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On the Selectivity of the Biomimetic Oxidation of the Saturated Hydrocarbon 1,3-Dimethyladamantane in a Gif-Type System Containing a Fe^{2+} Salt, Picolinic Acid, and Pyridine

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Abstract—The effects of the composition of a heterogeneous catalytic system based on $Fe_2SO_4 \cdot 7H_2O$, picolinic acid (pyridine-2-carboxylic acid), and pyridine and system preparation procedures on the selectivity of oxidation of 1,3-dimethyladamantane (1,3-DMA) with an aqueous 30% hydrogen peroxide solution in an aqueous acetonitrile solvent at room temperature and ambient pressure were studied. The yields of 1,3-DMA oxidation products were increased from fractions of a percent in initial experiments to the tens of percent under new catalytic conditions of final experiments. It was found that three different mechanisms can occur in the test system under various conditions; conceivably, these are radical, ion–molecule, and radical-cation mechanisms. In the first case, a statistical mixture of the products of 1,3-DMA oxidation at tertiary and secondary C–H bonds was formed. In the second and third cases, oxidation occurred only at secondary and tertiary C–H bonds, respectively. Unlike the first two cases, the selectivity of 1,3-DMA oxidation to a tertiary alcohol under conditions of the Gif-type test system corresponds to the selectivity of biological oxidation and, to the best of our knowledge, is the first example of this kind.

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INTRODUCTION

In 1972, Breslow was the first to introduce the term *biomimetic chemistry* designating a special area of organic chemistry that attempts to reproduce naturally occurring reactions and enzymatic processes in order to enhance the power of organic chemistry [1]. The main goal of studies in this branch of organic chemistry was to achieve high reaction selectivity, which approaches the selectivity of naturally occurring enzymatic reactions. As compared with the problem of reproducing the regioselectivity and stereoselectivity of naturally occurring reactions, other special features, including high rates, of these reactions were considered less important. This fact was reflected in the title of a more recent review of Breslow [2]: "Biomimetic Control of Chemical Selectivity."

The commonly used term *biomimetic* generally refers to any aspect in which a chemical process imitates a biochemical reaction [2]. In this context, attention should be focused primarily on the selectivity of processes.

The reproduction of the structure and operation of biological catalytic centers for the oxidative functionalization of hydrocarbons using chemical methods has been designated as *biomimetic oxidation* [3–5].

An attractive feature of the oxidative biotransformation of saturated hydrocarbons, which occur in considerable amounts in gases, petroleum, and gas condensates, consists in the possibility of using mild conditions (room temperature and ambient pressure) because the currently available industrial processes for the conversion of the above hydrocarbon raw materials are associated with high energy consumption [6–8]. At the same time, alternative technologies are now unable to meet competition in the oxidation of saturated hydrocarbons. They primarily belong to basic research oriented to studies of their capabilities, reaction mechanisms, and factors affecting selectivity [9, 10]. Therefore, any new reports on the appearance of much more simply organized and readily available chemical systems that efficiently operate under ordinary laboratory conditions have attracted considerable interest. These systems (in essence, model systems) are often accompanied by the epithet *biomimetic* even in the absence of a correspondence with the selectivity of naturally occurring processes in simulated biological systems.

Such an ambiguous situation [7, 8, 11–15], which was referred to as paradoxical [14, 15], takes place in the oxidation of saturated hydrocarbons in catalytic systems known as Gif systems [7, 8, 13]. Various researchers detected different selectivities in oxidation

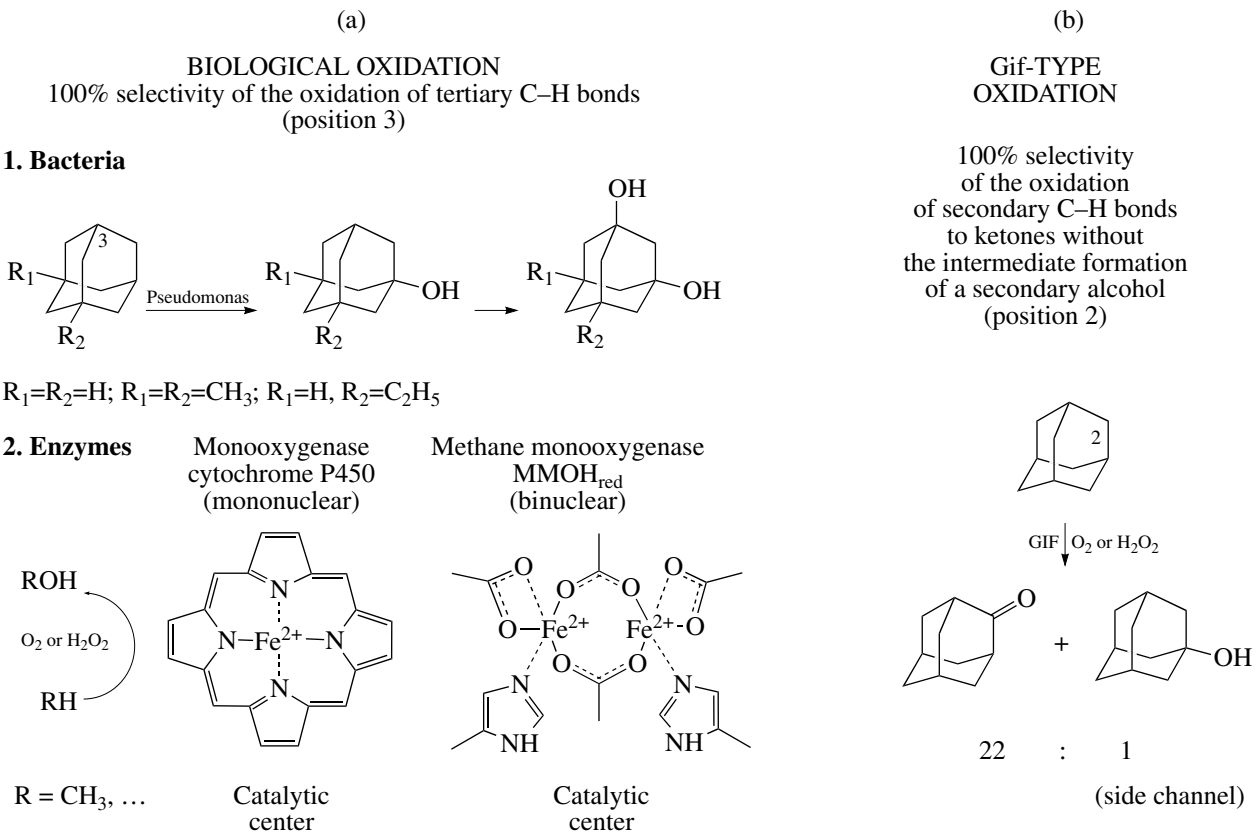


Fig. 1. Comparison between (a) the biological oxidation of saturated hydrocarbons RH and (b) the Gif-type oxidation of RH exemplified by methane and hydrocarbons from the adamantane series. The catalytic centers of enzymes are represented in simplified forms (see the text).

processes performed under uniform experimental conditions. In this paper, attention is focused on the fact that the selectivity of neither of the Gif systems studied previously corresponded to the selectivity of processes with the participation of biological materials.

Figure 1 shows that alcohols (tertiary alcohols in the case of adamantane hydrocarbons) are formed in the oxidation of saturated hydrocarbons in the presence of Pseudomonas bacteria [9] or enzymes (mononuclear monooxygenase containing cytochrome P450 or binuclear methane monooxygenase (MMO) [3, 4, 7, 8]). The selectivity of the processes is as high as 100%. The structures of electron-compensated (electrically neutral) catalytic centers of the oxidation of saturated hydrocarbons (RH) with oxygen or hydrogen peroxide are represented in a simplified form. We have restricted ourselves to the images of a mononuclear iron–porphyrin ring in the case of the catalytic center of cytochrome P450 or the most stable fragment of a binuclear complex containing four carboxylate groups ($-COO^-$) and imidazole rings in the case of the catalytic center of MMO. In both cases, we gave the reduced forms of catalytic centers containing the (six-coordinated) iron ions Fe^{2+}, because these forms are responsible for the fixation of oxygen and other oxidizing species. In order to indicate the catalytic center of MMO, a fragment of its reduced form ($MMOH_{red}$) was used. In the reproduction of the spatial arrangement of ligands in the structure of the $MMOH_{red}$ catalytic center, the presence of an additional $O–Fe^{2+}$ bond and water molecules in the coordination sphere of the second ion of iron is usually shown [3].

In 1983–1984, Barton was the first to combine reagents required for catalysis in a reaction volume based on the composition of the catalytic center and the catalytic cycle of monooxygenases containing cytochrome P450. These reagents are iron powder as a source of iron ions and as a reducing agent (a source of electrons), a carboxylic acid (a source of protons), molecular oxygen (an oxidizing agent), and pyridine as a solvent and nitrogen-containing ligand. It was found that organometallic complexes that catalyze the oxidation of C–H bonds in saturated hydrocarbons are spontaneously formed in this chemical system under ambient room conditions [7, 11–13].

However, it was found that, under new catalytic conditions, the oxidation selectivity of adamantane as a test hydrocarbon at secondary C–H bonds was higher than that at tertiary bonds by a factor of 22 (Fig. 1). In this case, ketones were primarily formed, and correspond-

ing alcohols did not serve as the precursors of these ketones. The formation of the second product (a tertiary alcohol) was related to the simultaneous occurrence of a side radical reaction. Thus, according to Barton, it follows that, ideally, the Gif-type oxidation, as well as biological oxidation, should be characterized by 100% selectivity. Under an attack of oxygen-containing radicals on adamantane, tertiary C–H bonds are primarily oxidized along with secondary C–H bonds (the value of 3° : 2° normalized to a C–H bond is 6.7 [7]). On this basis, a conclusion on the nonradical mechanism of oxidation was made and a hypothesis on the participation of the ferroxo complex Fe^{5+}=O in catalytic processes was formulated (by analogy with the catalytic cycle of monooxygenase containing cytochrome P450).

Thus, the problem of the assignment of new catalytic systems to biomimetically operating systems appeared since the early studies by Barton, because the main oxidation products (ketones) were other than alcohols (tertiary alcohols in the case of adamantane) [7, 11–13]. These products were not formed by well-known free-radical mechanisms. As a possible reason for the unusual selectivity of the oxidation of saturated hydrocarbons at methylene groups, Barton postulated that intermediate complexes with the iron–carbon (in more exact terms, iron–methylene) Fe^{5+}=C< bond are formed from the ferroxo complex Fe^{5+}=O.

Subsequently, it was demonstrated that almost all the types of reagents in the given chemical system can be varied over a very wide range with the retention of the ability to oxidize an organic substrate to ketones [7, 11–13]. In particular, Fe^{2+} or Fe^{3+} salts and various ligands, carboxylic acids, and solvents (in combination with pyridine) can be used as starting compounds, and hydrogen peroxide and other oxidizing agents can be used in place of oxygen. Experiments with various reducing agents and even metal ions were performed. As a result of this breadth, the concept of the Gif system became ambiguous and was replaced with the even more ambiguous concept of the Gif-type system, and several trivial abbreviations were introduced in order to denote various versions of the Gif systems [7, 13].

In order to systematize the study of various Gif systems, we tentatively subdivided all of the known and conceivable versions into four groups from the standpoint of the positional oxidation selectivity of C–H bonds in saturated hydrocarbons. As a criterion, we used the characteristic values of the 3° : 2° ratio normalized to a C–H bond for the oxidation of tertiary (position 3°) and secondary (position 2°) C–H bonds in adamantane (see Fig. 1). The first group consists of all of the systems in which the specific Gif effect occurs: the selective oxidation of methylene groups into keto groups without intermediate alcohol formation (3° : 2° ≤ 0.3) [7, 11–13]. The second group consists of the systems in which the nonselective (statistical) radical oxidation of tertiary C–H bonds primarily occurs along with the oxidation of secondary C–H bonds (3 ≤ 3° : 2° ≤ 7) [7, 14, 15]. The third group consists of the systems in which the decomposition of hydrogen peroxide to oxygen rather than the oxidation of a hydrocarbon is observed [12]. The systems with the selective oxidation of saturated hydrocarbons to alcohols (to a tertiary alcohol in the case of adamantane) (3° : 2° ≥ 10–50) [3, 4, 7, 9] should be assigned to the fourth group. The intermediate values of 3° : 2° = 0.3–3 and 7–10 may be indicative of the occurrence of a few (most likely, two) parallel reaction paths in the system.

From the standpoint of positional selectivity, the fourth group could pretend to be classified with biomimetically operating systems. However, conditions under which the biomimetic oxidation of substrates occurs in the framework of Gif systems are currently unknown. Thus, in the past two decades (1983–2003), considerable factual information and methodological experience has been accumulated in studies on the oxidation of saturated hydrocarbons in so-called Gif systems. However, this experience resulted in moving away from the initial goal: to find and study biomimetically operating chemical systems, primarily, from the standpoint of process selectivity. The aim of this work was to fill the above gap.

EXPERIMENTAL

1,3-Dimethyladamantane (1,3-DMA) was chosen as a substrate to be oxidized because its structure contains all of the types of C–H bonds (primary, secondary, and tertiary). The advantages of 1,3-DMA over adamantane are the following: the former contains three (rather than one) types of (positionally different) methylene groups; under ambient room conditions, 1,3-DMA is a liquid, which is easier to operate than solid adamantane; and 1,3-DMA is better soluble in acetonitrile. Moreover, considerable experience in the oxidation of 1,3-DMA under various conditions has been accumulated in our laboratory [9, 16–18]. For catalytic experiments, 1,3-DMA of 99% purity was taken. It contained approximately equal amounts (1%) of 1,2- and 1,4-dimethyladamantanes as impurities.

Two main procedures were used in this study for preparing the catalytic system. In standard experiment no. 1, solid reagents (iron(II) sulfate ($FeSO_4 \cdot 7H_2O$; 1.39 g, 5×10^{-3} mol), picolinic acid ($C_6H_5NO_2$; 1.23 g, 10×10^{-3} mol), and ascorbic acid ($C_6H_8O_6$; 1.761 g, 1×10^{-3} mol)) were added to a solvent mixture containing 27 ml of acetonitrile, 4 ml of distilled water, and 0.08 ml (1×10^{-3} mol) of pyridine (C_5H_5N). After the formation of a reddish brown precipitate, 0.5 ml (2.7×10^{-3} mol) of 1,3-DMA ($C_{12}H_{20}$) was introduced into the heterogeneous (solution/precipitate) system and oxidized with 0.4 ml (4×10^{-3} mol) of a 30% hydrogen peroxide solution for 1 h (four 0.1-ml portions at regular intervals of 15 min) under ambient room conditions. After this lapse of time, the organometallic complexes of the reaction mixture were decomposed with 30 ml of

distilled water, and the liberated 1,3-DMA and its conversion products were extracted with the use of 15 ml of diethyl ether. The resulting extract was analyzed by chromatography–mass spectrometry (GC–MS). For this purpose, a high-resolution Finnigan MAT 95 XL instrument (ionization energy, 70 eV; cathode current, 1 mA; mass range, 20–800 amu; resolution, 1000; source temperature, 200°C; scan rate, 1 s/decade) and an HP 6890+ chromatograph (capillary column 30 m in length and 0.25 mm in diameter with an SE-30 stationary liquid phase) were used. Helium was used as a carrier gas (split ratio of 1 : 30); temperature programming was as follows: from 30 to 120°C at a heating rate of 5 K/min; then, to 270°C at a rate of 10 K/min and an exposure of 10 min at 270°C.

A change from the initial conditions (experiment no. 1) to new standard conditions (experiment no. 13) was performed by removing ascorbic acid from the composition of reagents and decreasing the amount of water from 4 to 1 ml. The second difference was that the phases of a heterogeneous catalytic system were separated by centrifugation (MPW-340 centrifuge (Poland); 2000 rpm; time, 15 min) before the stage of oxidation. After the separation of solution, the sediment, which was predried in a desiccator over concentrated sulfuric acid, was taken for the oxidation of 1,3-DMA. Acetonitrile (27 ml) dried with fused calcium chloride was used as a solvent. The other conditions of catalyst preparation, oxidation reaction, and product separation and analysis were the same as in the first procedure (standard experiment no. 1). Special features of experiment nos. 2–12 and 14, as well as other experiments related to either experiment no. 1 or no. 13, are specified in the Results section as they first appear.

Because we started a study of the capabilities of a new catalytic system with previously unknown properties, we solved several methodological problems that appeared successively in the course of this study (these problems are typical of catalytic studies of this kind). First, we determined that the test catalytic system is a heterogeneous (solution/precipitate) rather than homogeneous system. Thereafter, we revealed the roles of individual phases in the reactions of 1,3-DMA oxidation. Second, at a fixed reaction time, we tested the occurrence of postreaction processes that can affect the composition of final products, which were monitored. Third, we determined the effect of catalysis and particular components that are necessary or additional for the occurrence of the effect of catalysis. Fourth, catalytic conditions were optimized in order to reach the highest selectivity of 1,3-DMA oxidation at tertiary C–H bonds. Fifth, the effect of the amount of an oxidant added on the selectivity of oxidation processes was studied. It is our opinion that the above list of methodological problems successively solved in the course of this study will considerably assist the reader in perceiving the entire sequence and logical structure of the results reported below.

RESULTS

The early experiments demonstrated that a solution/precipitate heterogeneous catalytic system occurred in acetonitrile. Several series of experiments (see Figs. 2–4 and Tables 1–3) were performed to determine the roles of phases and individual components of the solution/precipitate heterogeneous system based on iron, picolinic acid, and pyridine in the oxidation of 1,3-DMA with hydrogen peroxide in acetonitrile under room conditions. Along with the oxidation of 1,3-DMA to ketones, a tertiary alcohol, and secondary alcohols, the alkylation of acetonitrile and pyridine by 1,3-DMA was observed in the test system. The alkylation of picolinic acid did not occur. Figure 3 summarizes the structural formulas of parent 1,3-DMA, its oxidation products, and alkylation products. Tables 1 and 2 systematize the yields of oxidation and alkylation products with respect to the relative concentration of the parent hydrocarbon in the extract.

A comparison between data (Figs. 2, 3; Table 1) on the relative concentrations of oxidation products and the products of pyridine alkylation with 1,3-DMA in a standard experiment (no. 1) without phase separation and 1,3-DMA oxidation only in solution (experiment no. 2) or only at the precipitate (experiment no. 3) suggests that pyridine alkylation products were mainly formed in solution, whereas 1,3-DMA oxidation products were mainly formed at the precipitate. The oxidation of 1,3-DMA only in solution (experiment no. 2), as well as in standard experiment no. 1, resulted in equal ratios between the yields of four pyridine alkylation products. In this case, the total relative yields (~60×10^{-4}) of these products were also equal and higher than the total relative yield of oxidation products by a factor of 7–20. In contrast, in the oxidation of 1,3-DMA only at the precipitate (experiment no. 3), the total relative

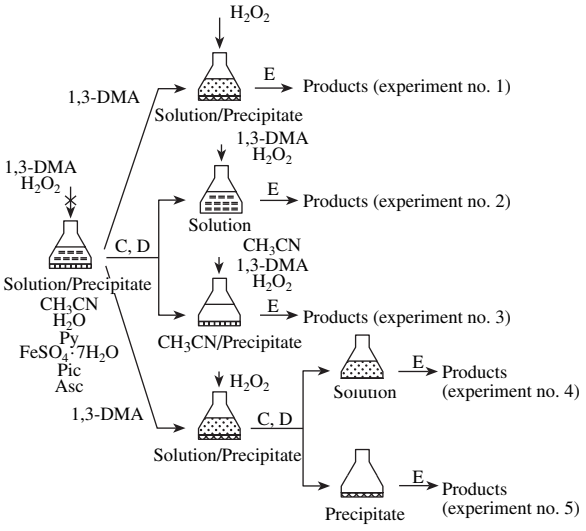
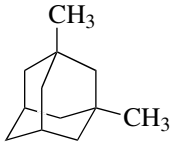


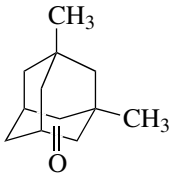
Fig. 2. Roles of solution/precipitate phases under the initial standard conditions of experiment no. 1. C, D, and E stand for centrifugation, decantation, and extraction, respectively.

PARENT HYDROCARBON

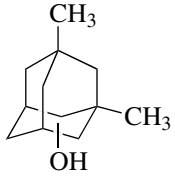


1,3-DMA (m/z = 164)

OXIDATION PRODUCTS

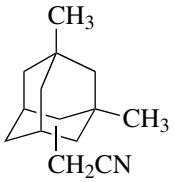


Ketone (m/z = 178)

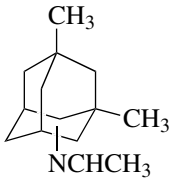


Alcohol (m/z = 180)

PRODUCTS OF ALKYLATION BY ACETONITRILE

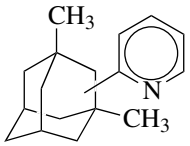


m/z = 203

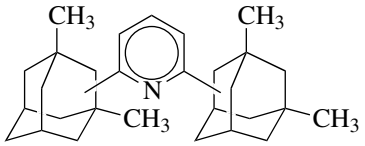


m/z = 205

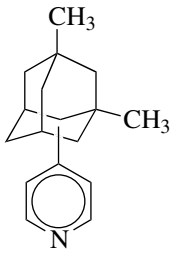
PRODUCTS OF ALKYLATION BY PYRIDINE



retention time of ~750 s

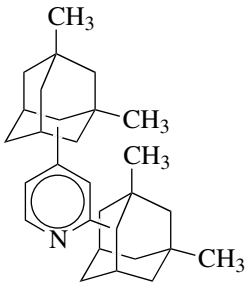


retention time of ~1000 s



retention time of ~800 s

m/z = 241



retention time of ~1040 s

m/z = 403

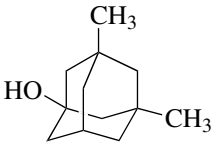
Fig. 3. Structural formulas of parent 1,3-DMA and its oxidation and alkylation products under initial standard conditions (experiment no. 1).

yield of oxidation products (143×10^{-4}) increased by two orders of magnitude, whereas the total yield of pyridine alkylation products decreased by an order of magnitude (4.7×10^{-4}). In this case, the ratio between 1,3-DMA oxidation channels at tertiary and secondary positions normalized to a C–H bond remained unaffected (3° : 2° = 6[3°]/[2°] ~ 8). This fact suggests that oxidation reactions also occurred at the precipitate in the standard experiment (no. 1). This conclusion was supported by the selective oxidation of 1,3-DMA at secondary positions in the case of hydrocarbon oxidation only in solution (experiment no. 2), in which the ratio is 3°/2° = 0.06. Different selectivities in the oxidation of 1,3-DMA primarily at tertiary positions (at the

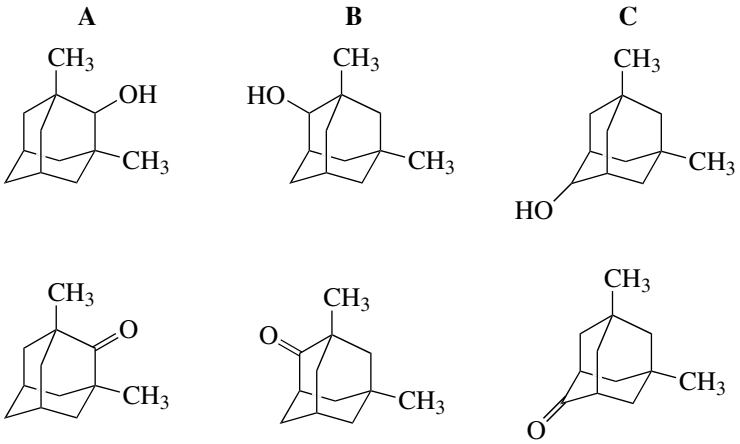
(a)

MONOOXYGENATION PRODUCTS

I. Oxidation of tertiary C–H bonds

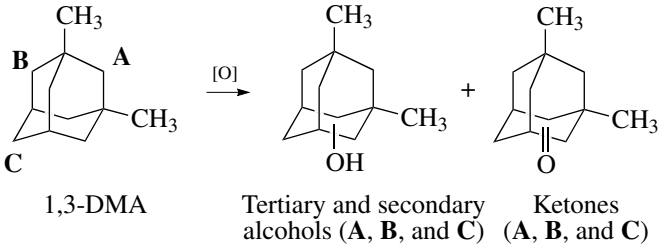


II. Oxidation of secondary C–H bonds



(b)

MONOOXYGENATION PRODUCTS



DIOXYGENATION PRODUCTS

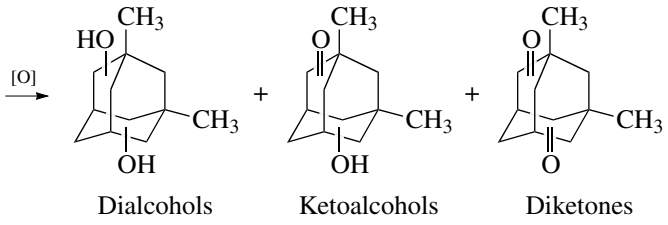


Fig. 4. Experiment no. 14: (a) products of 1,3-DMA oxidation by hydrogen peroxide at (I) tertiary and (II) secondary C–H bonds; (b) general reaction scheme of the mono- and dioxygenation of 1,3-DMA with hydrogen peroxide under new conditions. See the text for details.

Table 1. Relative concentrations ($\times 10^{-4}$) of 1,3-DMA* oxidation and alkylation products in the catalytic system based on $FeSO_4 \cdot 7H_2O$/picolinic acid/Py/H_2O_2 in CH_3CN/H_2O

Compound		*m*/*z*	Retention time, s	Experiment no.**				
				1	2	3	4	5
Fraction of 1,3-DMA		136	~300	1.0	1.0	1.0	0.53	0.47
1,3-DMA oxidation products								
Ketones		178	~500	0.6	0.3	62.0	12.0	1.4
Tertiary alcohol		180	~460	1.5	0.1	81.0	8.5	0.8
Secondary alcohols			~490	0.5	8.1	–	5.7	–
Ratio*** 3°/2°				8.18	0.06	7.86	2.88	3.42
1,3-DMA alkylation products								
With acetonitrile	1,3-DMA–CH_2CN	203	~700	1.7	0.3	–	12.0	0.6
	1,3-DMA–NC_2H_4	205	~800	3.1	0.3	0.3	–	1.6
With pyridine	1,3-DMA–Py	241	~750	9.2	21.0	3.7	28.0	19.0
			~800	4.2	4.2	1.0	13.0	14.0
	$(1,3\text{-DMA})_2$–Py	403	~1000	31.0	37.0	–	200.0	71.0
			~1040	18.0	–	–	290.0	–

*The 1,3-DMA content was used as an internal standard.

**For experiment numbering and specification, see Fig. 2 and the text; nos. 1–3, extraction immediately after completion of an experiment; nos. 4 and 5, extraction after a day.

***The ratio 3°/2° = 6[3°]/[2°] between 1,3-DMA oxidation products without consideration for alkylation products.

precipitate) and secondary positions (in solution) suggest the occurrence of at least two different mechanisms of hydrocarbon oxidation in the test system. The same conclusion follows from an analysis of the structures of two fundamentally different products of acetonitrile alkylation with 1,3-DMA (see Fig. 3 and Table 1). The product with *m*/*z* 203 corresponds to the recombination of neutral C-centered 1,3-DMA and acetonitrile radicals, and it is related to the loss of two hydrogen atoms from parent molecules. The product with *m*/*z* 205 corresponds to the addition of an acetonitrile molecule to 1,3-DMA at the nitrogen atom with the retention of the total mass of parent molecules. This addition mode corresponds to the interaction of acetonitrile with the tertiary C–H bond of the adamantane structure activated in the radical cation [19, 20].

The possibility of postreaction catalytic transformations was tested using the following simple experiment: Immediately after performing a standard experiment, the solution (extraction no. 4) and precipitate (extraction no. 5) containing reaction products were separated. The extraction was performed a day after phase separation. The samples were kept under room conditions away from light. It can be seen in Table 1 that 1,3-DMA was distributed between phases in approximately equal proportions. A common effect of keeping sample nos. 4 and 5 for a day consisted in an increase in the amount of 1,3-DMA oxidation and alkylation products by an order of magnitude both in solution and at the precipitate. We related this effect to the occurrence of postreaction catalytic transformations. This also follows from the total change rather than retention of the value 3° : 2° = 8.18 for experiment no. 1; in experiment no. 4 or 5, this value decreased in much the same manner to 2.88 or 3.42, respectively. We related postreaction catalytic transformations to the presence of a large amount of unreacted hydrogen peroxide in the system. A radical mechanism corresponds to slower postcatalytic reactions because the ratio 3° : 2° is ~3. In all of the other experiments, the decomposition of metal complexes with water in the reaction mixture and the extraction of 1,3-DMA oxidation products were performed immediately upon completion of the reaction.

A number of test experiments were performed in order to determine the roles of particular components and the presence of the effect of catalysis in the test heterogeneous system for 1,3-DMA oxidation with hydrogen peroxide in acetonitrile. It was found that $FeSO_4 \cdot 7H_2O$, picolinic acid, and pyridine are the main components of the system. Upon the removal of at least one of them, oxidation and alkylation products were not formed in the course of reaction for 1 h under the same conditions. Ascorbic acid and water are additional components; the systems retained the ability to oxidize

Table 2. Relative concentrations ($\times 10^{-4}$) of 1,3-DMA* oxidation and alkylation products under changes of reagent concentrations and procedures used for the preparation of the catalytic system

Compound		*m/z*	Retention time, s	Experiment no.**									
				1	6	7	8	9	10	11	12	13	14
1,3-DMA oxidation products													
Ketones		178	~500	0.6	1.7	33.0	3.4	2.3	1.5	–	8.5	73.0	2060.0
Tertiary alcohol		180	~460	1.5	1.5	19.0	3.1	1.4	1.9	–	39.0	400.0	860.0
Secondary alcohols			~490	0.5	–	–	1.6	–	–	–	–	–	29.0
Ratio*** 3°/2°				8.18	5.29	3.46	3.72	3.65	7.60	–	27.53	32.88	2.47
1,3-DMA alkylation products													
With acetonitrile	1,3-DMA–CH_2CN	203	~700	1.7	10.0	–	3.5	–	–	–	–	–	–
	1,3-DMA–NC_2H_4	205	~800	3.1	–	–	–	–	–	–	–	–	–
With pyridine	1,3-DMA–Py	241	~750	9.2	38.0	13.0	7.8	–	–	–	–	–	–
			~800	4.2	10.0	3.5	0.5	–	–	–	–	–	–
	$(1,3\text{-DMA})_2$–Py	403	~1000	31.0	61.0	4.6	3.9	–	–	–	–	–	–
			~1010	–	16.0	0.8	0.1	–	–	–	–	–	–
			~1040	18.0	10.0	1.5	0.9	–	–	–	–	–	–
Varied concentrations****													
Asc		$\times 10^{-3}$ mol		10	1	0	10	10	0	0	0	0	0
H_2O		mL		4	4	4	1	0	0	1	1	1	1
H_2O_2		mL		0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	2.0

*The 1,3-DMA content was used as an internal standard.

**For experiment numbering and specification, see the text.

***The ratio 3°/2° = 6[3°]/[2°] between 1,3-DMA oxidation products without consideration for alkylation products.

****Fixed concentrations: $FeSO_4 \cdot 7H_2O$, 0.5×10^{-3} mol; Py, 1×10^{-3} mol; picolinic acid, 1×10^{-3} mol; 1,3-DMA, 2.7×10^{-3} mol.

Table 3. Ratio (%) between 1,3-DMA and its oxidation products (alcohols and ketones) under new standard conditions (catalysis on a reddish orange precipitate dried over H_2SO_4 (conc)) according to chromatographic data

Experiment no.	1,3-DMA	(2°) total secondary alcohols and ketones	(3°) tertiary alcohol	Ratio* 3°/2°	H_2O_2, ml
13	58	4	38	57.0	0.4
14	24	44	32	4.2	2.0

* The ratio 3°/2° = 6[3°]/[2°] between 1,3-DMA oxidation products.

1,3-DMA in the absence of these components. Hydrogen peroxide (without organometallic complexes) did not oxidize 1,3-DMA under the conditions chosen. Thus, indeed, the effect of catalysis was observed in the test Gif-type system.

In order to determine effects on the selectivity of 1,3-DMA oxidation and alkylation processes, we performed experiments with various concentrations of additional components (ascorbic acid and H_2O) (Table 2, experiment nos. 1, 6–10) and somewhat modified experimental procedures (Table 2, experiment nos. 11–14).

At a fixed amount of water added (4 ml) with respect to standard experiment no. 1, the concentration of ascorbic acid (Asc) was decreased by an order of magnitude (experiment no. 6), whereas [Asc] = 0 in experiment no. 7. It can be seen in Table 2 that the decrease in the concentration of ascorbic acid by one order of magnitude did not cause a considerable increase in the yield of alkylation products at an almost unchanged amount of oxidation products (3.2×10^{-4} in place of 2.6×10^{-4}). However, the complete removal of ascorbic acid increased the yield of oxidation products by an

order of magnitude (52×10^{-4} in place of 2.6×10^{-4} or 3.2×10^{-4}) and decreased the yield of pyridine alkylation products with 1,3-DMA by a factor of 3–6 (23.4×10^{-4} in place of 62.4×10^{-4} or 135.0×10^{-4}). As the concentration of ascorbic acid was decreased, the 3° : 2° ratio decreased: 8.18, 5.29, and 3.46 for experiment nos. 1, 6, and 7, respectively. The experimental results indicate that, in standard experiment no. 1, ascorbic acid actively inhibited both alkylation and oxidation processes. Ascorbic acid acts as an interfering factor rather than serves as a necessary component for performing oxidation. Subsequently, we abandoned the introduction of ascorbic acid as a reducing agent into the system.

At a fixed ascorbic acid amount (10×10^{-3} mol), we varied the amount of water added: 4, 1, and 0 ml in standard experiment no. 1 and experiment nos. 8 and 9, respectively. As can be seen in Table 2, as the concentration of water was decreased, the yield of alkylation products decreased (to zero at 0 ml of H_2O). The yield of oxidation products passed through a maximum (8.1×10^{-4} at 1 ml of H_2O). In experiment no. 9, as well as in experiment no. 10, the structure and catalytic properties of the precipitate changed at 0 ml of H_2O (in the presence of 10×10^{-3} mol of ascorbic acid). The color of the precipitate became white. In all of the other experiments, the precipitates were reddish orange. At the same time, the 3° : 2° ratio in experiments with 0 and 1 ml of H_2O was the same (~3.7, which corresponds to the occurrence of radical reactions). By this is meant that, most likely, the products of 1,3-DMA oxidation in the presence of a standard concentration of ascorbic acid have the same origin and are mainly formed in solution.

Unlike experiment no. 3, in which only the precipitate was taken for oxidation reaction, the total amount of oxidation products (3.4×10^{-4}) did not increase considerably in experiment no. 10 with the complete removal of H_2O (0 ml) and ascorbic acid (0 mol). Therefore, based on the results of experiment nos. 3 and 8, we modified the catalyst preparation procedure and reaction conditions (with respect to standard experiment no. 1) by maximally decreasing an excess amount of water in the system in order to improve the selectivity and product yield in the oxidation of 1,3-DMA with hydrogen peroxide.

First, we repeated the separation of the reaction system into a solution and a precipitate followed by the independent oxidation of 1,3-DMA in them. Unlike experiment nos. 2 and 3, ascorbic acid was not introduced and only 1 ml of H_2O was added in place of 4 ml in subsequent experiment nos. 11 and 12. The precipitate exhibited a stable reddish orange color.

Upon the separation of the solution and the precipitate, excessive water passed into solution. As can be seen in Table 2, oxidation and alkylation products were completely absent from the solution thus prepared upon 1,3-DMA oxidation (experiment no. 11). Thus, the residual amount of water in solution was insufficient for the formation of catalytic complexes. In the oxidation of 1,3-DMA on the precipitate, which was freshly separated from solution, to which 27 ml of acetonitrile was added, only oxidation products were formed; in this case, a tertiary alcohol was predominant (experiment no. 12). In this experiment, the ratio 3° : 2° = 27.53 dramatically increased, as compared with the ratio 3° : 2° = 7.86 in analogous experiment no. 3 (see Table 1), in which the precipitate was formed in the presence of ascorbic acid and 4 ml of H_2O. Even better results were obtained in the oxidation of 1,3-DMA on the precipitate (as in experiment no. 12), which was predried in a desiccator over concentrated H_2SO_4 for a day (experiment no. 13). The reddish orange color of the precipitate remained unchanged. The yield of 1,3-DMA oxidation products increased by an order of magnitude, whereas the 3° : 2° ratio increased to 32.88.

An increase in the amount of water, which was introduced together with the oxidant H_2O_2 (2 ml of a 30% solution), by a factor of 5 resulted in the degradation of the catalytic centers of 1,3-DMA oxidation at tertiary C–H bonds and in the formation of new catalytic centers of 1,3-DMA oxidation at secondary C–H bonds (experiment no. 14). This follows from the fact that a further increase in the yields of 1,3-DMA oxidation products was accompanied by a dramatic decrease in the 3° : 2° ratio to 2.47.

A detailed analysis of the percentage ratios between the parent hydrocarbon 1,3-DMA and the total amount of secondary alcohols and ketones (position 2°) or a tertiary alcohol (position 3°) in experiment nos. 13 and 14 was performed using not only ion currents with specified values of *m*/*z* (Tables 1, 2) but also, additionally, chromatographic data (Table 3) because the yields of oxidation products became as high as tens of percent. As can be seen in Table 3, the concentrations of the tertiary alcohol in experiment nos. 13 and 14, in which 0.4 and 2.0 ml of an aqueous 30% H_2O_2 solution, respectively, were used, were practically equal (38 and 32%, respectively). On going from 0.4 to 2.0 ml of the H_2O_2 solution, the consumption of 1,3-DMA increased because of the oxidation of the parent hydrocarbon at secondary C–H bonds. In experiment nos. 13 and 14, the products of 1,3-DMA oxidation at the position 2° or the residual amounts of 1,3-DMA accounted for 4 and 44 or 58 and 24%, respectively. Because the aqueous H_2O_2 solution was added in four 0.5-ml portions at regular intervals of 15 min, the percentage of the tertiary alcohol (32–38%) may indicate that this alcohol was formed in the first 15 min of the reaction (the amount of H_2O_2 in the first portion (0.5 ml) was close to the total H_2O_2 content (0.4 ml) used in experiment no. 13). This hypothesis was supported by a direct experiment (0.5 ml of an aqueous 30% H_2O_2 solution; reaction time of 15 min). Next, in experiment no. 14, water affected the catalyst structure and the selectivity of oxidation

changed: oxidation occurred at position 2° rather than 3°. The overall effect was that the 3° : 2° ratio decreased from 57.0 in experiment no. 13 to 4.2 in experiment no. 14 (according to data in Table 3).

More detailed information was obtained by varying the added amount of the hydrogen peroxide solution from 0.2 to 4 ml. On the addition of 0.2 ml of H_2O_2, the detected amount of the tertiary alcohol was half as large as that with 0.4 ml (experiment no. 13); correspondingly, the consumption of 1,3-DMA was smaller. Consequently, at the initial stage of oxidation (0–0.4 ml of the solution of H_2O_2), the yield of the tertiary alcohol was a linear function of the amount of the oxidant added (Fig. 4a, I).

As the added amount of the H_2O_2 solution was increased, starting with 0.4 ml, the fraction of the products of 1,3-DMA oxidation at secondary C–H bonds increased. In all cases, the chromatograms exhibited two groups of three peaks, which generally retained a characteristic ratio between each other. The first group (with shorter retention times) corresponded to three secondary alcohols, and the second group corresponded to three ketones (see Fig. 4a, II). On the average, the **A** : **B** : **C** ratios between the peaks of secondary alcohols and ketones were close to 1 : 4.6 : 1 and 1 : 3.6 : 1, respectively. These ratios between oxidation products correspond to the ratio 1 : 4 : 1 between the numbers of C–H bonds for three types of methylene groups in 1,3-DMA. This is consistent with the assignment of chromatographic peaks with respect to retention times and with the fragmentation of molecular ions in mass spectra. The ratio between the concentration of ketones in the extract and the concentration of secondary alcohols also remained almost constant and, on average, equal to 1.4.

As the added amount of the H_2O_2 solution was increased above 2 ml, the chromatogram clearly exhibited a new group of peaks due to heavier products of 1,3-DMA oxidation. The majority of the most intense new peaks were identified based on an analysis of mass spectra, retention times, and peak intensity ratios. These peaks corresponded to the products of the further oxidation of monooxygenated 1,3-DMA oxidation products: a tertiary diol and a set of other diols, ketoalcohols, and diketones (see Fig. 4b). The total yield of 1,3-DMA dioxygenation products was higher than 10% upon the addition of 4 ml of the hydrogen peroxide solution.

As the added amount of the H_2O_2 solution was increased above 3 ml, the intense evolution of gas (oxygen) bubbles came into play; that is, the third type of Gif systems took place.

Thus, as a result of this study, we found new conditions for the reaction of 1,3-DMA oxidation with hydrogen peroxide in the presence of complexes based on iron, picolinic acid, pyridine (Py), and water. The conversion of the parent hydrocarbon increased from fractions of a percent in initial standard experiment no. 1 to the tens of percent in new standard experiment no. 13 and experiment no. 14. The selectivity of 1,3-DMA oxidation processes increased to 100% because the products of acetonitrile and pyridine alkylation by 1,3-DMA were completely absent under new conditions. In principle, the selective oxidation of 1,3-DMA at tertiary C–H bonds can be changed to the selective oxidation of 1,3-DMA at secondary C–H bonds within the framework of a single catalytic system by varying the amount of water present in the system.

From the formal standpoint of the positional selectivity of oxidation processes, all of the four types of Gif systems, which were systematized in the Introduction, were implemented in the course of this study under various conditions but within the framework of a single catalytic system. In particular, the first case of biomimetic oxidation, the selective oxidation of 1,3-DMA to a tertiary alcohol, was implemented.

DISCUSSION

The unusual selectivity of 1,3-DMA oxidation at tertiary rather than secondary C–H bonds found in this study is inconsistent with either of the two alternative mechanisms proposed previously. According to Barton, in the nonradical mechanism with a Fe^{3+}/Fe^{5+} reaction path, the oxidation of saturated hydrocarbons (RH) with hydrogen peroxide occurs selectively at secondary C–H bonds [7, 11–13]. The three-electron oxidation of RH with $XO^{+\bullet}$, where X = Py, results in analogous selectivity (according to published hypotheses and data [7, 21, 22], which are consistent with the results of Ryzhakov [23]). In the radical oxidation of RH with hydrogen peroxide via a Fe^{2+}/Fe^{4+} reaction path according to Barton [7, 11–13] (in accordance with the results obtained by Stavropoulos with coworkers [14, 15]), the tertiary and secondary C–H bonds of RH are nonselectively oxidized simultaneously by the same mechanism (the ratio 3° : 2° is ~3). Thus, in the occurrence of radical reaction paths, the oxidation of tertiary C–H bonds in saturated hydrocarbons, in particular, adamantane, is only predominant over the oxidation of RH at secondary C–H bonds rather than positionally selective, as in our case (the ratio 3° : 2° = 57 for experiment no. 13), where the oxidation of 1,3-DMA at tertiary and secondary C–H bonds certainly occurred at different catalytic centers via two different mechanisms.

In this context, it was necessary to find a new selective mechanism for 1,3-DMA oxidation that occurs exclusively at tertiary C–H bonds (100%). Based on data on the oxidation of 1,3-DMA and the structure and reactivity of its radical cation under model radiation-chemical conditions, we believe that a radical-cation mechanism occurred under new catalytic conditions (experiment no. 13). According to this mechanism, the key step is the insertion of an oxygen atom into the activated tertiary C–H bond of the 1,3-DMA radical cation. Figure 5 illustrates a conceivable mechanism of the

RADICAL-CATION OXIDATION
100% selectivity of the oxidation of tertiary C–H bonds in 1,3-DMA (position 3)

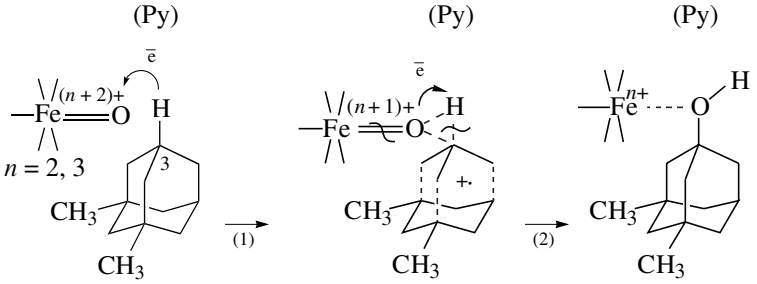


Fig. 5. Mechanism proposed for 1,3-DMA oxidation at tertiary C–H bonds (with the participation of the pyridine molecule).

selective biomimetic oxidation of 1,3-DMA to a tertiary alcohol under new standard conditions of experiment no. 13, which consists in the intermediate formation of the 1,3-DMA radical cation (step (1)) and the concerted insertion of the oxygen atom (oxene) into the activated radical cation.

The structure of the 1,3-DMA radical cation was determined by EPR spectroscopy and supported using PM3 semiempirical quantum-chemical calculations [24]. In the 1,3-DMA radical cation, one tertiary C–H bond is selectively elongated (by 0.04 Å) and, consequently, weakened. In condensed media, this bond can be selectively involved in the subsequent chemical transformations; in particular, it can undergo deprotonation to form a neutral tertiary radical. In advancing our hypothesis, we used the well-known empirical rule: the deprotonation of a radical cation occurs at sites with the greatest spin density (with 100% selectivity) [25], as well as the results of EPR-spectroscopic studies [24]. In the EPR spectra, the greatest isotropic hyperfine-interaction constant (a_{iso}(H) = 143 G (1 G = 0.1 mT)) corresponds to the hydrogen atom of a weakened tertiary C–H bond in the 1,3-DMA radical cation [24].

In addition to the selectivity of 1,3-DMA oxidation to a tertiary alcohol under new standard conditions (experiment no. 13), the hypothesis on the intermediate formation of the 1,3-DMA radical cation allowed us to explain other two unusual facts found in this work: the formation of a product with m/z = 205 by the addition of an acetonitrile molecule to 1,3-DMA in initial standard experiment no. 1 and the selectivity of processes and the composition of four products of the alkylation of pyridine by 1,3-DMA radicals in the above experiment no. 1.

We related the above three cases of the chemical behavior of the 1,3-DMA radical cation with a rapid reaction of the 1,3-DMA radical cation with the catalytic center of the precipitate, a slower reaction of the 1,3-DMA radical cation that escaped into the bulk solvent with the acetonitrile molecule, and a reaction of the deprotonation products of the 1,3-DMA radical cation (neutral tertiary radicals of 1,3-DMA that escaped into the bulk solvent) with pyridine molecules, respectively (Fig. 6).

The first two cases were briefly discussed above. Our concepts of the radical-cation mechanisms of the oxidation of 1,3-DMA and the alkylation of acetonitrile by 1,3-DMA are considered elsewhere [24]. Here, we consider in more detail the reaction of pyridine alkylation by the saturated hydrocarbon 1,3-DMA.

Each particular component of the catalytic test system can perform several functions. Pyridine is a necessary constituent of the catalytic system. Along with the role of a ligand, which forms a complex with the Fe^{2+} ion, it is an effective scavenger of free carbon-centered radicals [7, 14, 15]. Previously, it was reported that cyclohexylpyridine accounted for 77% of the total reaction products in the oxidation of cyclohexane in some Fe^{2+}/H_2O_2 systems, in which free-radical Fenton-type mechanisms occur [7]. In the case of standard experiment no. 1 (see Table 1), four products of pyridine alkylation by 1,3-DMA (see Fig. 3) accounted for 89% of the total reaction products. At the early stage of this work, attention was not focused on the analysis and identification of the products of pyridine alkylation by 1,3-DMA because it was necessary to find new conditions for selective oxidation rather than alkylation. The results obtained in the selective oxidation of 1,3-DMA to a tertiary alcohol, hypothetically, with the intermediate formation of the 1,3-DMA radical cation, under new standard conditions (Tables 2, 3, experiment no. 13) allowed us to give a new look at the selectivity of pyridine alkylation by 1,3-DMA under initial standard conditions (Table 1, experiment no. 1).

Previously [14, 15], a reaction scheme, which is shown in Fig. 7, was proposed for the alkylation of pyridine protonated at nitrogen by adamantyl radicals with the intermediate formation of radical-cation complexes. Four products (*t*2, *t*4, *s*2, and *s*4) were formed in the radical activation of the C–H bonds of adamantane. In the cases when only two products were observed in place of the four products (two tertiary

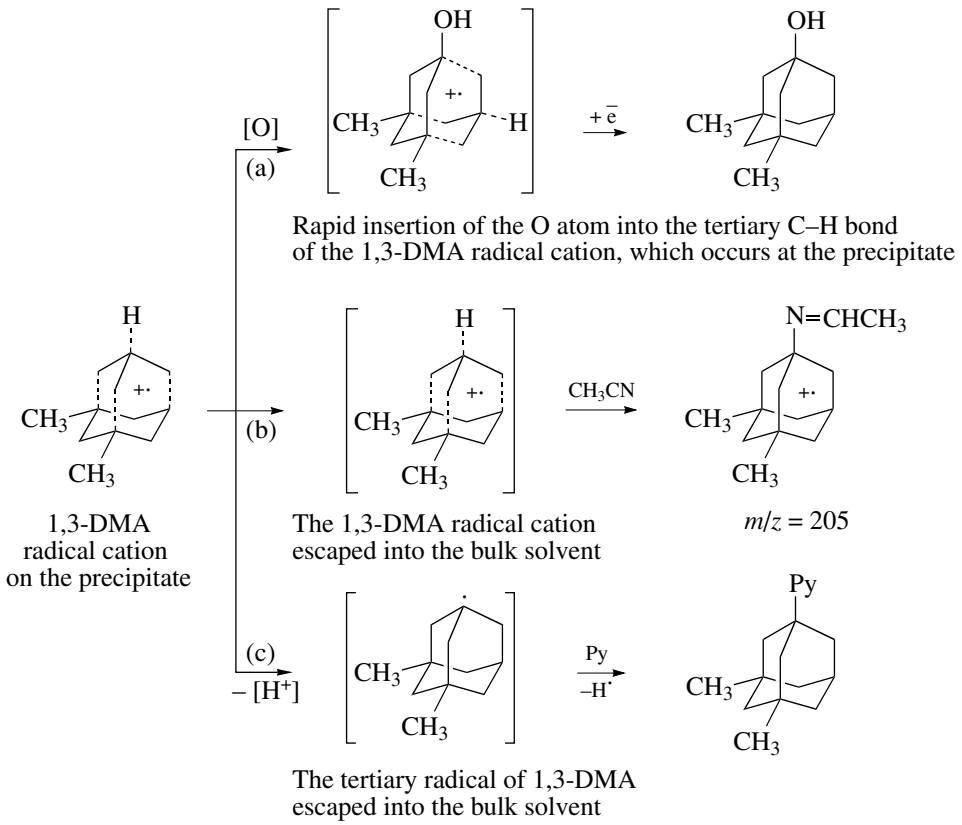


Fig. 6. Reactivity of the 1,3-DMA radical cation associated with (a) the rapid insertion of the [O] atom of the catalytic center into the tertiary C–H bond of the 1,3-DMA radical cation, which occurs at the precipitate and slower processes of the escape of (b) the 1,3-DMA radical cation and (c) the neutral tertiary radical of 1,3-DMA into the bulk solvent.

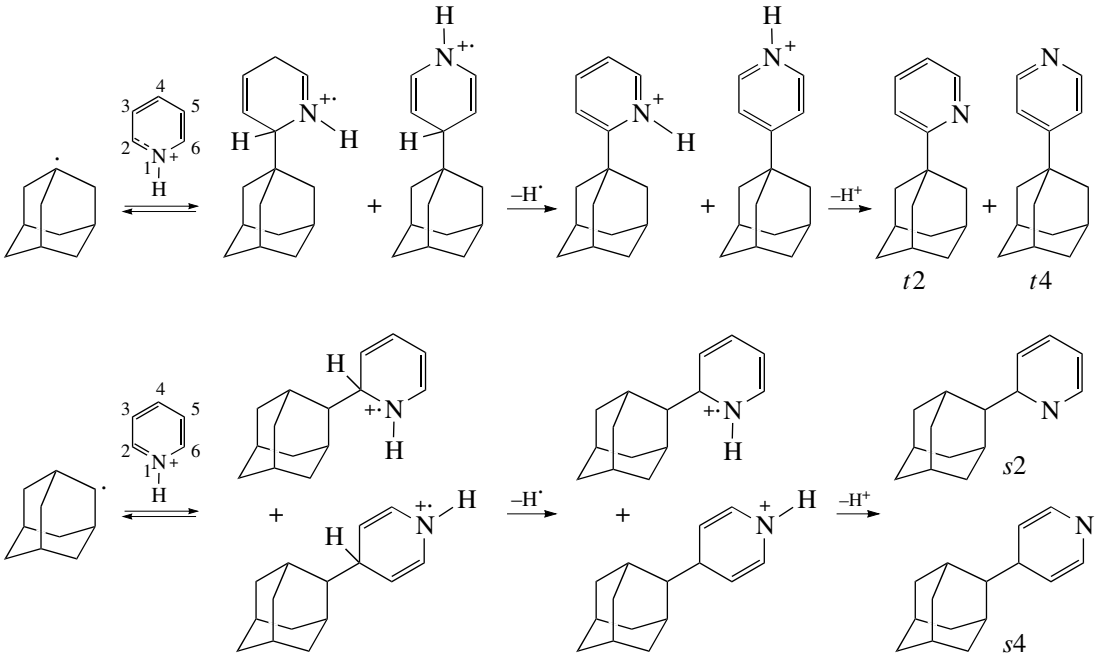


Fig. 7. Alkylation of pyridine protonated at nitrogen with adamantyl radicals with the intermediate formation of radical-cation complexes according to Stavropoulos and coauthors [14, 15] with the radical activation of the C–H bonds of adamantane in a Gif-type system.

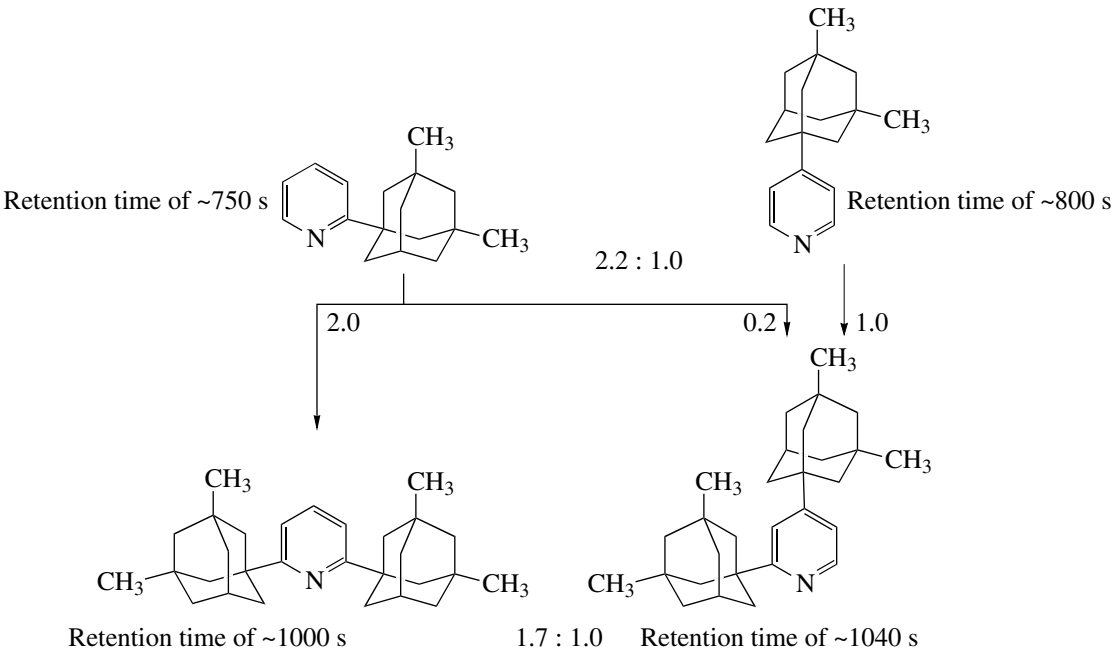


Fig. 8. Structures of the products of pyridine mono- and dialkylation by the tertiary radicals of 1,3-DMA based on the consecutive reaction scheme of pyridine dialkylation product formation.

products *t*2 and *t*4 and two secondary products *s*2 and *s*4), these were tertiary products *t*2 and *t*4. The parallel addition of an alkyl radical at the second and fourth positions of the pyridine ring is typical [7, 14, 15].

In our experiment (no. 1), only two monoalkylated products and two doubly alkylated products were present. This fact allowed us to unambiguously interpret them as the addition products of tertiary 1,3-DMA radicals at the 2- and 4-positions of the pyridine ring. Figure 8 specifies the ratios of 2.2 : 1 and 1.7 : 1 between products in the pairs of pyridine mono- and dialkylation by tertiary 1,3-DMA radicals based on the data of experiment no. 1 (see Table 1). The ratio of 2.2 : 1 between the monoalkylation products with retention times of ~750 and ~800 is close to the ratio of 2 : 1 between the numbers of equivalent positions in the pyridine ring (2, 6, and 4). The reaction scheme in Fig. 8 indicates that the two dialkylation products correspond exactly to the two monoalkylation products. The monoalkylation product with the retention time of ~800 s can add another tertiary 1,3-DMA radical only at the 2- or 4-positions of the pyridine ring to result in a product with the retention time of ~1040 s.

The monoalkylation product with the retention time of ~750 s can add another tertiary 1,3-DMA radical at either of the nonequivalent positions (6 and 4) of the pyridine ring to result in two dialkylation products with the retention times of ~1000 and ~1040 s. The ratio of 1.7 : 1 between the two last-named pyridine dialkylation products was formed from the ratio of 2.2 : 1 between the initial pyridine monoalkylation products with the addition of a tertiary 1,3-DMA radical at the 6-position of the pyridine ring in the mono precursor with the retention time of ~750 s, which is more effective than the addition at the 4-position by a factor of 10. Taking into account small contributions of the tertiary alcohol and the products of acetonitrile alkylation by 1,3-DMA, which also add to the tertiary carbon atom of 1,3-DMA in both a product with *m*/*z* 205 and, likely, a product with *m*/*z* 203, and the trapping of two tertiary 1,3-DMA radicals by a pyridine ring (products with *m*/*z* 403), the fraction of the tertiary C–H bond activation products of 1,3-DMA in experiment no. 1 is 99%, whereas the fraction of the secondary C–H bond activation products of 1,3-DMA is only 1%. This high selectivity of the formation of tertiary 1,3-DMA radicals can also be understood with consideration for the intermediate formation of the 1,3-DMA radical cation, the deprotonation of which selectively leads to the tertiary 1,3-DMA radical. In this case, the selective formation of the tertiary 1,3-DMA radical–pyridine protonated at the nitrogen atom pair can be reproduced by a reaction scheme (Fig. 9) with the participation of the 1,3-DMA radical cation without the subsequent discussion by analogy with the reaction scheme in Fig. 7.

Thus, in all of the studied modifications of standard conditions (experiment nos. 1 and 13), tertiary C–H bonds were selectively activated in 1,3-DMA. This selectivity of the activation of C–H bonds in adamantane or another saturated hydrocarbon in the catalytic system based on Fe^{2+}/H_2O_2 in the presence of picolinic acid, pyridine, and water in acetonitrile or other solvents was not described previously. Reports on the formation of dialkylpyridinium compounds in similar cat-

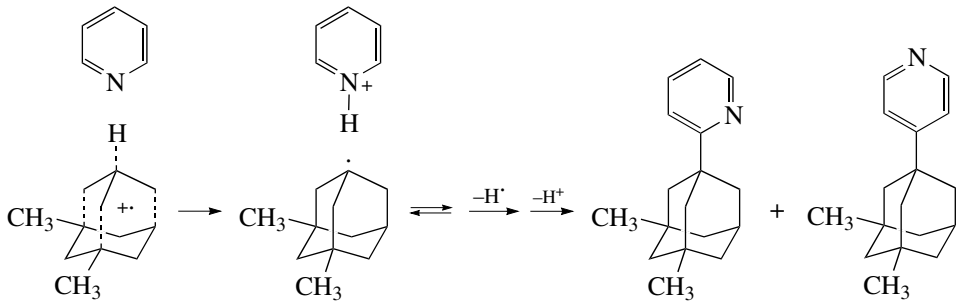


Fig. 9. Formation of the products of pyridine monoalkylation by the tertiary radicals of 1,3-DMA with consideration for the intermediate formation of the 1,3-DMA radical cation.

alytic systems (experiment no. 1 etc.) are also unknown to us.

It is our opinion that the unusual selectivity of reactions, including the alkylation of 1,3-DMA by pyridine, under the test conditions was related to the intermediate formation of the 1,3-DMA radical cation. An analysis of published data showed that the 1,3-DMA molecules are the most readily ionizable chemical species in our catalytic system (PI_v = 9.155 eV, according to data obtained by photoelectron spectroscopy in a gas phase) [26].

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