

Liquid Phase Oxidation of Alkenes with Nitrous Oxide to Carbonyl Compounds

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Abstract: A variety of substrates including linear, cyclic, heterocyclic alkenes and their derivatives were tested in the liquid phase non-catalytic oxidation with nitrous oxide (N_2O). The structure and composition of the alkenes have a significant effect on the reaction selectivity. With many alkenes, N_2O oxidation provides a selective way for the preparation of carbonyl

compounds. The generation of carbene (or diazomethane) species is a remarkable feature of the oxidation of terminal alkenes.

Keywords: alkenes oxidation; carbene; carbonyl compounds; cycloheptatriene; cyclopropane; methylene; nitrous oxide

Introduction

In the past decade, nitrous oxide has attracted a great deal of attention from researchers as a selective oxygen donor for conducting the catalytic oxidation of hydrocarbons. It is being used especially widely in the gas phase oxidation of aromatic compounds. The most successful reaction of this type is direct oxidation of benzene to phenol over Fe-containing zeolites:



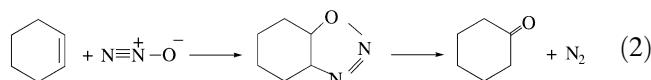
Based on this reaction, a new phenol process has been developed and successfully tested with a pilot plant providing 97–98% yields of phenol.^[1] The results of many studies in this field were discussed in a number of reviews.^[2–7]

Besides great opportunities, the gas phase oxidation also has some difficulties. Product desorption from the catalyst surface is a main problem. It needs elevated temperatures, which frequently lead to degradation of products and deactivation of the catalyst.

In order to solve these problems, we tried to transfer the oxidation into the liquid phase, assuming that this should facilitate product removal from the surface, thus increasing the number of possible catalytic reactions. This idea has come true only partly, but instead it brought us to the unexpected discovery of a non-catalytic oxidation of alkenes with nitrous oxide to carbonyl compounds.^[8]

Later, we learned that actually this reaction type had been discovered and extensively studied already in 1951 by Bridson-Jones et al.^[9,10] This group of ICI researchers tested a broad variety of substrates and, in spite of the

semi-quantitative nature of their study (efficient analytical techniques such as GC, GC-MS, NMR were not available that time), could correctly describe the main reactivity patterns of various alkenes. They also suggested a 1,3-dipolar N_2O cycloaddition mechanism involving the intermediate formation of 1,2,3-oxadiazoline, decomposition of which leads to the carbonyl compounds. The following equation for the case of cyclohexene oxidation is an example:



This mechanism well explains the experimental data^[8–11] and was supported by recent quantum-chemical calculations.^[12,13] But the authors^[9,10] presented no numbers for selectivity, conversion, or yield. The selectivities in refs.^[9,10], when the reported data allow one to make an estimation, were quite low. Thus, in the case of cyclohexene oxidation, which is one of the most selective examples, the selectivity to cyclohexanone did not exceed 64%. Low selectivities are possibly related to the harsh conditions of the experiments, which typically were conducted at 300 °C and 500 atm. To provide such a high pressure and to decrease the danger of an explosion when compressing N_2O , the authors^[9,10] used a specially designed mercury compressor. One may think that low selectivities coupled with harsh reaction conditions, which are difficult to provide in laboratory practice, are a reason why since 1951 no attempt has been made to reproduce or to improve results of Bridson-Jones et al.^[9,10]

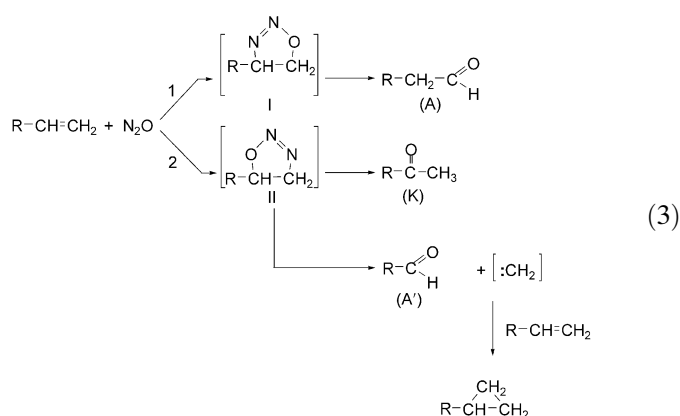
The main distinctive features of our work are the milder and easily available experimental conditions, and

the higher selectivity. Oxidations of cyclohexene to cyclohexanone^[8] and cyclopentene to cyclopentanone^[11] were shown to proceed in the temperature range 150–250 °C under 30–100 atm with 96–99% selectivity. The latter remains nearly unchanged at increasing conversion up to over 90%.^[11] The simplicity and high selectivity of these reactions stimulated our efforts to extend this approach to other substrates. The present work is devoted to a screening of alkenes including several alkenes identical to those tested in refs.^[9,10] The main purpose of the study is to obtain a quantitative basis for estimating the prospects and limitations of the liquid phase N₂O oxidation for preparing carbonyl compounds. The results are discussed further according to alkene types.

Results and Discussion

Linear Alkenes

The oxidation of linear alkenes (Table 1) exhibits particular features depending on the position of the double bond in the molecule. For the case of terminal alkenes (entries 1–4), a general scheme of the oxidation may be suggested as follows:



Equation (3) shows that the reaction may proceed *via* two routes leading to the formation of an aldehyde (A) or ketone (K). These routes are assumed to relate to different configurations of the intermediate 1,2,3-oxadiazoline complexes, with the oxygen being attached to the first (complex I) or the second carbon atom (complex II). Decomposition of complex II may occur in two ways, i.e., without cleavage and with cleavage of the C–C bond. The latter route leads to an aldehyde with a smaller number of carbon atoms (A') and the methylene (or diazomethane) species, which is immediately intercepted by another alkene molecule yielding the corresponding derivative of cyclopropane.

From Equation (3) one can see that the ratio between reaction routes 1 and 2 may be expressed *via* the concentrations of corresponding products:

$$R_1/R_2 = C_A / (C_K + C_{A'}) \quad (4)$$

In the case of ethylene, due to the symmetrical location of double bond in the molecule, only one configuration of the intermediate complex is possible. Decomposition of this complex leads to the formation of 91% acetaldehyde and minor products resulting from methylene reactions generated by cleavage of the C–C bonds (entry 1). For the other alkenes, the ratio R_1/R_2 may be calculated with the experimental results presented in Table 1. The calculation reveals a dominating role of route 2. Thus, in the case of propylene (entry 2), the ratio equals 1:2.3; in the case of 1-hexene (entry 3), 1:3.7; and in the case of 1-octene (entry 4), 1:4.2.

For these alkenes one may also calculate a fraction of the cleavage type decomposition of complex II:

$$F_{\text{cleav.}} = C_{A'} / (C_K + C_{A'}) \quad (5)$$

This fraction slightly increases from propylene (42%) to 1-hexene (48%) and 1-octene (48%). The resulting methylene generated by the cleavage may react with, apart from a starting alkene, also the solvent benzene. It mainly incorporates into the aromatic nucleus yielding cycloheptatriene, which is responsible for a significant part of the reaction products (12–18%). Small amounts of toluene (*ca.* 0.5%) are also produced.

The widening of the aromatic nucleus by the methylene generated from diazomethane is known in the literature.^[14] But with the methylene generated by N₂O oxidation of an alkene, this reaction is probably reported here for the first time.

Similar to ref.^[9], with all terminal alkenes studied here, no expected formaldehyde was detected.

The oxidation of unsubstituted non-terminal alkenes is exemplified by 2-pentene (entry 5). The reaction proceeds with a smaller cleavage, producing 2- and 3-pentanones comprising in sum 88% of the reaction products. A number of substituted non-terminal alkenes were also studied including crotyl alcohol, crotononitrile, mesityl oxide, 3-methyl-2-buten-1-ol, styrene, and stilbene. They all contain a functional group located in the vinyl or allyl position, and all exhibit low selectivity due to various side reactions (polymerization, dehydration, etc.).

Carbocyclic Alkenes

Results for this type of alkene are presented in Table 2. Due to the symmetrical location of the double bond in

unsubstituted rings (entries 1–4), their oxidation may provide a single ketone, which in all cases forms with high selectivity (94–99%). One may note a slight tendency towards an increasing contribution of side reactions in the cyclopentene to cyclododecene sequence, which is mainly due to opening of a ring leading to the formation of aldehydes. Minor products of aldol condensation are also detected in the reaction mixture.

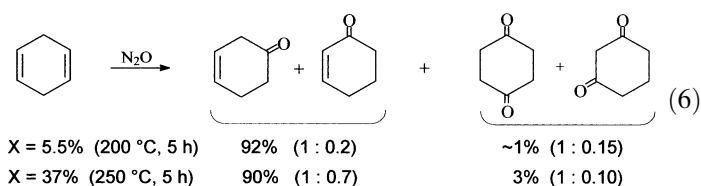
The presence of a substituent at a distant position from the double bond provides for the formation of isomeric ketones, in most cases keeping the high total selectivity. For example, 4-methyl-1-cyclohexene (entry 5) and 4-(3-cyclohexen-1-yl)pyridine (entry 6), having substituents in position 3, give the two expected isomeric cyclic ketones with total selectivities of 95% and 97%, respectively. In the case of 6-methyl-3-cyclohexene-1-methanol (entry 7), the selectivity is lower, which seems to be caused mainly by dehydration of the alcohol.

However, the oxidation of 1-methyl-1-cyclohexene having a substituent in position 1 (entry 8), proceeds much less selectively, providing only 44% of a cyclic ketone (2-methyl-1-cyclohexanone) in the reaction products. In this case, the reaction is accompanied by a significant cleavage of double bonds leading to formation of 1-cyclopentyl-1-ethanone and 6-hepten-1-one. An aldehyde $C_7H_{12}O$ (presumably 5-heptenal) is also found in the reaction products (2–3%).

Cycloalkadienes

These compounds contain two double bonds, which can consecutively react with N_2O , yielding accordingly unsaturated monoketones and diketones. We studied 1,4-cyclohexadiene and 1,5-cyclooctadiene which have isolated double bonds, and 1,3-cyclohexadiene which has conjugated bonds.

The distribution between mono- and diketones is an interesting feature of the reaction. In the oxidation of 1,4-cyclohexadiene (equation 6), 3- and 2-cyclohexen-1-ones are the main products comprising 90–92%:



Note that with 1,4-cyclohexadiene, 20–25% of the converted alkene was consumed for a polymerization process, which is not taken into account when calculating the product composition shown in Equation (6). With 1,5-cyclooctadiene, no polymerization was noted. The concentration of diketones is very small and at conversion $X = 37\%$ comprises only 3% instead of the expected statistical 9%. This low amount of diketones may indicate that the introduction of the first carbonyl

Table 1. Oxidation of linear alkenes ($P_{N_2O}^0 = 10$ atm, 220 °C, 12 h).

Entry	Substrate	Conversion [%]	Product composition [mol %]
1	Ethylene, 0.08 mol in 50 mL benzene	27	acetaldehyde, 91 cyclopropane, 4 cycloheptatriene, 3
2	Propylene, 0.08 mol in 50 mL benzene	26	propanal, 23 acetone, 31 acetaldehyde, 22 methylcyclopropane, 4 cycloheptatriene, 15
3	1-Hexene, 0.08 mol in 50 mL benzene	35	hexanal, 15 2-hexanone, 29 pentanal, 27 butylcyclopropane, 14 cycloheptatriene, 12
4	1-Octene, 0.06 mol in 50 mL benzene	30	octanal, 13 2-octanone, 28 heptanal, 26 hexylcyclopropane, 9 cycloheptatriene, 18
5	2-Pentene, 0.14 mol in 50 mL benzene	22	2-pentanone, 41 3-pentanone, 47 acetaldehyde, 5 propanal, 3 cyclopropanes, 1

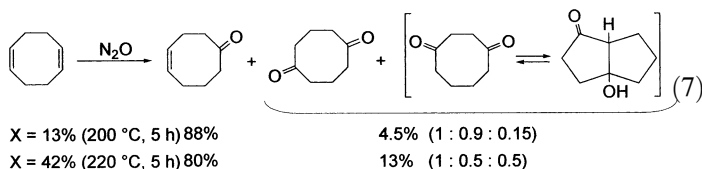
Table 2. Oxidation of carbocyclic alkenes (25 mL, $P_{N_2O}^0 = 25$ atm).

Entry	Substrate	T [°C]	Time [h]	Conv. [%]	Product composition [mol %]
1		200	20	67	99
2		250	5	27	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	75, 75
8		250	12	33	44, 34, 5

group into 1,4-cyclohexadiene deactivates the remaining double bond and makes it more resistant to oxidation. An approximately 10-fold predominance of 1,4- vs. 1,3-cyclohexanedione is observed.

The formation of two cyclohexenone isomers in the oxidation of 1,4-cyclohexadiene is a noteworthy result, since addition of one oxygen atom to any position of the starting molecule should lead to the formation of only 3-cyclohexen-1-one. Formation of 2-cyclohexen-1-one may be explained by migration of the double bond under the reaction conditions to the thermodynamically more favorable conjugated position. This process intensifies with the increasing reaction temperature. Thus, at 200 °C, the ratio between the cyclohexenone isomers is 1:0.2 [Equation (6)], while at 250 °C it is 1:0.7.

Oxidation of 1,5-cyclooctadiene also leads to the formation of mono- and diketones [Equation (7)]:



However, unlike 1,4-cyclohexadiene, this diene forms only one monoketone isomer. Besides, there is no deactivation effect of the C=O group, so that in this case the diketone fraction is much greater, being close to the statistical value. These distinctions are probably ex-

plained by a more distant location of the double bonds in the 1,5-cyclooctadiene molecule.

It is interesting that among the oxidation products of 1,5-cyclooctadiene, thorough NMR analysis identifies reliably 3 α -hydroxyhexahydro-1(2*H*)-pentalenone. Most probably, this compound forms as a result of intramolecular aldol condensation of 1,4-cyclooctanedione, the contribution of which increases with the temperature and at 220 °C consumes 50% of the latter [Equation (7)].

The oxidation of conjugated 1,3-cyclohexadiene is strongly complicated by the Diels–Alder side reaction. Therefore, the main part of the diene is consumed by a dimerization process, and only 25–30% are involved in the oxidation, yielding cyclic ketones.

Bicyclic Alkenes

Results for this type of alkene are presented in Table 3. The oxidation of norbornylene (entry 1) leads to the formation of both ketone (norcamphor) and aldehyde (1-formyl-3-methylenecyclopentane) in approximately equal amounts, indicating that a significant cleavage of the double bond occurs. There is also a set of other reaction products, which we have not yet identified with certainty.

The oxidation of 1,2-dihydronaphthalene proceeds with a minor cleavage and yields α - and β -tetralones with the total selectivity of 93% (entry 2). Oxygen adds predominantly to the α -position, and the amount of α -tetralone is approximately twice that of β -tetralone.

In the oxidation of indene, where the double bond is located in a 5-membered ring (entry 3), oxygen also adds to both positions, but the preference for the α -position becomes even greater. The ratio of α -indanone to β -indanone is 4.5:1. Presumably, 2-ethenylbenzaldehyde also forms ($\sim 10\%$) as a result of the double bond cleavage in the indene molecule.

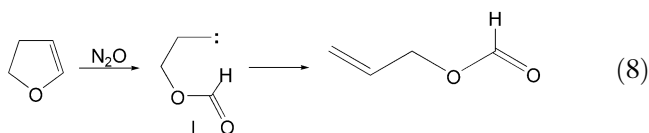
Table 3. Oxidation of bicyclic alkenes ($P_{N_2O}^0 = 10$ atm).

Entry	Substrate	T [°C]	Time [h]	Conv. [%]	Product composition [mol %]
1	 0.053 mol in 45 mL cyclohexane	180	4	42	28, 29
2	 0.039 mol in 20 mL benzene	250	5	46	65, 28
3	 0.043 mol in 20 mL benzene	250	5	35	63, 14, 10

Heterocyclic Alkenes

Among alkenes of this type we tested rings containing oxygen, nitrogen and sulfur (Table 4). 5-Membered heterocycles with similar molecular structures (2,5-dihydrofuran, 3-pyrroline, butadiene sulfone) exhibit different reaction patterns depending on the nature of the heteroatom. The oxygen-containing ring of 2,5-DHF (entry 1) is oxidized selectively yielding the corresponding ketone (94%), while the rings containing nitrogen (entry 2) and sulfur (entry 3) show a strong tendency toward side reactions resulting in a set of unidentified products.

Comparison of the several oxygen-containing rings presented in Table 4 allows one to follow an effect of double bond's location in the heterocyclic molecule. Results with 2,3-DHF (entry 4) and 3,4-dihydro-2H-pyran (entry 5) show that double bonds located nearer to the oxygen atom exhibit an increased disposition towards cleavage. Indeed, oxidation of 2,3-DHF proceeds exclusively *via* the cleavage route. It leads to 71% of allyl formate in the products:



Besides, a set of other formates was identified as a result of addition of the intermediate carbene **I** [Equation (8)] to the components of reaction mixture. No sign of butyrolactone was detected. Oxidation of 3,4-dihydro-2H-pyran also proceeds primarily *via* the cleavage route, giving 48% of 3-butenyl formate. But in this case, a significant contribution of a non-cleavage route is also observed, which is evidenced by the presence of 31% of δ -valerolactone in the products.

Unlike that, oxidation of 2,5-DHF (entry 1) and 4,7-dihydro-1,3-dioxepin (entry 6), having more distant location of double bonds (position 3), proceeds essentially without cleavage leading in both cases to the formation of corresponding ketones with 94% selectivity.

Note that oxidation of 3,4-dihydro-2H-pyran has been studied earlier by Bridson-Jones et al.^[9] They found that the reaction proceeds via non-cleavage route giving small amount of δ -valerolactone as the only oxidation product. The distinction from our results may be explained by more severe reaction conditions in ref. [9], which might cause fast secondary transformations of 3-butenyl formate.

Conclusion

Results of the substrate screening presented above show that liquid-phase oxidation with nitrous oxide can be

Table 4. Oxidation of heterocyclic alkenes.

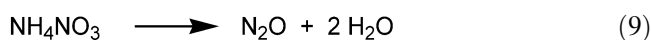
Entry	Substrate	P ^o _{N₂O} [atm]	T [°C]	Time [h]	Conv. [%]	Product composition [mol %]
1	 0.13 mol in 50 mL benzene	10	220	12	16	 94
2	 0.13 mol in 30 mL benzene	25	180	10	13	unidentified products
3	 0.085 mol in 50 mL acetonitrile	10	210	5	8	butadiene, ~50
4	 0.13 mol in 60 mL cyclohexane	10	200	5	34	 71
5	 0.11 mol in 50 mL benzene	25	240	5	20	 48 31
6	 0.10 mol in 15 mL benzene	25	220	5	16	 94

applied to a variety of alkenes including aliphatic, cyclic, heterocyclic alkenes and their derivatives. The oxidation proceeds non-catalytically in the temperature range of 150–250 °C yielding ketones and aldehydes as main products. Although the reaction selectivity depends significantly on the alkene structure and composition, each type of alkenes was shown to include compounds whose oxidation proceeds selectively yielding 90–99% of carbonyl compounds.

Trying to test as many substrates as possible, we did not have an opportunity to study effect of temperature and N₂O concentration on the reaction performance. As a first approximation one may assume this effect to follow the kinetics observed with the oxidation of cyclopentene and cyclohexene.^[8,11]

Due to evolution of high energy, N₂O oxidation may cause cleavage of an alkene molecule over the double bond. This undesirable process increases the number of reaction products and decreases the selectivity. But in the case of terminal alkenes, where this process is most intensive, it may deserve a special interest as a way for generating carbenes, which may be used for conducting fine synthetic reactions.

With regard to a possible practical application of nitrous oxide in chemical reactions, it is worth mentioning that N₂O is an inexpensive compound. Presently it is used for medical application and prepared mainly by decomposition of ammonium nitrate:



Recently, an efficient process for N_2O preparation has been developed using direct oxidation of ammonia:



The process has been successfully tested with a pilot unit.^[15] The reaction is accomplished using a Mn/Bi/Al oxide catalyst, and 87–88% selectivity to nitrous oxide has been achieved at almost complete conversion of ammonia. According to estimation,^[16] the cost of active oxygen in N_2O produced by this method is 4 times lower than its cost in H_2O_2 . This fact coupled with remarkable oxidation chemistry makes nitrous oxide to be especially attractive oxygen donor, and stimulates further studies in this promising field.

Warning. Oxidation of alkenes with N_2O involves no free radicals^[8] and therefore is less explosive as compared with similar reactions involving O_2 . However, one should remember that nitrous oxide can form explosive mixtures with organic substrates,^[17,18] and should use precautionary measures to ensure a safe work.

Experimental Section

Oxidation of alkenes with N_2O was performed batchwise in a stainless-steel Parr autoclave reactor of 100 c.c. capacity, equipped with a stirrer and manometer. The vessel was typically charged with 25 c.c. of a liquid substrate. In order to remove dioxygen, the system was blown off with nitrous oxide fed from a cylinder, and then an initial N_2O pressure, $P_{\text{N}_2\text{O}}^0$, was set at 10 or 25 atm. The vessel was closed and heated (at 6 °C/min ramp) to the reaction temperature 150–250 °C. Due to heating, the pressure increased to 30–100 atm depending on the initially admitted amount of N_2O and an equilibrium pressure of the alkene. When the reaction was completed, the vessel was cooled to room temperature and, after performing analysis of the gas phase composition, the pressure released slowly.

In many cases, in particular with gaseous or solid alkenes, the oxidation was conducted in solvents. The type of solvent (benzene, cyclohexane or acetonitrile) and amount of a dissolved alkene are given in Tables 1, 3, 4 together with the corresponding experimental results. All the solvents were shown to be inert with respect to N_2O oxidation.

Reaction products were analyzed using the GC, GCMS and NMR methods. GC analysis of the gas phase composition (N_2O , N_2 , CO , CO_2 , low hydrocarbons) was performed at room temperature with a Cristall-2000 instrument using a TCD and a packed column filled with Poropak Q. For a more accurate measurement of small CO and CO_2 amounts, these compounds were hydrogenated over a nickel catalyst and then analyzed as methane using an FID. However, even with this sensitive method, no complete oxidation products were detected. In all cases CO_x concentration was less than 0.001 mol %.

GC analysis of the liquid phase products was typically performed at the programmed elevation of temperature from 40 °C to 250 °C with a capillary column (50 m, 0.2 mm, SE-52 phase) using an FID. In most cases, authentic compounds or their isomers were used as calibration standards. In the case of low selective reactions, the analysis was usually limited by identification of main products.

GCMS analysis was performed using VG Analytical Ltd. 7070 HS, and Varian Saturn 2000 instruments equipped with a set of capillary columns. The type of a column as well as operation conditions were selected depending on the reaction under study, so as to provide more efficient separation and identification of the products.

NMR analysis of reaction products was performed using a resulting reaction mixture without its any further treatment or modification. ^1H and ^{13}C NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, using a Bruker MSL-400 spectrometer. The following operating conditions were used: sweep width 6 kHz (^1H) or 25 kHz (^{13}C), 10–20° pulse of 1–2 μs (^1H), 45° pulse of 12 μs (^{13}C), relaxation delay 5–60 s. To provide an increased accuracy of measurements, large scan numbers were collected, in the range of 10^2 – 10^4 scans depending on the composition and concentration of the products.

Quantitative ^{13}C NMR relative intensity measurements were made with inverse gated proton decoupling (to avoid the nuclear Overhauser effect) and long relaxation delays. These results, together with the GC data, were used for calculating alkene conversions and reaction selectivities.

High purity organic substrates were used in the work, purchased from Aldrich, Fluka and ACROS. Medical grade nitrous oxide (99.8%) was purchased from Cherepovets Azot Co. (Russia). The latter was supplied in cylinders in a liquefied form under equilibrium pressure of about 50 atm.

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