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Phenazine di-*N*-oxide radical cation and its reactions with hydrocarbons

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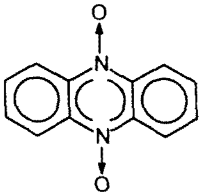
The absorption spectra of phenazine di-*N*-oxide radical cation ($OPO^{+\cdot}$) in dichloromethane were recorded by the spectroelectrochemical method in the range from 300 to 700 nm. The reactions of the electrochemically generated $OPO^{+\cdot}$ with *para*-substituted toluenes, ethylbenzene, and cumene were studied. Using differential cyclic voltammetry, relative rate constants of reactions of $OPO^{+\cdot}$ with substrates were determined; their correlations with σ^{+}_{para} constants of substituents gives $\rho = -2.7$, which attests to the nonradical character of the reaction of $OPO^{+\cdot}$ with RH. This conclusion is confirmed by the study of the effect of O_2 on oxidation of ethylbenzene and cumene.

Key words: phenazine di-*N*-oxide, radical cation, hydrocarbons, oxidation, mechanism, O_2 effect.

We have previously shown that photo-[1] or electrochemically[2—6] generated radical cations of heteroaromatic *N*-oxides are capable of oxidizing hydrocarbons and other organic substrates. The formation of an intermediate complex radical cation—substrate[1] was suggested for several systems; and it is established for phenazine di-*N*-oxide that its radical cation can be a donor of the oxygen cation, and the transfer of O^+ can occur in both one[5—6] and several[3] stages. Phenazine di-*N*-oxide (OPO)



turned out to be a convenient object for study, because its radical cation ($OPO^{+\cdot}$) is stable (lifetime τ in acetonitrile ~20 s) in a time scale of cyclic voltammetry (CVA). The product of one-electron oxidation of the complex of OPO with a proton of composition 2 : 1, radical dication $[OPOH^{+}OPO]^{+\cdot}$, also can oxidize hydrocarbons.[4]

Application of flash photolysis and radiolysis methods in a frozen matrix made it possible to record the absorption spectrum of the radical cation of pyridine *N*-oxide,[1] which exhibits a broad maximum in the visible spectral range at 430 to 460 nm. In this work, data on absorption bands of $OPO^{+\cdot}$ were obtained by the spectroelectrochemical method; the non-nucleophilic solvent dichloromethane was used to increase τ.

In order to study in more detail the nature of reactions of radical cations of heteroaromatic *N*-oxides with hydrocarbons, we systematically studied the reactivity of the electrochemically generated radical cation of phenazine di-*N*-oxide relative to *para*-substituted toluenes, ethylbenzene, and cumene. In addition, the effect of the presence of oxygen on oxidation of some substrates was studied.

Experimental

Cyclic voltammograms were recorded on a PI-50-1 potentiostat with a PR-8 programmer and on a Pine Instrument RDE-3 (PARC) potentiostat. A disk platinum electrode 1 mm in diameter sealed into glass and polished with a diamond paste (grain diameter <1 μm) served as a working electrode. Measurements were carried out in solutions of acetonitrile or dichloromethane with Et_4NClO_4 or Bu_4NPF_6, respectively, as supporting electrolytes. All potentials were determined relative to an aqueous saturated calomel electrode (SCE) by calibrating a reference electrode (Ag/AgCl/4 *M* aqueous LiCl separated from the studied solution placed in a cell by a bridge filled with the corresponding solution of the supporting electrolyte) relative to potentials of the redox transitions ferrocene/ferrocenium (0.42 V, SCE) or decamethylferrocene/decamethylferrocenium (−0.10 V, SCE). All measurements were carried out in an argon atmosphere or, if it was specially mentioned, in an oxygen atmosphere at room temperature.

For preparative electrooxidation in a regime of potentiostatic electrolysis (EPE), a diaphragm (glass filter) electrolyzer with a platinum wire anode was used. Spectroelectrochemical measurements in a thin-layered cell (optical length 0.1 mm) with an optically transparent gold miniwire electrode (200 lines per cm, 60 % transmittance) were carried

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out on a Cary Model 2400 spectrophotometer. Spectrophotometric measurements were carried out on a Specord M-40 instrument in a cell 10 mm in width in acetonitrile or chloroform.

Dichloromethane (Aldrich Gold Label) was boiled for 1—2 h over P_2O_5 and distilled directly to electrochemical or spectroelectrochemical cells in an argon atmosphere. Methods for synthesis and/or purification of other reagents were described previously.[2,3,6]

To interpret the data obtained, electronic structures of OPO^+ and its derivatives were calculated by the MNDO method. The N—O bond length was taken as equal to 1.36 Å, and the other geometric parameters of molecules were standard.

Results and Discussion

The cyclic voltammograms of OPO in CH_2Cl_2 and MeCN contain a diffusionally controlled ($I_p \cdot \upsilon^{1/2}$ = const, where I_p is the current in a maximum of the peak, and υ is the velocity of the linear scanning of potential) quasi-reversible one-electron peak with a half-wave potential $E^0 = E_{1/2} = (E_p{}^a + E_p{}^c)/2 = 1.48$ V, where $E_p{}^a$ and $E_p{}^c$ are the potentials of anode and cathode peaks, respectively. The value $\Delta E_p = E_p{}^a - E_p{}^c$, which is a criterion of reversibility of the electron transfer stage, is 85 mV at $\upsilon = 100$ mV s^{-1} and somewhat exceeds the value of 60 mV for the reversible process. This is probably caused by a high ohmic resistance of dichloromethane, because for the *a fortiori* reversible redox pair ferrocene/ferrocenium the ΔE_p value reaches 80 mV under these conditions. The heights of the anode and cathode peaks are equal and retain equality as υ decreases from 200 to 20 mV s^{-1}, which makes it possible to conclude that the lifetime of $OPO^{+\cdot}$ in CH_2Cl_2 is not shorter than 50 s. An order of magnitude of this value agrees with that previously obtained in MeCN (20 s).[2]

The results of spectroelectrochemical studies of OPO in the visible spectral range upon its oxidation to $OPO^{+\cdot}$ in CH_2Cl_2 are presented in Fig. 1. The intensities of the absorption bands of the initial OPO (sh 430, 460, and 490 nm) decrease during electrolysis at $E = 1.7$ V (the spectra were recorded each 15 s), which is accompanied by the group of absorption bands in the spectral range from 300 to 420 nm. It is known from our previous works[3,4] that the electrolysis of OPO is accompanied by both its deoxygenation and formation of the $OPOH^+OPO$ complex due to the reaction of OPO with protons formed in the reaction of the oxidized form of OPO with a solvent. This circumstance forces us to take into account the possibility of the absorption of $OPOH^+OPO$ (350, 367, 387, and 430—500 nm) and phenazine mono-*N*-oxide (OP) in the initial (sh 340, sh 370, 381, 397, and 421 nm) and protonated forms (342, 370, 384, and 430—500 nm) (Fig. 2) in the analysis of spectroelectrochemical data. To isolate absorption bands inherent in $OPO^{+\cdot}$ (along with the radical dication $OPOHOPO^{2+\cdot}$) of the group of absorption bands, the polarization at 1.0 V (Fig. 3, spectrum *2*) was performed immediately after the polarization at 1.7 V. Subtracting spectrum *2*

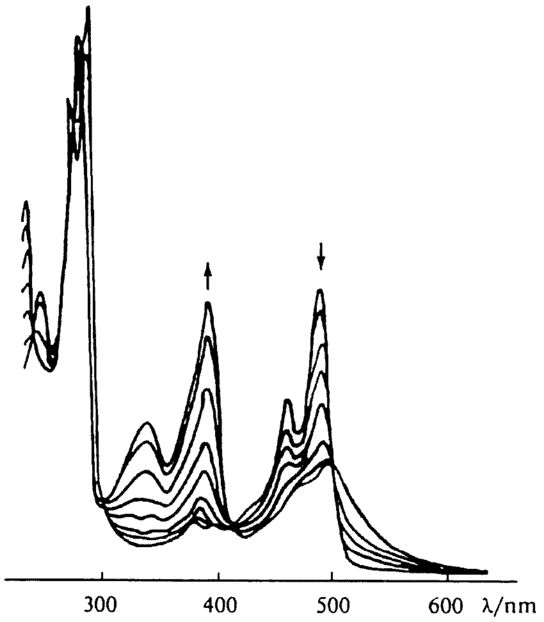


Fig. 1. Spectral changes accompanying oxidation of OPO (10^{-3} mol L^{-1}) in CH_2Cl_2/0.1 *M* Bu_4NPF_6 at E = +1.7 V. Arrows show the evolution of absorption bands in the spectrum.

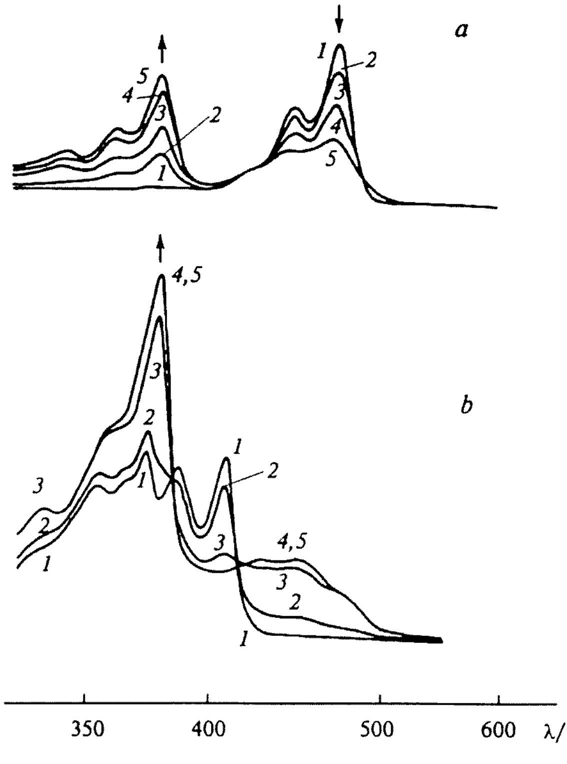


Fig. 2. Spectral changes accompanying protonation of OPO ($6.7 \cdot 10^{-6}$ mol L^{-1}) (*a*) and OP ($6.7 \cdot 10^{-6}$ mol L^{-1}) (*b*) upon the addition of $HClO_4$; OPO : $HClO_4$ was *a.* 1 : 0 (*1*), 1 : 2 (*2*), 1 : 4 (*3*), 1 : 10 (*4*), 1 : 15 (*5*); *b.* 1 : 0 (*1*), 1 : 1 (*2*), 1 : 2 (*3*), 1 : 4 (*4*), and 1 : 10 (*5*). Arrows show the evolution of absorption bands upon protonation.

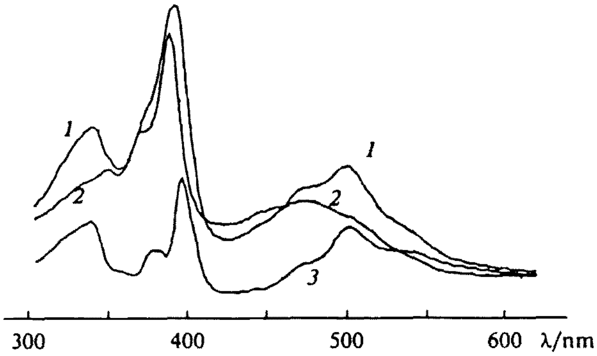


Fig. 3. Spectral changes accompanying oxidation of OPO (for conditions, see Fig. 1): *1*, polarization at E = 1.7 V for 4 min; *2*, subsequent polarization at E = 1.0 V for 30 min; *3*, result of subtraction of spectrum *2* from spectrum *1*.

from spectrum *1* gives the sum of absorption spectra of the radical cations $OPO^{+\cdot}$ and $OPOHOPO^{2+\cdot}$ (338, 376—382, 396, and 502 nm) (Fig. 3, spectrum *3*). It is noteworthy that it is difficult to isolate the absorption spectrum of $OPO^{+\cdot}$, because the oxidation potentials of OPO (1.4 V) and $OPOH^{+}OPO$ (1.6 V) are close.

The known data on the structure of the $(PyO)_2H^+$ complex, where PyO is pyridine *N*-oxide,[7] show that a substantial nonequivalence of the N→O bonds (1.39 and 1.29 Å) is retained despite the existence of a strong hydrogen bond (the O—O distance is 2.29 Å). This makes it possible to suppose that in the $(OPO)_2H^+$ complex a proton is also bound nonsymmetrically: $(OPOH^+)OPO$. Therefore, it can be expected that the spectrum of the protonated form of OPO is a superposition of the spectra of the components $OPOH^+$ and OPO. In fact, the spectral measurements (see Fig. 2) show that the bands of OPO are retained (with a somewhat changed ratio of intensities) as their total intensity decreases by approximately 50 % in the presence of excess acid. The structures of additional absorption bands in the near UV range resemble absorption bands of OPO. This seems quite reasonable in terms of the given model, because the addition of a proton to OPO should result in both a shift of absorption bands in the system of conjugated bonds of OPO and a change in their intensities due to polarization of the molecule.

It can be assumed that the oxidation of the $(OPOH^+)OPO$ complex facilitates its existence in the nonsymmetric form $(OPOH^+)(OPO^{+\cdot})$ due to the nonequivalent distribution of an additional charge over two initially nonequivalent OPO molecules. According to the data of the quantum-chemical calculation, a small negative charge on oxygen atoms is retained in $OPO^{+\cdot}$, which provides for the possibility of their participation in hydrogen bonds. Therefore, it should be expected that the absorption spectrum of the radical dication $[OPOHOPO]^{2+\cdot}$ simultaneously contains absorption bands of $OPO^{+\cdot}$ and $OPOH^+$ modified by their mutual influence. It can be accepted by analogy with the spectra of OPO and $OPOH^+$ that the result of this influence is a change in intensities of the absorption bands, although they continue to belong to a certain spectral range, namely: the absorption spectrum of $OPO^{+\cdot}$ itself lies in the range from 450 to 500 nm, while the absorption spectrum of $(OPOH^+)OPO^{+\cdot}$ occupies two regions, 300 to 400 and 450 to 550 nm. This assignment correlates well with the recorded[1] broad absorption maximum of $PyO^{+\cdot}$ in the same region from 400 to 500 nm in which the absorption maximum of PyO is observed.

The reactivity of $OPO^{+\cdot}$ was studied relative to toluene and its *para*-substituted derivatives (*p*-xylene, 4-bromo-, 4-iodo-, and 4-nitrotoluenes) as well as ethylbenzene and cumene using the differential cyclic voltammetry method,[8] according to which the following dependence is fulfilled

$$\ln(I_0/I) = a\ln(kC^m/v) + b, \tag{1}$$

where I_0/I is the ratio of the direct and inverse peaks of the differentiated signal of the current peak, v is the scanning velocity, k is the rate constant of the chemical stage, C is the concentration of a substrate, m is the order of the chemical reaction with respect to a substrate (in our case, m = 1), and a and b are constants that are the same for the same class of reactions. The dependences of $\ln(I_0/I)$ on $\ln C$ obtained for reactions of $OPO^{+\cdot}$ with the aforementioned substrates at v = 100 mV s^{-1} are presented in Fig. 4. Their approximation by straight lines with the same slopes a = 0.271 by the least-squares method in the region of $\ln(I_0/I) > 0.3$ gives an absolute error of 0.02 to 0.05. The relative rate constants k/k_0 thus determined (where k_0 is the rate constant of the reaction of $OPO^{+\cdot}$ with toluene) increase in the series of substituents NO_2 < Br < I < H < Me (Table 1).

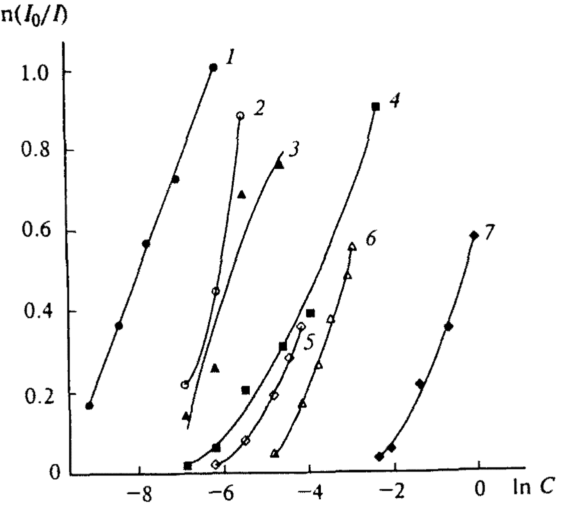


Fig. 4. Dependence of $\ln(I_0/I)$ on $\ln C$ for reactions of $OPO^{+\cdot}$ with various substrates at v = 100 mV s^{-1}: *p*-xylene (*1*), ethylbenzene (*2*), cumene (*3*), toluene (*4*), *p*-iodotoluene (*5*), *p*-bromotoluene (*6*), and *p*-nitrotoluene (*7*).

Table 1. Effect of the nature of substituents at the *para*-position on relative rate constants for reactions of $OPO^{+\cdot}$ with substituted toluenes

Parameters of reaction	Substituent				
	Me	H	I	Br	NO_2
$\log k/k_0$	1.56*	0	−0.04	−0.30	−1.51
σ_{para}**	−0.129	0	0.18	0.232	0.778
σ^{+}_{para}**	−0.311	0	0.135	0.150	0.790

* Calculated for the "effective" concentration of methyl groups, which is equal to the doubled true concentration of *p*-xylene.
** σ_{para} and $\sigma_{para}{}^{+}$ are published[9] values of Hammett constants of substituents.

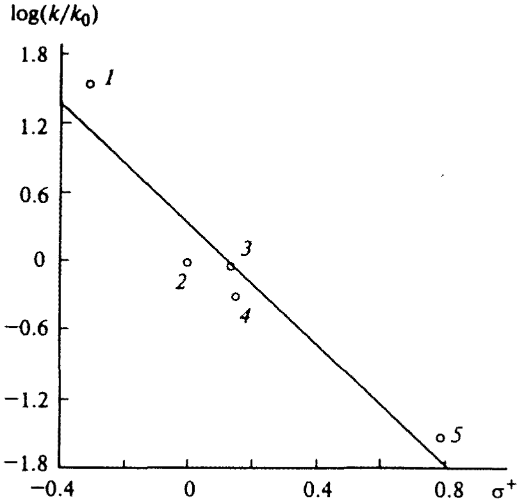


Fig. 5. Dependence of relative rate constants k/k_0 on values of constants of substituents σ^{+}_{para} for *p*-xylene (*1*), toluene (*2*), *p*-iodotoluene (*3*), *p*-bromotoluene, and *p*-nitrotoluene (*5*).

The dependence of k/k_0 on the values of Hammett constants of substituents is better linearized when electrophilic constants σ^{+}_{para} are used (the use of constants σ_{para} results in a twofold increase in error of the value of the slope ρ), which is evidence for a strong resonance interaction between the reaction center of the electrophilic reaction and a substituent[9] (Fig. 5). The absolute value of the calculated $\rho = -2.6\pm0.4$ is sufficiently high, which attests to a rather high degree of polarity of the transition state of the limiting stage of the reaction with a substrate and, hence, to a considerable effective electronegativity of the reaction center.* This contradicts the mechanism of the simple elimination of an H atom from the substrate molecule

$$OPO^{+\cdot} + RH \rightarrow OPOH^{+} + R^{\cdot}$$

(as a rule, the ρ values for reactions of atoms and free radicals with aromatic compounds range[10] from −1 to 0).

In fact, it has previously been shown[1] by the flash photolysis method that in reactions of pyridine *N*-oxide with toluene and other substrates an intermediate complex is formed (with the equilibrium constant, for example, for the reaction with toluene, of 200 L mol^{-1}). Based on the published data,[11] it can be assumed that such a complex contains the five-coordinated carbon atom, where the fifth ligand is the oxygen atom of an attacking electrophilic particle, and it can be accepted by analogy that reactions of $OPO^{+\cdot}$ with substituted toluenes also occurs *via* the formation of the complex

$$OPO^{+\cdot} + RH \rightarrow OPO^{+\cdot}...RH.$$

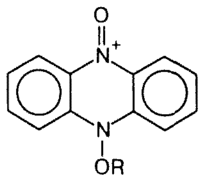
However, in the $OPO^{+\cdot}...RH$ complex, unlike the previously considered[11] complex $LFe^{IV}O...RH$, the rearrangement accompanied by the transfer of an H atom from the C atom to the O atom seems improbable, because the nucleophilic character of the N atom is retained when the deoxygenated OP molecule is ionized (according to the data of calculation by the MNDO method, the charge on the N atom increases only from −0.21 to −0.09). As a result, such a transfer leads to the energetically unfavorable arrangement of $OP^{+\cdot}...O<^{R}_{H}$ of OP and ROH molecules. Therefore, the elimination of H^{+} by the base

$$OPO^{+\cdot}...RH \xrightarrow[-H^{+}]{} OPOR^{\cdot} \xrightarrow[-e]{} OPOR^{+}$$

or of an H atom by an appropriate acceptor seems to be a more probable route of decomposition of the complex with the five-coordinated carbon atom. In the latter case, the final product, $OPOR^{+}$ ion, is formed immediately

$$OPO^{+\cdot}...RH \xrightarrow[-H]{} OPOR^{+} .$$

The formal structure of the oxoammonium cation



should be assigned to the $OPOR^{+}$ ion on the basis of the data on charge distribution (the calculation by the MNDO method showed that for R = Me in the NO fragment $q_N = +0.29$, and in the NOR fragment $q_N = -0.03$). This, however, also follows from the fact that the corresponding neutral compound OPOR is the nitroxyl radical.

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* Calculations by the MNDO method show that the initial negative charge −0.39 on the oxygen atom in OPO decreases to −0.04 in $OPO^{+\cdot}$, so the $OPO^{+\cdot}$ species can be considered as a soft electrophile.

As for determination of relative rate constants of reactions of $OPO^{+\cdot}$ with ethylbenzene and cumene, it is difficult due to the difference in slopes of the dependences of $\ln(I_0/I)$ on $\ln C$ (see Fig. 4). However, the following qualitative estimations can be made. First, the substitution of the H atom (toluene) in the reaction center for the Me group (ethylbenzene) results in an increase in the reactivity of the substrate, which corresponds to both a greater electron-donating ability of the methyl group (induction constant $\sigma_I = -0.05$)[9] and a lower energy of the benzyl C—H bond in ethylbenzene (357 kJ mol^{-1}) compared to toluene (368 kJ mol^{-1}).[12] Second, the methyl group at the *para*-position to the reaction center in *p*-xylene exerts a greater effect on the reactivity of a substrate relative to $OPO^{+\cdot}$ than the Me group attached to the reaction center in ethylbenzene, despite the greater energy of the benzyl C—H bond in *p*-xylene (363 kJ mol^{-1})[12] compared to that in ethylbenzene. This agrees with the values of the corresponding constants of the methyl substituent ($\sigma_I = -0.05$, $\sigma_{para} = -0.170$, $\sigma^+_{para} = -0.311$)[9] and likely attests to the appearance of some steric hindrances in the reaction center for ethylbenzene. Third, the reactivities of ethylbenzene and cumene calculated per benzyl C—H bond with respect to $OPO^{+\cdot}$ turned out to be close despite the existence of the additional electron-donating methyl group and a lower value of the bond energy (353 kJ mol^{-1})[13] in cumene. This is evidence for considerable steric hindrances for the formation of the $OPO^{+\cdot}$—cumene complex and agrees qualitatively with the concept of transition state with the five-coordinated carbon atom or for the different mechanism of the reaction with cumene.

Additional data in favor of this conclusion are provided by the study of the effect of oxygen on the character of the cyclic voltammograms of OPO in the presence of hydrocarbons. It is known[1] that the complex of pyridine *N*-oxide with hydrocarbon can react with O_2 (the rate constant for the complex with toluene is $50 \cdot 10^{-7}$ L mol^{-1} s^{-1}). In addition, it is shown[4] that the CVA of OPO in the presence of ethylbenzene and bubbling of oxygen is accompanied by a 50 % increase in the current of the peak at $E = 1.6$ V. Under the same conditions but in the presence of *p*-xylene, the current of the peak increases by a factor of two. However, in the presence of cumene (as well as in the presence of 1-phenylethanol[4]), O_2 exerts almost no effect on heights and potentials of peaks of CVA in the anodic region of potentials (Fig. 6). This is evidence for the qualitatively different character of the primary reaction of cumene with $OPO^{+\cdot}$. The addition of cumene to the ethylbenzene—OPO system also results in a gradual decrease in the effect of O_2 on the character of the voltammogram up to its complete disappearance (for the ethylbenzene—OPO system, 50 : 1, with a threefold excess of cumene compared to ethylbenzene). In our opinion, this is evidence for a noticeably higher rate constant of the reaction with cumene compared to that with ethylbenzene in the primary elementary process (which are qualitatively different for these two substrates). As a result, a small excess of cumene is already enough to completely intercept the active species $OPO^{+\cdot}$.

From the viewpoint of the suggested mechanism of oxidation of hydrocarbons with primary and secondary C—H bonds by the radical cation $OPO^{+\cdot}$, which is

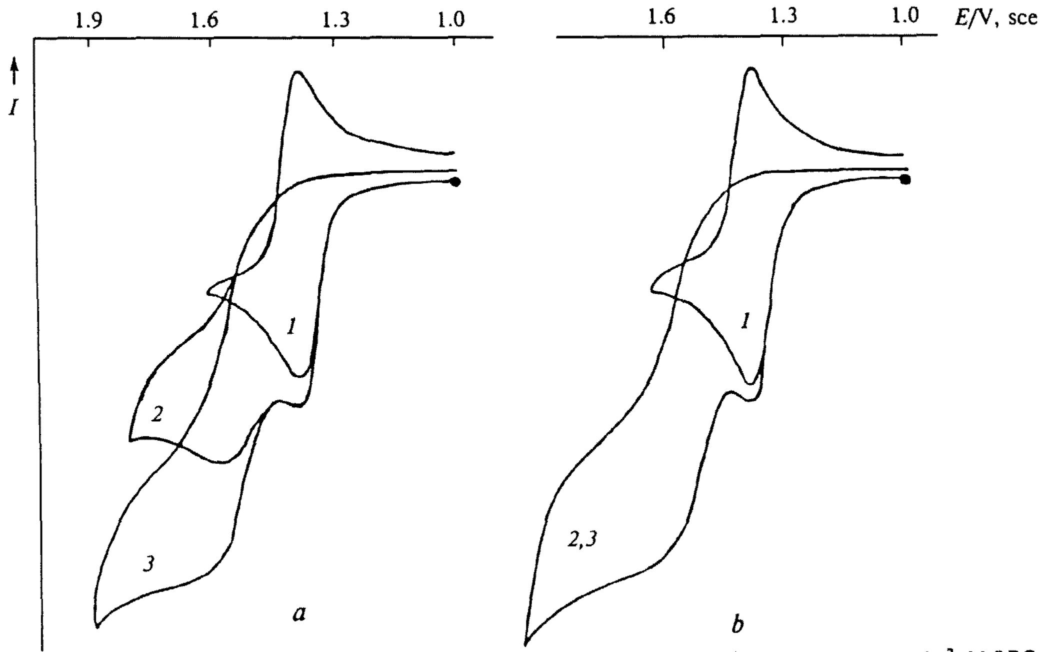
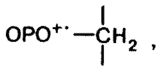


Fig. 6. Effect of ethylbenzene ($2 \cdot 10^{-3}$ mol L^{-1}) (*a*) and cumene ($2 \cdot 10^{-3}$ mol L^{-1}) (*b*) on CVA $2 \cdot 10^{-3}$ *M* OPO (MeCN, 0.1 *M* Et_4NClO_4, Pt anode, v = 100 mV s^{-1}): *1*, without hydrocarbon, Ar or O_2; *2*, with hydrocarbon, Ar; and *3*, with hydrocarbon, O_2.

realized *via* the formation of an intermediate complex with the five-coordinated carbon atom



$$OPO^{+\cdot}-CH_2\ ,$$

the data presented above point to the possibility of the effect of the H...H interaction on the stabilization of the complex. The known equilibrium structure CH_5^+ is[15] also a tight complex of CH_3^+ and H_2. The low strength of the C—H bond in this complex easies its cleavage under the action of an appropriate agent. (In the limiting case, the reaction of O^+ with CH_4 followed by the formation of OCH_3^+ and yield of H occurs without an activation barrier.[13]) In our opinion, the reason for the different behavior of cumene is a decrease in strength of the tertiary C—H bond, on the one hand, and the difficult formation of the complex with the five-coordinated carbon atom, on the other hand, which increases the probability of the tertiary H atom in cumene by the radical cation $OPO^{+\cdot}$. In fact, as in the case of 1-phenylethanol,[4] when excess cumene was added, catalysis resulting in a 2.5-fold increase in the height of the peak of the anode response was observed with a potential of the peak of the $OPOH^+OPO$ oxidation of 1.6 V ($k \approx 10^2$ L mol^{-1} s^{-1}).

Since the oxidizability of tertiary radicals is very high and the complex of OPO with H^+ possesses noticeable oxidative properties ($E_{1/2}$ = 0.35 V),[4] it should be assumed that the electron transfer occurs immediately after the elimination of the H atom from the cumene molecule

$$OPO^{+\cdot} + RH \rightarrow OPOH^+ + R^\cdot \rightarrow OPOH^\cdot + R^+.$$

Then R^+ is accepted by a base, most likely OPO, and $OPOH^\cdot$ undergoes two-electron oxidation. Thus, in the case of cumene, the final product of the oxidation, oxoammonium $OPOR^+$, is formed *via* a more complicated route. The appearance of the neutral species $OPOH^\cdot$, which oxidizes at potentials >0.35 V, in principle decreases the $\ln(I_0/I)$ value. This explains the effect of inhibition of the O_2 effect on the CVA of the ethylbenzene+OPO system by cumene and its seeming lower reactivity. On the other hand, the regeneration of the $OPOH^{2+\cdot}$ oxidant provides for the phenomenon of catalysis.

For substrates with primary and secondary C—H bonds, the formation of a relatively long-lived intermediate complex with the five-coordinated carbon atom with a weak, but stable to regeneration C—H bond occurs without this regeneration of an oxidant, and the phenomenon of catalysis is not observed. However, the reaction of the $OPO^{+\cdot}$...RH complex with O_2 gives the $HO_2^\cdot$ radical.

$$OPO^{+\cdot}...RH + O_2 \rightarrow OPOR^+ + HO_2^\cdot.$$

It is important that the decay of this radical in the reaction with a substrate

$$RH + HO_2^\cdot \rightarrow R^\cdot + H_2O_2$$

results in the formation of hydrogen peroxide, whose oxidation potential in acetonitrile is small in the presence of a base.[16] The specific feature of our system is that the oxidant $OPO^{+\cdot}$ accepts an electron to turn into a base, which is capable of subsequent addition of a proton. Thus, the oxidation of H_2O_2 by two $OPO^{+\cdot}$ particles

$$2\ OPO^{+\cdot} + H_2O_2 \rightarrow O_2 + 2\ OPOH^+$$

finally results in the regeneration of oxygen and formation of two protonated OPO molecules, whose oxidation results in an increase in the anode response at E = 1.6 V in an atmosphere of O_2.

The formation of the $HO_2^\cdot$ radical initiates the subsequent oxidation chain:

$$RH + HO_2^\cdot \rightarrow R^\cdot + H_2O_2,$$

$$R^\cdot + O_2 \rightarrow RO_2^\cdot,$$

$$RH + RO_2^\cdot \rightarrow R^\cdot + ROOH.$$

Protons that are present in the system catalyze the decomposition of ROOH to ketone and water. The process of decay of $ROO^\cdot$ radicals in the disproportionation reaction also yields ketone and alcohol, which oxidizes to ketone. The oxidative medium ($OPO^{+\cdot}$, electrode) determines several peculiarities in the behavior of alkyl (benzyl) radicals. In addition to the simple recombination of two radicals

$$R^\cdot + OPO^{+\cdot} \rightarrow OPOR^+,$$

resulting in the normal product of oxidation in the absence of oxygen, there is a competitive process of their oxidation followed by the reaction of R^+ with bases, OPO or H_2O, which finally results in the formation of $OPOR^+$ or ketone.*

In fact, the preparative electrooxidation of OPO and ethylbenzene in concentrations of $2\cdot10^{-3}$ and $2\cdot10^{-1}$ mol L^{-1}, respectively, at E = 1.4 V in an oxygen atmosphere and passing of ~$12\cdot10^{-3}$ F ($1.2\cdot10^3$ C) resulted in the formation of $6.1\cdot10^{-3}$ mol L^{-1} acetophenone and hydroxyammonium cation $OPOR^+$. The decomposition of $OPOR^+$ additionally gave

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* The possible reaction of R^+ with oxygen

$$R^+ + O_2 \rightarrow ROO^+,$$

is of interest, because it results in the formation of highly reactive ROO^+ species, which can enter into various reactions. In particular, a possibility of branching of the oxidation chain with participation of these species and the direct formation of ketone accompanied by the regeneration of R^+

$$ROO^+ + RH \rightarrow R^+ + H_2O + \text{ketone}.$$

cannot be excluded.

$0.4 \cdot 10^{-3}$ mol L^{-1} ketone and $(0.4-0.5) \cdot 10^{-3}$ mol L^{-1} OP, and the overall consumption of OPO in the reaction also was $(0.4-0.5) \cdot 10^{-3}$ mol L^{-1}.

Thus, these results can be interpreted on the basis of concepts of the formation of an intermediate complex with the five-coordinated carbon atom in the reaction of $OPO^{+\cdot}$ with hydrocarbons with primary and secondary C—H bonds.

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