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Ketonization of 1,5-Cyclooctadiene by Nitrous Oxide

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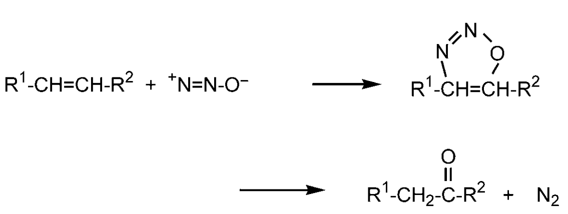
Abstract: The kinetics and mechanism of the liquid phase ketonization of 1,5-cyclooctadiene (COD) by nitrous oxide have been studied. The reaction proceeds without catalyst in the temperature range 473–553 K with the activation energy 113 kJ mol^{-1} and is first order with respect to the initial reactants. The mechanism includes consecutive ketonization of two C=C bonds in the COD molecule, with the intermediate formation of an unsaturated monoketone (MK). Further ketonization of MK leads to two isomeric diketones (DK): 1,4- and 1,5-cyclooctanedione. The 1,5-DK is a stable final product while the 1,4-DK undergoes further intramolecular aldol transformation leading to two bicyclic compounds, that retain the same number of carbon atoms. The distribution of mono- and diketones in the course of reaction is described by theoretical dependences pointing to identical reactivities of the C=C double bonds residing in COD and MK molecules. The ketonization of COD by nitrous oxide exemplifies a prospective way for the preparation of valuable organic products in perfect harmony with the strategy of green chemistry.

Keywords: 1,5-cyclooctadiene; cyclooctanediones; 1,3-dipolar cycloadditions; ketonization; nitrous oxide; oxidation

Introduction

Starting from the 1990s, nitrous oxide has attracted the ever-growing attention of researchers. This is caused by two reasons. The first reason is the negative environmental impact of N_2O resulting in greenhouse and ozone-depleting effects, which may contribute to global climate changes. This makes necessary the development of effective methods for N_2O abatement in industrial off-gases.[1] The second reason relates to the unique features N_2O exhibits as a selective oxygen donor. This gives a strong incentive to search for its useful chemical applications. These features were first discovered in catalytic oxidation in the gas phase[2] and later in the liquid phase.[3] In particular, the use of nitrous oxide and FeZSM-5 zeolites allowed the development of a pilot-scale process for the oxidation of benzene to phenol providing 97–98% selectivity. Numerous works on catalytic oxidation by N_2O are considered in some reviews.[4]

But the most remarkable feature of nitrous oxide is its ability to perform the *non-catalytic* oxidation of alkenes to carbonyl compounds. The oxidation of this type was discovered in the 1950s.[5] However, the active interest in this field arose only in recent years, after the rediscovery of these reactions as exemplified by the oxidation of cyclohexene and cyclopentene to the corresponding cyclic ketones with 96–99% selectivity.[6] The reaction proceeds by a 1,3-dipolar cycloaddition mechanism *via* a 4,5-dihydro[1,2,3]oxadiazole intermediate:[5–7]



(1)

where R^1 and R^2 are hydrocarbon radicals or hydrogen atoms. Decomposition of the oxadiazole intermediate generally occurs by a hydrogen shift with the formation of ketone group on one of the carbon atoms at the double bond [Eq. (1)]. The decomposition may proceed also by the so-called diazo mechanism[7b] including C=C bond cleavage and formation of an aldehyde.

This type of N_2O oxidation was denoted as 'carboxidation'.[4b] However, since in most cases the oxidation leads to ketones, it can be called also the ketonization following Hermans et al.[7b]

By now, several fields have been revealed in which the ketonization was shown to be a promising approach. Screening of various alkenes including linear, cyclic and heterocyclic compounds showed that the reaction selectivity depends on the alkene composition and structure, and often exceeds 90%.[8] This allowed the BASF company to develop a new process for the production of cyclododecanone (the intermediate for nylon-12) *via* ketonization of cyclododecene by the N_2O recovered from off-gases at the adipic acid production.[9]

Rather promising is the N_2O ketonization of polymeric compounds. In particular, ketonization of polydiene rubbers makes it possible to obtain a new type of material, that is, unsaturated liquid polyketones.[10] Recently, the opportunities of N_2O chemistry have been explored in relation to unsaturated renewable resources like fatty esters and triacylglycerols.[11] The corresponding keto products were obtained with a selectivity 95–99%, the volume-time yield being one order of magnitude higher than that provided by the conventional Wacker process.

Nevertheless, even now the number of works in this non-catalytic field is still quite limited and hardly exceeds a dozen. Therefore, it is important both to keep on searching for new N_2O reactions and to study in more detail the known ones.

This work presents a study of cyclooctadiene (COD) ketonization. Previously, within substrates screening,[8] we carried out a couple of experiments with this diene. The interest in a more thorough investigation of this reaction is caused by both the value of the main expected products (cyclic mono- and diketones) and the need to accumulate more experimental results on a detailed ketonization mechanism for individual substrates. With a cyclic diene such a detailed study has now been performed for the first time.

Results and Discussion

Identification of Reaction Oroducts

Prior to a systematic study of the reaction, we performed some preliminary experiments in the temperature range 473–553 K for 12 h. In the reaction mixtures obtained with these experiments, GC, GC-MS and NMR methods identified five main products presented in Figure 1.

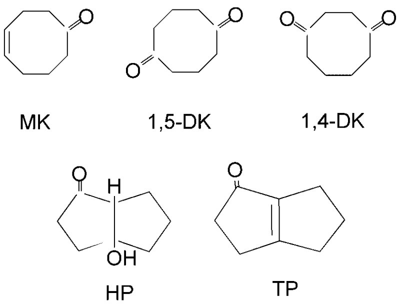


Figure 1. Main reaction products.

The first three compounds, 4-cyclooctenone (MK) and two isomeric diketones [1,5-cyclooctanedione (1,5-DK) and 1,4-cyclooctanedione (1,4-DK)], are the expected products of the consecutive ketonization of two COD double bonds. Two other two compounds, also with 8 carbon atoms, 3α-hydroxyhexahydropentalen-1-one (HP) and 3,4,5,6-tetrahydro-2*H*-pentalen-1-one (TP), are secondary products of the reaction, as we will see later. There is also a minor amount of some other compounds, but their low concentration hinders their identification. They are denoted as "other products".

Table 1 presents the results of the above experiment: conversions of N_2O, COD, and C═C bonds; composition of the reaction mixtures; and selectivities for products. These results will be discussed later together with the results of other experiments.

Effect of Reaction Time

The progress of consecutive ketonization of COD can be conveniently monitored in dependence on the reaction time. Based on the data of Table 1, we chose 523 K as the reaction temperature to perform a series of experiments lasting from 1 to 30 h. Results are presented in Table 2. One may see that, starting from the initial value (4.5 mol%), the COD concentration de-

Table 1. Ketonization of COD at various temperatures.[a]

T [K]	Conversion, X_i [%]			Composition of reaction mixture [mol%]							Selectivity, S_i [mol%]					
	N_2O	COD	C═C	COD	MK	1,5-DK	1,4-DK	HP	TP	O[b]	MK	1,5-DK	1,4-DK	HP	TP	O[b]
473	2.1	11.7	6.2	4.07	0.50	0.014	0.01	0	0	0.01	92.9	2.6	1.9	0	0	2.6
493	6.7	30.7	17.7	3.19	1.20	0.10	0.08	0	0	0.03	84.9	7.1	5.7	0	0	2.4
523	21.9	84.5	67.3	0.62	1.59	1.11	0.41	0.45	0.06	0.27	40.8	28.5	10.5	11.7	1.4	7.0
553	31.3	100	97.7	0	0.20	2.25	0	1.05	0.72	0.38	4.3	48.9	0	22.9	15.6	8.3

[a] *Reaction conditions:* 0.096 mol N_2O, 0.016 mol COD, 30 mL C_6H_6, 12 h.

[b] Other products.

Table 2. Effect of reaction time on ketonization of COD at 523 K.[a]

Time [h]	Conversion, X_i [%]			Composition of reaction mixture [mol%]							Selectivity, S_i [mol%]					
	N_2O	COD	C=C	COD	MK	1,5-DK	1,4-DK	HP	TP	O[b]	MK	1,5-DK	1,4-DK	HP	TP	O[b]
1	2.7	16.4	9.2	3.85	0.67	0.021	0.017	0	0	0.05	88.3	2.8	2.2	0	0	6.7
3.5	9.0	45.2	28.1	2.49	1.58	0.21	0.16	0	0	0.13	75.8	10.1	7.7	0	0	6.4
8	15.6	71.7	51.4	1.16	1.87	0.67	0.33	0.19	0.01	0.23	56.6	20.3	10.0	5.9	0.3	6.9
12	21.9	84.5	67.3	0.62	1.59	1.11	0.41	0.45	0.06	0.27	40.8	28.5	10.5	11.7	1.4	7.0
18.5	29.4	93.7	83.5	0.19	0.94	1.67	0.17	1.07	0.15	0.32	21.8	38.6	3.9	24.8	3.5	7.4
24	31.7	100	96.6	0	0.25	2.20	0	1.39	0.41	0.32	5.5	48.0	0	30.4	9.0	7.1
30	33.7	100	98.3	0	0.04	2.26	0	1.12	0.79	0.34	0.9	49.6	0	24.6	17.3	7.6

[a] *Reaction conditions:* 0.096 mol N_2O, 0.016 mol COD (4.5 mol%), 30 mL C_6H_6.

[b] Other products.

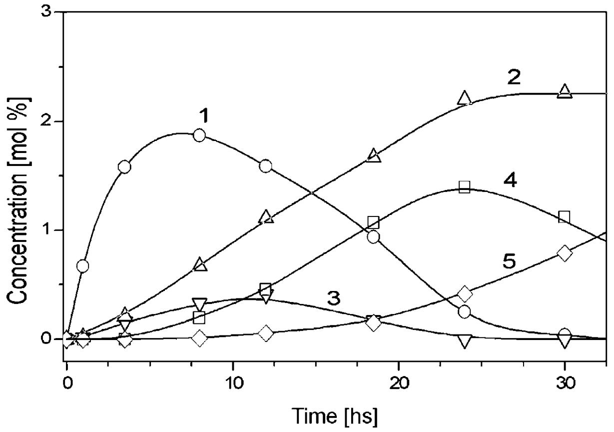


Figure 2. Product concentrations *vs.* ketonization time of COD at 523 K: MK (line 1), 1,5-DK (line 2), 1,4-DK (line 3), HP (line 4), TP (line 5).

creases monotonically and in 24 h approaches zero. Changes in the product concentrations are more complicated, which is clearly seen in Figure 2. Thus, the MK concentration (line 1) first increases, attains a maximum at 7–8 h, and then drops, approaching zero at the end of experiment. Such a behaviour indicates a consecutive reaction mechanism with the unsaturated MK to be an intermediate compound.

Further ketonization of the remaining double bond transforms MK into two isomeric diketones, 1,4-DK and 1,5-DK, depending on the carbon atom to which the second oxygen atom adds. Indeed, an increase in the MK concentration is accompanied by an increasing concentration of 1,5-DK (line 2), which attains its limiting value by the end of experiment. The behaviour of 1,4-DK (line 3) is quite different. Its concentration, being comparable with concentration of 1,5-DK at the initial period, increases more slowly, passes over a maximum (*ca.* 12 h), and disappears at the end of experiment. Along with the decrease in 1,4-DK concentration, there is an increase in the concentrations of HP (line 4) and TP (line 5). This gives an idea that the two latter compounds may be the products of further 1,4-DK transformation. To verify this idea we performed a more detailed analysis of the reaction mechanism.

Reaction Mechanism

Figure 3 shows a proposed general scheme of the reaction mechanism. In the first step, COD ketonization proceeds along the first C=C bond to give a monoketone MK. Ketonization of the second bond results in the formation of diketones and follows two routes. Route I leads to stable 1,5-DK, and route II – to unstable 1,4-DK, which further undergoes an intramolecular aldol reaction and turns into a bicyclic isomer containing keto and hydroxy groups (HP). This type

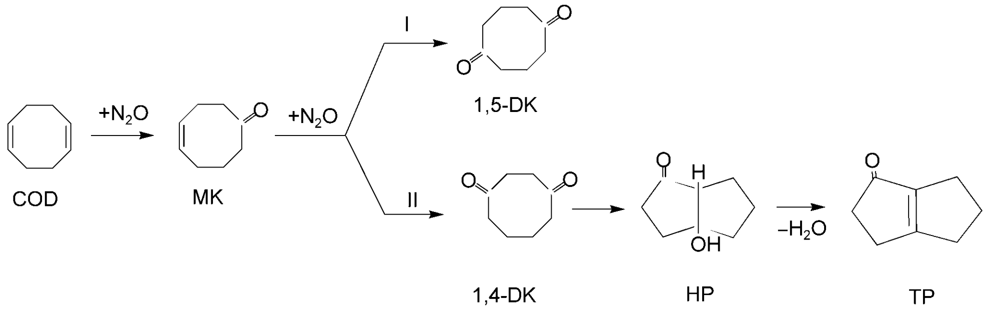


Figure 3. Mechanistic scheme for COD ketonization.

of transannular aldolization is of a significant interest in organic chemistry. In particular, the latter reaction of 1,4-cyclooctanedione and its derivatives was studied recently by Chandler and List[12] using *trans*-4-fluoroproline as a catalyst at room temperature. At the high temperatures used in our study, this reaction proceeds *via* a thermal route. However, the resulting HP is also not stable under these conditions and, eliminating H_2O, gradually transforms into the bicyclic unsaturated monoketone (TP).

If this mechanistic scheme is correct, then, despite secondary transformations of 1,4-DK, products fractions formed by route I (1,5-DK) and route II (1,4-DK + HP + TP) should be independent of time and remain constant in the reaction course. To verify this expectation one may calculate fractions F_i of each product of the MK ketonization [Eq. (2)]:

$$F_i = C_i / \sum C_i \tag{2}$$

where C_i is the concentration of 1,5-DK, 1,4-DK, HP, and TP in the reaction mixture (Table 2).

The results are given in Table 3 and Figure 4. As Table 3 shows, the fraction $F_{1,5\text{-}DK}$ is 55±1.5% and remains approximately constant to the point of complete transformation of MK. The fractions of other products change with the reaction time, which is seen most clearly in Figure 4. The value of $F_{1,4\text{-}DK}$, comprising initially 43–45%, decreases monotonically and approaches zero by the end of reaction (line 1).

Table 3. Product fractions of MK ketonization.[a]

Entry	Time [h]	Product fractions, F_i [%]				
		1,5-DK	1,4-DK	HP	TP	Σ[b]
1	1	55.3	44.7	0		44.7
2	3.5	56.7	43.2	0	0	43.2
3	8	55.5	27.4	16.2	0.9	44.5
4	12	54.6	20.2	22.4	2.8	45.4
5	18.5	54.6	5.6	35.0	4.9	45.5
6	24	55.0	0	34.8	10.2	45.0
7	30	54.2	0	26.9	18.9	45.8

[a] Calculated with the data of Table 2.

[b] Sum 1,4D-K; HP; TP.

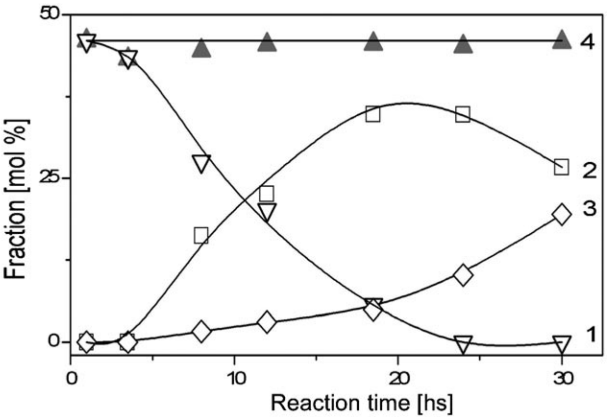


Figure 4. Fractions of MK ketonization products formed *via* route II (Figure 3) *vs.* reaction time: 1,4-DK (line 1), HP (line 2), TP (line 3), the sum 1,4-DK+HP+TP (line 4). Plotted with the data of Table 3.

In contrast, F_{HP} increases starting from zero and then passes a maximum (line 2), whereas F_{TP} monotonically increases over the entire period (line 3). Such a picture may indicate the following consecutive transformations: 1,4-DK→HP→TP. Indeed, the sum fraction of these three compounds remains constant (line 4) and comprises 45±1.5% of the total MK ketonization products, thus supporting the mechanism presented in Figure 3.

A similar analysis of the data reported in Table 1 gives the same ratio between routes I and II (0.55:0.45) regardless of variable reaction temperatures.

Effect of Solvent

The nature of the solvent is known to play an important role in organic reactions and can change the reaction rate by several orders of magnitude.[13] We tried several solvents differing in their dielectric constants ε and dipole moments μ. Experiments were carried out

Table 4. Solvent effect on COD ketonization.[a]

Solvent	Solvent properties[14]		Conversion, X_i [%]			Rate constant [h^{-1}]	Selectivity, S_i [mol%]					
	ε	μ [D]	N_2O	COD	C=C		MK	1,5-DK	1,4-DK	HP	TP	Other
Benzene	2.28	0	21.9	84.5	67.3	0.15	40.8	28.5	10.5	11.7	1.4	7.0
Cyclohexane	2.02	0	19.8	81.3	58.3	0.12	45.6	28.0	7.3	11.6	1.5	6.0
Acetonitrile	33.0	3.87	21.0	82.5	61.6	0.13	44.1	26.5	4.2	14.7	2.4	8.1
THF	7.52	1.75	20.2	82.3	59.5	0.12	45.8	26.8	7.7	12.9	1.2	5.6
1,4-Dioxane	2.22	0	26.0	93.6	76.4	0.27	26.8	37.0	1.7	24.8	3.6	6.0
Ethanol	25.3	1.69	18.1	72.9	53.2	0.09	54.2	20.4	1.1	3.5	13.1	7.7

a) *Reaction conditions:* 0.096 mol N_2O, 0.016 mol COD, 30 mL solvent, 12 h, 523 K.

at 523 K for 12 h with the same composition of feed mixture (0.016 mol COD, 0.096 mol N_2O, 30 mL solvent). The change of a solvent has only a slight effect on the reaction rate (Table 4). The rate constants estimated assuming a first-order reaction are virtually close for most solvents and equal to $0.13 \pm 0.02\ h^{-1}$. This value becomes somewhat higher with 1,4-dioxane ($k = 0.27\ h^{-1}$) and lower with ethanol ($k = 0.09\ h^{-1}$). However, the distinctions do not exceed a factor of three. According to the literature, a minor solvent effect is typical of other reactions of the 1,3-dipolar addition type.[13]

Interestingly, the ratio between routes I and II is also independent of the solvent. In all cases the value of $F_{1,5\text{-}DK}$ is *ca.* 55%, leaving the other 45% for 1,4-DK and its derivatives. However, the solvent has a pronounced effect on the stability of 1,4-DK towards secondary transformations. Thus, for benzene the fraction of 1,4-DK in the sum of products (1,4-DK+HP+TP) is 45%, for acetonitrile 20%, and for dioxane and ethanol only 5–6%. The mechanism of this effect is unclear.

Reaction Kinetics

To describe the ketonization kinetics, we measured the activation energy and the reaction orders with respect to N_2O and COD. Therewith, the reaction conditions (temperature and time) were chosen so as to provide conversions of the reactants not higher than 15–20%, which allows calculation of the reaction rate using the approximation of a differential reactor.

Table 5 presents the temperature effect on the rate of ketonization. Rising the temperature from 473 to 523 K increases the rate by more than an order of magnitude. The dependence is satisfactorily described by an Arrhenius plot with the activation energy $E = 113 \pm 4\ kJ\,mol^{-1}$. Earlier E values were measured for two other reactions of the liquid phase ketonization: $88\ kJ\,mol^{-1}$ for cyclopentene[6b] and $92\ kJ\,mol^{-1}$ for 2-butene.[15] In our case, the E value is noticeably higher, which possibly may relate to a higher stability of THE COD molecule as compared, in particular, with a strained five-membered cycle of the cyclopentene molecule.

Table 5. Temperature effect on the rate of COD ketonization.[a]

T [K]	Time [h]	Conversion, X_i [%]			Reaction rate
		N_2O	COD	C=C	[10^{-2} mol/L h]
473	12	2.1	11.7	6.2	0.52
493	5	2.8	17.5	9.7	1.9
503	2.5	2.6	13.7	7.6	2.9
523	1	2.7	16.4	9.2	8.7

[a] *Reaction conditions:* 0.096 mol N_2O, 0.016 mol COD, 30 mL C_6H_6.

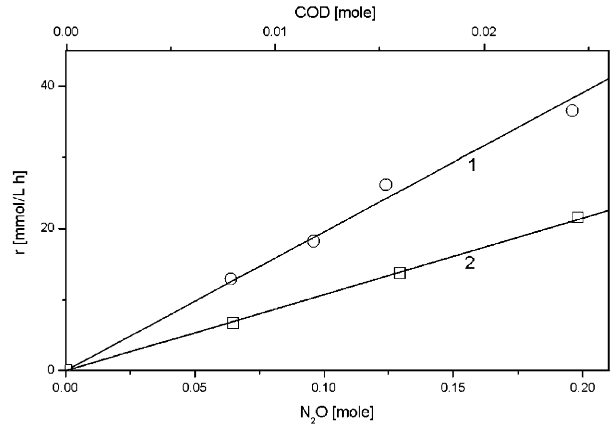


Figure 5. The rate of ketonization at 493 K *vs.* amount of N_2O (1) and COD (2) in the reaction mixture.

To determine the reaction order, two series of experiments were performed at 493 K. In the first series, the reaction rate was measured upon introduction in the reaction system of different amounts of COD (0.0082–0.0245 mol), while in the second series upon introduction of different amounts of N_2O (0.064–0.196 mol). In both cases the reaction rate is satisfactorily described by linear dependences issuing out of the origin of THE coordinates (Figure 5), which indicates their first order nature with respect to initial reactants. Therefore, the reaction rate can be described by the following kinetic equation [Eq. (3)]:

$$r = A \cdot e^{-\frac{E}{RT}} \cdot C_{COD} \cdot C_{N_2O} \tag{3}$$

where A is a pre-exponential factor; E is an activation energy, C_{COD} and C_{N_2O} are concentrations of the reactants in liquid phase. Since the precise N_2O concentration in the liquid phase is not known, we assume it to be proportional to the N_2O mole amount introduced into the system. This circumstance does not prevent measurement of the reaction order, but prevents calculation of the A value.

On the Reactivity of C=C Bonds Residing in the COD and MK Molecules

The screening of alkenes showed that the reactivity of C=C bonds toward N_2O may considerably depend on the molecule's composition.[8] It is interesting to elucidate whether ketonization of the first C=C bond in a COD molecule affects the reactivity of the remaining double bond. This question is quite pertinent because the C=O group was shown to exhibit a significant deactivating effect at ketonization of 1,4-cyclohexadiene.[8]

At equal reactivity of C=C bonds, their reaction with N_2O should proceed statistically, no matter whether the bond resides in COD or MK. In this case, one may calculate the concentrations of ketonized products versus C=C conversion by the following theoretical equations [Eq. (4), Eq. (5), and Eq. (6)]:

$$C_{COD} = (1 - X_{C=C})^2 \tag{4}$$

$$C_{MK} = 2X_{C=C} \cdot (1 - X_{C=C}) \tag{5}$$

$$C_{DK} = X_{C=C}^2 \tag{6}$$

Figure 6 compares experimental data (dots) with the theoretical dependences (solid lines). The C_i values were calculated with the results of Table 1 and Table 2. The value of C_{DK} includes not only diketones proper (1,5-DK and 1,4-DK), but also HP and TP. It is seen that experimental data satisfactorily agree with the theoretical curves, which confirms the equivalence of the C=C reactivities.

In the case of non-equivalence, there would be a deviation from the theoretical curves, most pronounced for C_{MK}. In the extreme case, with the bond reactivity in the initial COD far exceeding that in MK ($r_{COD} \gg r_{MK}$), the MK concentration would follow the dotted line 1 and attain 100% at $X_{C=C} = 0.5$. And *vice versa*, at $r_{COD} \ll r_{MK}$, the value of C_{MK} would always remain zero (dotted line 2).

The bonds equivalence at ketonization of COD may relate to the fact that, in distinction to 1,4-cyclohexadiene, the double bonds in this molecule are more distant from each other, so ketonization of one of these bonds has a weak to no effect on the reactivity of other one.

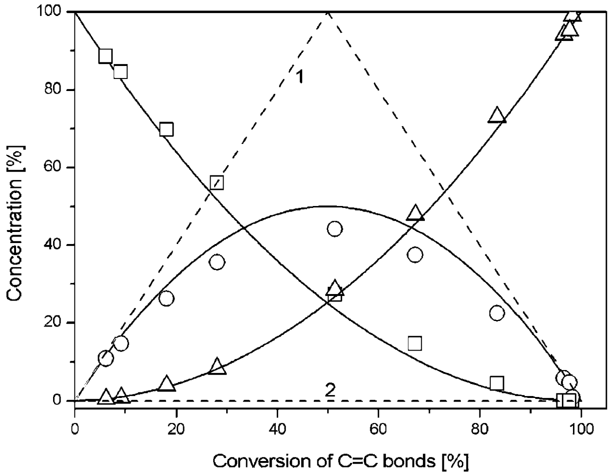


Figure 6. Concentration of COD (□), MK (○) and DK (△) in the reaction mixture *vs.* C=C conversion. Dots are experimental results; solid lines are calculated dependences assuming identical reactivity of C=C bonds in COD and MK ($r_{COD} = r_{MK}$); dashed line 1 is a calculated C_{MK} dependence assuming $r_{COD} \gg r_{MK}$; dashed line 2 is a calculated C_{MK} dependence assuming $r_{COD} \ll r_{MK}$.

Conclusions

Cyclic mono- and diketones are of considerable interest as solvents, reagents for organic syntheses, and as intermediates in the production of medicinal and aromatic substances. The methods of their preparation are quite complicated and expensive.[16] The studied reaction suggests a new simple approach for the synthesis of C_8 cyclic ketones *via* the oxidation of ready available 1,5-cyclooctadiene by nitrous oxide. The total yield of ketonized products exceeds 90%.

A thorough study on the kinetics and the mechanism of COD ketonization carried out in this work extends our knowledge of nitrous oxide as a remarkable and prospective oxygen donor, which affords unique oxidation of C=C bonds into carbonyl groups not allowed with other donors.

The N_2O oxidant has a particular value within the concept of green chemistry.[17] Its use not only creates no problems for the environment, but on the contrary, opens a way for useful application of this ecologically unfriendly component present in many industrial off-gases.

Experimental Section

The ketonization was usually carried out with a 4.5 mol% solution of 1,5-cyclooctadiene (COD) using a 100-mL steel Parr reactor equipped with manometer and stirrer. To provide a reliable NMR analysis of the reaction products, in most cases benzene was used as a solvent. In a typical run 2 mL of COD (99%, Aldrich) and 30 mL of benzene (99%, Khimmed) were loaded into the reactor. After pumping out the air, the reactor was filled with a measured amount of medical grade nitrous oxide. Then the reactor was heated ($6\,\mathrm{K\,min^{-1}}$) to the reaction temperature and kept for some time. Pressure at the reaction temperature was 3.5–8.5 MPa.

The reaction products were analyzed by the GC, GC-MS, and NMR methods. The gas phase GC analysis (N_2O, N_2, CO, CO_2, low hydrocarbons) was performed using a TCD and a packed column with Porapak Q. N_2 was the only product detected in the gas phase. Based on the N_2 amount, conversions of N_2O and C=C bonds were calculated [Eq. (7) and Eq. (8)]:

$$X_{N_2O} = n_{N_2} \big/ n_{N_2O}^0 \tag{7}$$

$$X_{C=C} = n_{N_2} \big/ n_{C=C}^0 \tag{8}$$

where $n_{C=C}^0$ is the amount of C=C bonds in the initial COD.

GC analysis of the liquid phase was performed on heating (3 K min^{-1}) from 423 K to 493 K using an FID and capillary column (50 m, 0.2 mm, SE-52). GC-MS analysis was performed using a Varian Saturn 2000 instrument equipped with a quartz capillary column (30 m, 0.25 mm, CP-Sil 24 CB) on heating (7 K min^{-1}) from 323 to 523 K. ^{13}C NMR spectra were recorded at 100.61 MHz using a Bruker MSL-400 spectrometer. ^{13}C NMR spectral data of the COD and its ketonization products were as follows.

1,5-COD: $\delta = 128.93$ (4 C, $-\mathrm{CH}=$), 28.5 (4 C, $-\mathrm{CH_2}-$).

MK: $\delta = 211.87$ (1 C, C=O), 130.85 (1 C, $=\mathrm{CH}-$), 130.68 (1 C, $=\mathrm{CH}-$), 47.24 (1 C, $-\mathrm{CH_2}-$), 40.24 (1 C, $-\mathrm{CH_2}-$), 26.62 (1 C, $-\mathrm{CH_2}-$), 24.19 (1 C, $-\mathrm{CH_2}-$), 22.19 (1 C, $\mathrm{CH_2}-$).

1,5-DK: $\delta = 211.20$ (2 C, C=O), 42.18 (4 C, $-\mathrm{CH_2}-$), 22.33 (2 C, $-\mathrm{CH_2}-$).

1,4-DK: $\delta = 211.95$ (2 C, C=O), 41.38 (2 C, $-\mathrm{CH_2}-$), 40.83 (2 C, $-\mathrm{CH_2}-$), 24.87 (2 C, $-\mathrm{CH_2}-$).

HP: $\delta = 218.06$ (1 C, C=O), 87.05 (1 C, C−OH). 60.15 (1 C, CH), 40.88 (1 C, $-\mathrm{CH_2}-$), 38.60 (1 C, $-\mathrm{CH_2}-$), 34.65 (1 C, $-\mathrm{CH_2}-$), 28.30 (1 C, $-\mathrm{CH_2}-$), 25.81 (1 C, $-\mathrm{CH_2}-$).

TP: $\delta = 202.16$ (1 C, C=), 185.43 (1 C, C=), 149.06 (1 C, C=O), 41.22 (1 C, $-\mathrm{CH_2}-$), 31.77 (1 C, $-\mathrm{CH_2}-$), 27.95 (1 C, $-\mathrm{CH_2}-$), 25.44 (1 C, $-\mathrm{CH_2}-$), 24.94 (1 C, $-\mathrm{CH_2}-$).

Quantitative ^{13}C NMR relative intensity measurements were made with inverse gated proton decoupling and long relaxation delays (30–60 s). These results together with the GC data were used to calculate the COD conversion and that of double bonds [Eq. (9) and Eq. (10)]:

$$X_{COD} = \sum C_i \big/ C^0_{COD} \tag{9}$$

$$X_{C=C} = X_{COD} - C_{MK} \big/ 2 \cdot C^0_{COD} \tag{10}$$

Experimental results were reproducible within ±5 rel.%, the mass balance based on carbon was 100 ± 3%, and balance based on oxygen was 100 ± 8%.

More experimental information is given elsewhere.[8]

References

[1] a) G. Centi, S. Perathoner, F. Vazzana, M. Marella, M. Tommaselli, M. Mantegazza *Advances Environm. Res.* **2000**, *4*, 325–338; b) J. Perez-Ramirez, F. Kapteijn, K. Schoffel, J. A. Moulijn, *Appl. Catal. B: Envir.* **2003**, *44*, 117–151.

[2] a) E. Suzuki, K. Nakashiro, Y. Ono, *Chem. Lett.* **1988**, *6*, 953–956; b) A. S. Kharitonov, T. N. Aleksandrova, L. A. Vostrikova, K. G. Ione, G. I. Panov, USSR Patent 1,805,127, **1988**.

[3] a) T. Yamada, K. Hashimoto, Y. Kitaichi, K. Suzuki, *Chem. Lett.* **2001**, *30*, 922–923; b) R. Ben-Daniel, R. Neumann, *Angew. Chem.* **2003**, *115*, 96–99; *Angew. Chem. Int. Ed.* **2003**, *42*, 92–95; c) T. L. Stuchinskaya, M. Muzevir, E. F. Kozhevnikova, I. V. Kozhevnikov, *J. Catal.* **2005**, *231*, 41–47.

[4] a) G. I. Panov, *CATTECH*, **2000**, *4*, 18–31; b) V. N. Parmon, G. I. Panov, A. Uriarte, A. S. Noskov, *Catal. Today* **2005**, *100*, 115–131; c) G. I. Panov, K. A. Dubkov, A. S. Kharitonov, in: *Modern Heterogeneous Oxidation Catalysis*, (Ed.: Mizuno), Wiley-VCH, Weinheim, **2009**, Chap 7, pp 217–252.

[5] F. S. Bridson-Jones; G. D. Buckley; L. H. Cross, A. P. Driver, *J. Chem. Soc.* **1951**, 2999–3008.

[6] a) G. I. Panov, K. A. Dubkov, E. V. Starokon, V. N. Parmon, *React. Kinet. Catal. Lett.* **2002**, *76*, 401–406; b) K. A. Dubkov, G. I. Panov, E. V. Starokon, V. N. Parmon, *React. Kinet. Catal. Lett.* **2002**, *77*, 197–205.

[7] a) V. I. Avdeev, S. Ph. Ruzankin, G. M. Zhidomirov, *Chem. Commun.* **2003**, *1*, 42–43; b) I. Hermans, B. Moens, J. Peeters, P. Jacobs, B. Sels, *Phys. Chem. Chem. Phys.* **2007**, *9*, 4269–4274.

[8] E. V. Starokon, K. A. Dubkov, D. E. Babushkin, V. N. Parmon, G. I. Panov, *Adv. Synth. Catal.* **2004**, *346*, 268–274.

[9] BASF news Release, April 03, **2006** (press.contact@basf.com).

[10] a) K. A. Dubkov, S. V. Semikolenov, D. E. Babushkin, L. G. Echevskaya, M. A. Matsko, D. P. Ivanov, V. A. Zakharov, V. N. Parmon, G. I. Panov, *J. Polym. Science Part A* **2006**, *44*, 2510–2520; b) K. A. Dubkov, S. V. Semikolenov, D. P. Ivanov, D. E. Babushkin, M. A. Matsko, G. I. Panov, *J. Appl. Polymer Sci.* **2009**, *114*, 1241–1249.

[11] I. Hermans, K. Janssen, B. Moens, A. Philippaerts, B. Van Berlo, J. Peeters, P. A. Jacobs, B. Sels, *Adv. Synth. Catal.* **2007**, *349*, 1604–1608.

[12] C. L. Chandler, B. List, *J. Am. Chem. Soc.* **2008**, *130*, 6737–6739.

[13] C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd edn., Weinheim, Wiley-VCH, **2003**, 187–198.

[14] *Handbook of Chemistry and Physics*, 85th edn., (Editor-in-Chief: D. R. Lide), CRC Press, Boca Raton, **2004**, pp 15–17.

[15] S. V. Semikolenov, K. A. Dubkov, E. V. Starokon, G. I. Panov, D. E. Babushkin, *Russ. Chem. Bull.* **2005**, *54*, 948–956.

[16] a) S. L. Schreiber, D. B. Smith, G. Schulte, *J. Org. Chem.* **1989**, *54*, 5994–5996; b) S. S. Mahajan, M. M. Sharma, T. Sridhar, *Ind. Eng. Chem. Res.* **2005**, *44*, 1390–1395; c) G. Süss-Fink, G. B. Shul′pin, L. S. Shul′pina, US Patent 7,015,358 B2, **2006**.

[17] R. A. Sheldon, I. Arends, U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, **2007**, pp 133–221.