

High-Temperature Carboxidation of Cyclopentene with Nitrous Oxide

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Abstract—It is demonstrated by the example of cyclopentene that the noncatalytic oxidation of alkenes with nitrous oxide to carbonyl compounds (carboxidation), which is known to occur in the liquid phase at 150–250°C, can also take place in the gas phase at higher temperatures (300–475°C). Like liquid-phase carboxidation, the gas-phase reaction likely proceeds via a dipolar 1,3-addition mechanism. However, 4-pentenal is formed along with cyclopentanone in the gas phase. The 4-pentenal selectivity increases from 2.5 to 23% as the reaction temperature is raised. High-temperature cyclopentene carboxidation can be carried out in a paraffin melt (bp ~ 400°C). Filling the reactor with paraffin accelerates the reaction and reduces its activation energy.

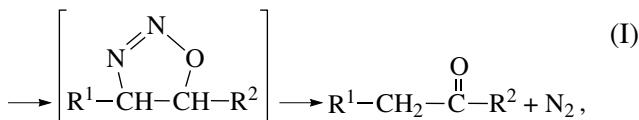
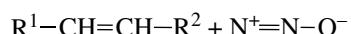
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INTRODUCTION

Nitrous oxide is used as a selective oxygen donor in various catalytic oxidation reactions [1]. The unusual ability of nitrous oxide to perform liquid-phase alkene oxidation has evoked considerable interest in recent years. The interaction of N₂O with alkenes takes place at the C=C bond to form carbonyl compounds (aldehydes and ketones). The compounds containing no such bonds cannot react with N₂O. The double bonds of unsaturated polymers can also be involved in reactions of this type. We call these reactions carboxidation [2, 3].

The role of aldehydes and ketones as solvents and by-products in the syntheses of various chemicals is well known. The syntheses of these compounds, except for their simplest representatives, are usually difficult to carry out and are accompanied by the formation of noxious waste. Aldehydes and ketones can be synthesized by the oxidation of primary and secondary alcohols with O₂ and H₂O₂ [4]. However, alcohols are often expensive and poorly available substances. Therefore, search for new routes for the synthesis of carbonyl compounds is of great scientific and practical interest. One promising method of solving this problem is by alkene carboxidation.

Liquid-phase alkene carboxidation is usually carried out at 150–250°C and 3–12 MPa using, if necessary, such traditional solvents as cyclohexane, benzene, acetonitrile, etc. [5, 6]. The reaction is believed to proceed via the dipolar mechanism of N₂O 1,3-cycloaddition to the double bond of alkene, forming an intermediate oxadiazoline cycle [5–10]:



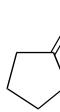
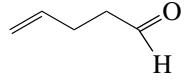
where R¹ and R² are alkyl groups or hydrogen atoms. The carboxidation of linear, cyclic, heterocyclic, and other alkenes [5] can be of practical interest. In particular, using reaction (I), the BASF Company has recently developed a new process for cyclododecanone synthesis by the liquid-phase oxidation of cyclododecene with nitrous oxide [11, 12].

Gas-phase reactions have several technological advantages over liquid-phase processes. Earlier [13], we demonstrated the possibility of the gas-phase carboxidation of cyclohexene and the selective formation of cyclohexanone at very high temperatures (320–450°C). In the present work, we consider the high-temperature (300–425°C) carboxidation of cyclopentene not only in the gas phase but also in a paraffin melt acting as a high-temperature solvent. The results obtained allow one to compare the kinetic parameters and efficiencies of the reactions carried out in the gas phase and in the solvent at the same temperature and pressure.

EXPERIMENTAL

Experiments were carried out using an automated setup with a stainless-steel tubular flow reactor. The reactor was fed with a gas mixture of the following composition (mol %): C₅H₈, 20; N₂O, 20; He, 60. The reaction mixture was sampled at the reactor outlet at intervals of 20 min and was analyzed on a Biokhrom-1 chromatograph. Light gases (N₂O, N₂, CO₂) were

Table 1. Carboxidation of cyclopentene in the gas phase

T, °C	Conversion, %		Selectivity, %		Reaction rate, mol cm ⁻³ h ⁻¹
		N ₂ O			
300	0.35	0.4	95	2.5	0.009
325	0.9	1.1	94	4.0	0.024
350	1.8	2.3	92	6.5	0.049
375	3.6	4.4	89	9.0	0.097
400	9.5	10.3	78	18	0.25
425	16.5	19.5	73	23	0.43

determined at room temperature using a Porapak Q column and a thermal-conductivity detector. To enhance the accuracy of the measurements of small amounts of CO and CO₂, these oxides were pre-hydrogenated on a nickel catalyst and were then quantified as methane using a flame-ionization detector. In all cases, the CO_x concentration did not exceed 0.01 mol %. Dinitrogen was virtually the only gas-phase reaction product, and its content was consistent with the amount of the resulting carbonyl compounds.

Organic products were identified on a DB-1701 capillary column (J&W Scientific) at 100°C using a flame-ionization detector. For more reliable identification, in some entries the reaction products were condensed and then analyzed by NMR spectroscopy. The spectra were recorded on a Bruker MSL-400 spectrometer operating at 400.13 MHz (¹H) and 100.61 MHz (¹³C).

The following reagents were used: cyclopentene (99.9%, Aldrich), medical nitrous oxide (99.8%, OAO Cherepovetskii azot), and medical paraffin (mp 54.6°C, bp ~ 400°C, OAO Slavneft' - Yaroslavnefteorgsintez).

The reactor for gas-phase cyclopentene carboxidation had a diameter of 0.7 cm and a volume of 5 cm³. A 10-cm³ reactor was used in the experiments involving paraffin. It was loaded with 8 g of solid paraffin, which melted upon heating. The reaction mixture as small bubbles was introduced into the melt through a disperser. The top of the reactor was fitted with a refluxer (150°C) for paraffin condensation and downflow.

In the gas-phase experiments, the reaction soon reached a steady-state regime. In the experiments with paraffin, this took a longer time because the solvent (paraffin) was saturated with the initial reactants and reaction products. Depending on the experimental conditions, this time sometimes was as long as 3–4 h. After the steady-state regime was achieved, the reaction was performed for another 2–3 h, its parameters remaining unchanged. The cyclopentene conversion (x_R) and the

nitrous oxide conversion (x_{N_2O}) were calculated using the results of analysis of the gas phase:

$$x_R = (C_{\text{one}} + C_{\text{al}})/C_R^0, \quad (1)$$

$$x_{N_2O} = C_{N_2}/C_{N_2O}^0, \quad (2)$$

where C_{one} , C_{al} , and C_{N_2} are the concentrations of cyclopentanone, 4-pentenal, and nitrogen at the reactor outlet, respectively; C_R^0 and $C_{N_2O}^0$ are the initial concentrations of cyclopentene and nitrous oxide (mol/l). Taking into account comparatively low conversions, the rate of cyclopentene oxidation was calculated using the equation

$$r = C_R^0 x_R v_0/V, \quad (3)$$

where v_0 is the gas space velocity, which in our experiments was 1500 cm³/h (under normal temperature and pressure), and V is the reactor volume (cm³).

RESULTS AND DISCUSSION

Carboxidation in the Gas Phase

The results of the experiments in an empty flow reactor at 1.0 MPa are presented in Table 1. At 300°C, the reaction proceeds to an insignificant extent, but its rate increases considerably as the temperature is raised. The temperature dependence of the reaction rate is well described by a straight line in the Arrhenius coordinates (Fig. 1, line 1), whose slope corresponds to an activation energy of 24 ± 1 kcal/mol.

The major reaction products are cyclopentanone and 4-pentenal, and the total selectivity of their formation is 96–98% and is virtually temperature-independent. However, the proportions of these compounds change significantly. As can be seen from the data in Table 1, as the temperature increases from 300 to 425°C, the cyclopentanone selectivity decreases from 95 to 73%,

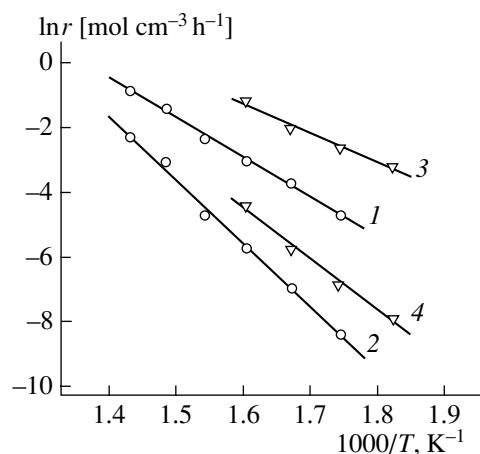
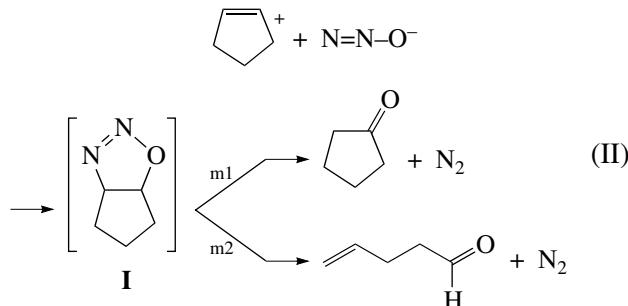


Fig. 1. Temperature dependences of the cyclopentene carboxidation rate: (1) overall reaction rate in the gas phase, (2) 4-pentenal formation rate in the gas phase, (3) overall reaction rate in the paraffin melt, and (4) 4-pentenal formation rate in the paraffin melt.

whereas the 4-pentenal selectivity increases from 2.5 to 23%. The reaction products include small amounts of some other compounds, whose formation selectivity ranges between 0.2 and 2%. These compounds were not identified.

The formation of 4-pentenal as a reaction product was unexpected. This product was not observed in liquid-phase cyclopentene oxidation at 140–230°C [14], and the cyclopentanone selectivity was about 100%. The assumption that 4-pentenal is the product of cyclopentanone isomerization at high temperatures was not confirmed experimentally. Passing pure cyclopentanone or its mixture with N₂O through the reactor at 425°C did not cause cyclopentanone isomerization or any other reaction. Therefore, both carbonyl compounds form via parallel pathways.

It seems natural to assume that the gas-phase carboxidation of cyclopentene, like the liquid-phase reaction, proceeds via the dipolar 1,3-cycloaddition mechanism. This mechanism is widely used to explain experimental results and has recently been convincingly proved by quantum-chemical calculations [8, 9]. According to the dipolar 1,3-cycloaddition mechanism, the reaction of nitrous oxide with cyclopentene proceeds through the formation of intermediate oxadiazoline complex I:



The decomposition of intermediate complex I without C–C bond cleavage (pathway m1) results in cyclopentanone. 4-Pentenal is formed if the C–C bond is cleaved upon the decomposition of the complex (pathway m2).

The fact that the pathway m2 is not observed in the liquid phase [14] but appears when the reaction is carried out in the gas phase can be attributed to specific features of the temperature dependences of these two pathways. Knowing the overall reaction rate and the formation selectivities of both carbonyl compounds at different temperatures (Table 1), one can calculate the activation energy for either pathway. The corresponding Arrhenius plots are presented in Fig. 1. Since the overall reaction rate is mainly determined by pathway m1, the activation energy of this pathway almost coincides with that of the overall reaction, being 24 ± 1 kcal/mol. The activation energy of pathway m2, which leads to 4-pentenal, is equal to 38 ± 1 kcal/mol; i.e., it is 14 kcal/mol higher. As a result, the contribution of pathway m2 decreases considerably with decreasing temperature and becomes negligible below 230°C. It cannot be ruled out that the insufficient efficiency of energy dissipation in the gas-phase reaction can exert an effect on the contribution from pathway m2. Owing to this, intermediate complex I in the gas phase can possess some excess energy compared to its energy in the liquid-phase process. This facilitates surmounting the high energy barrier via pathway m2.

Note that the radical-chain mechanism does not substantially contribute to the gas-phase oxidation of cyclopentene with nitrous oxide, although the temperature of the reaction is high and the reaction is exothermic (~70 kcal/mol). The addition of such efficient free-radical quenchers as benzoquinone and hydroquinone (3–5% on the cyclopentane basis) to the reaction mixture exerted no effect on the rate or selectivity of the reaction.

The nonradical character of the process is also indicated by the high reaction order. This order was derived from the plot of the reaction rate versus pressure (0.27–2.0 MPa) on the $\sqrt{r} - P$ coordinates (Fig. 2). The pressure dependence is described satisfactorily by a straight line coming out of the origin. Therefore, the overall reaction order is two. Since the reaction order with respect to each reactant is unity according to an earlier kinetic study of the oxidation of butenes in the liquid phase [6], it can be assumed with good reason that the rate of cyclopentene oxidation is described by the equation

$$r = k_0 e^{-E_a/RT} P_{N_2O} P_R, \quad (4)$$

where k_0 is the preexponential factor, E_a is the activation energy, and P_R and P_{N_2O} are the partial pressures of cyclopentene and nitrous oxide.

Carboxidation in Paraffin

The results of experiments on cyclopentene carboxidation in the paraffin melt are presented in Table 2. The reaction was carried out at the same pressure and in the same temperature region as the gas-phase reaction. Similar results were obtained in both cases. Both cyclopentanone and 4-pentenal form in the melt. The total selectivity of their formation is 97–99%. The Arrhenius plots presented in Fig. 1 show that the activation energy of the overall reaction in the melt (line 3) and that of 4-pentenal formation (line 4) differ significantly, as in the gas-phase reaction, being 18 and 31 kcal/mol, respectively. This indicates that the kinetics and mechanism of carboxidation undergo no substantial changes on passing from one variant of the reaction to the other.

However, it is seen from the data in Table 3 that the solvent significantly affects the rate and activation energy of the reaction. In the reactor filled with paraffin, the reaction rate at 325°C is 5 times higher and the activation energy of the overall reaction is lower by 6 kcal/mol. These changes can be caused both by an increase in the concentrations of the initial reactants due to their dissolution in paraffin and by the solvation factors that affect the activation energy and entropy of the reaction. It seems difficult to estimate the relative contributions from these factors without performing further studies.

The presence of the solvent (paraffin) affects the activation energies of both reaction pathways to equal extents, decreasing it by 6–7 kcal/mol. This agrees well with mechanism (II), according to which both reaction pathways involve the same intermediate complex. The formation of 4-pentenal in the paraffin melt indicates that pathway m2 (with the C–C bond cleavage) is not a unique feature of the gas-phase reaction. However, the selectivity of 4-pentenal formation in the melt decreases (from 4.0% in the gas phase to 2.5% in paraffin). This possibly indicates some influence of energy dissipation on the process, although this influence is insignificant.

The order of the reaction in paraffin was not determined in the present work. However, since the overall order was previously found to be 2 for both the gas [13]

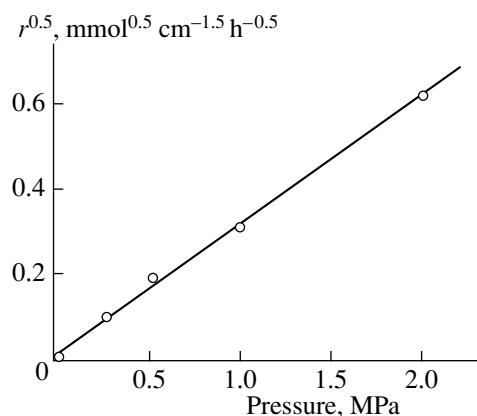
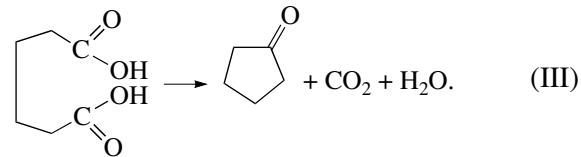


Fig. 2. Rate of cyclopentene formation in the gas phase versus pressure.

and liquid [6, 14] phases, it can be assumed that the reaction in molten paraffin is also second-order.

Cyclopentanone is a valuable chemical product. In particular, it is used as an intermediate in the synthesis of glutaric acid and some types of nylons. Cyclopentanone is not widely used because of its high cost. Presently, the main method of cyclopentanone synthesis is the decomposition of adipic acid [15]



The theoretical yield is only 57.5 wt %. Therefore, the reaction of cyclopentene carboxidation with N₂O can be of significant practical interest, all the more so as nitrous oxide is a very cheap and available product [1]. Although the reaction occurs in the liquid phase when the paraffin melt is used as the reaction medium, an important advantage of the gas-phase process is retained in this variant: the gaseous reaction products are removed from the reactor, eliminating the problem of their separation from the solvent.

As for 4-pentenal, presently we have no information on methods of its synthesis and use. However, it can be

Table 2. Carboxidation of cyclopentene in the paraffin melt

T, °C	Conversion, %		Selectivity, %		Reaction rate, mol cm ⁻³ h ⁻¹
		N ₂ O			
275	3.3	3.5	98.3	0.9	0.04
300	5.2	5.7	98.4	1.5	0.07
325	10.1	11.4	96.6	2.4	0.13
350	21.5	21.0	93.4	4.0	0.30

Table 3. Comparison of the parameters of cyclopentene carboxidation in the gas phase and paraffin melt

Method of reaction	Reaction rate, mol cm ⁻³ h ⁻¹	Selectivity, %		Activation energy, kcal/mol	
				overall reaction	formation of 4-pentenal
In the gas phase	0.024	94.0	4.0	24 ± 1	38 ± 1
In paraffin melt	0.13	96.6	2.4	18 ± 2	31 ± 2

expected that this unsaturated aldehyde can also be used in organic synthesis.

The rather low reaction rates achieved in the present work (see Tables 1 and 2) can be increased by using more concentrated reaction mixtures and increasing the pressure. Since the reaction order is 2, the second method should be recognized as more efficient. When the pressure increases from 10 to 40 MPa, the increase in the reaction rate is expected to be 16 times, which provides a rather high productivity of the process.

The reactions considered in the present work are classified as noncatalytic. Of course, this reaction could become particularly attractive for the synthesis of cyclopentanone and many other carboxyl compounds if a catalytic method were developed for alkene carboxidation with nitrous oxide. No information concerning this problem has been reported, while our efforts have demonstrated that it will be very difficult to find catalysts for these syntheses. However, a successful solution of this problem could be a worthy tribute to researchers working in this area.

It is important to keep in mind that nitrous oxide can form explosive mixtures with organic substances [16, 17] and, hence, the corresponding protective measures should be provided when working with this oxide.

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