molecular structure of N_2O enables its selective reactions with the C=C double bonds of alkenes and oxygen atom transfer to the unsaturated carbon atom to give ketones and aldehydes.

Unlike the reactions of alkenes with molecular oxygen, the oxidation with nitrous oxide proceeds with high selectivity, which is due to the non-radical reaction mechanism and inertness of N_2O to other types of bonds. Nitrous oxide has also a number of advantages over another popular oxidant, hydrogen peroxide, which is used, for example, for the catalytic epoxidation of propene.[109] In particular, N_2O is rather readily soluble in organic compounds and is rather thermally stable, which allows for a considerably wider range of suitable reaction conditions.

A specific feature of ketonization is that it proceeds selectively without a catalyst. This makes this approach especially attractive, as this eliminates typical catalyst-related problems such as deactivation, regeneration, separation from the reaction mixture, periodic replacement, *etc*. The good prospects of practical application of this type of reactions has been demonstrated by BASF in the new industrial processes for the production of valuable cyclic ketones using nitrous oxide recovered from the exhaust gas of adipic acid production.

Apart from the oxidation of diverse alkenes, the reaction with nitrous oxide can be successfully employed for the selective formation of functional carbonyl groups within various diene rubbers containing numerous carbon – carbon double bonds. This provides the synthesis of a broad range of unsaturated polyketones — a new class of functionalized oligomers and materials based on them.

Thus, the use of nitrous oxide as the oxygen donor in the partial oxidation of unsaturated compounds opens up a new area of research and offers broad opportunities for its targeted use.

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109. F Cavani *Catal. Today* **157** 8 (2010)