ethane) are formed in the case of propylene than for propane (Tables 1 and 2). Cracking of the initial alkane should thus be considered the source of light hydrocarbons in the case of propane. Incorporation of zinc in the zeolite changes the rate of cracking of propane very little. At the same time, the aromatizing activity increases markedly due to acceleration of the first stage of dehydrogenation of propane and also due to acceleration of the following stages.

On the whole, quantitative data which characterize the promoting effect of Zn in the Zn/HTsVM system both on conversion of propane into propylene and on subsequent conversions of propylene into ArH were obtained in the study. Experimental data which support the occurrence of the reaction of aromatization of propane in the kinetic region were obtained.

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### KINETICS OF THE REACTION OF SUPEROXIDE ANION-RADICAL WITH OLEFINS

 M. Ya. Meskina, L. M. Baider,
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 and I. P. Skibida
 546.21-128.2:547.538

Kinetic investigation of the reaction of electrochemically generated  $O_2$  with perfluorooctene, styrene, and cyclohexene in acetonitrile, in the presence of tetraethylammonium perchlorate used as a background electrolyte, revealed that  $O_2$  reacts with styrene and perfluorooctene at the double bond, and the reactivity of the olefins with respect to  $O_2$  decreases with decrease in the electrophilicity of the substituents at the double bond: perfluorooctene > styrene > cyclohexene. The main transformation products of styrene are phthalic and benzoic acid esters.

The superoxide anion-radical  $0_2$ , plays an important role in biochemical processes. Three basic types of reaction of  $0_2$ , with substrates in aprotic media were established: a one-electron transfer [1, 2], a nucleophilic substitution [3, 4], and deprotonation [5, 6], in which  $0_2$ , acts as a medium-strength reducing agent, a nucleophile, and a weak base, repsectively. The mechanism of the reaction of  $0_2$ , with alkenes has not been clarified up to this day.

Nonactivated alkenes are generally fairly inert to  $0_2$ , and can be oxidized only in the presence of activating additives such as a sulfo-ion, acyl chloride, or sulfonyl chlorides.

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The role of the additives consists in the generation of the  $RC(0)00^{\circ}$  or  $RS(0)00^{\circ}$  ions, acting as epoxidizing agents [7].

In the study of the reaction of styrene with  $O_2^{\cdot}$ , it was shown that this reaction is possibly accompanied by an electron transfer to the substrate, without formation of oxygen-containing products [8].

The rate of reaction of  $0_2$ , with olefins is substantially influenced by the introduction of substituents. Nitro- and cyano-substituted olefins react at fairly high rates with  $0_2$ , at the double bond to form oxidative degradation products [9]. It is assumed that the mechanism of the oxidative cleavage of the double bond entails the formation of dioxetane, followed by its dissociation at the C-C bond.

However, in the case of halogen-substituted olefins, the reaction of  $O_2^{\cdot}$  with these olefins proceeds by a nucleophilic substitution mechanism with the formation of a vinylperoxy radical, which subsequently decomposes with the cleavage of the C-C bond [10].

In view of the possibility that the dioxetane mechanism may be substantially dependent on the nucleophilicity of the olefin, we studied in the present work the reaction of  $O_2$  with three olefins with different degrees of nucleophilicity - cyclohexene, styrene, and perfluorooctene.

## EXPERIMENTAL

The  $O_2^{-1}$  anion-radical was generated by the electrochemical reduction of oxygen in acetonitrile. The electrolytic cell was fitted with a mercury cathode and a platinum anode. Tetraethylammonium perchlorate served as the background electrolyte. Oxygen, preliminarily dried over  $H_2SO_4$  and  $CaCl_2$ , was bubbled into the system at a rate of 1.5 liters/h. The reduction of oxygen was carried out for 80-120 min at a constant current strength of 1.5-2.0  $\Omega/A$ . The anion radical obtained was identified according to UV and EPR spectra. The integral intensity of the EPR spectrum of (I) obtained by the method of a double integration of the spectrum was used as a measure of  $O_2^{-1}$  concentration in the course of the reaction. The initial concentration of the electrochemically generated  $O_2^{-1}$  was measured spectrophotometrically according to the absorption intensity in the region of the maximum ( $\lambda$  249 nm), using the k values of the extinction of 1760 liter·mole<sup>-1</sup>·cm<sup>-1</sup> [12].

The optical measurements were carried out on a Beckman UV 5270 spectrophotometer directly after the generation of  $O_2$ . The EPR spectra were recorded at 77 K on a Bruker R-200 spectrometer. The analysis of the products of the reaction of  $O_2$ , with styrene was carried out on a Ribermag R10-10 chromato-mass spectrometer.

The acetonitrile used as solvent was dehydrated by boiling over  $P_2O_5$  and  $K_2CO_3$  and then was distilled. A "pure" brand of cyclohexene was washed with a 10% solution in  $H_2SO_4$ , and then with a 10% aqueous solution of alkali and distilled water to a neutral reaction. The purified cyclohexene was dried over calcined  $CaCl_2$ , and distilled in an argon current over metallic sodium. Styrene, stabilized by hydroquinone, was washed with a 5% solution of alkali, and then with distilled  $H_2O$ . After being dried over  $CaCl_2$ , styrene was distilled under vacuum in an argon current. Perfluorooctene was synthesized by the pyrolysis of a sodium salt of perfluorononanoic acid at 320°C [13].

# DISCUSSION OF RESULTS

The kinetics of the reaction of  $0_2$ , with perfluorooctene, styrene, and cyclohexene was studied at room temperature in an acetonitrile solution. As known,  $0_2$ , may be spontaneously consumed in aprotic solvents, due to reaction with impurities (mainly traces of water) and disproportionation [14, 15]

$$O_2^{\tau} + O_2^{\tau} \to O_2^{=} + O_2$$
 (1)

We have therefore preliminarily measured the rate of consumption of  $O_2$ , under the experimental conditions used (acetonitrile, tetraethylammonium perchlorate as the background electrolyte). The characteristic EPR spectrum of  $O_2$  and the typical curve of the spontaneous consumption of  $O_2$  are given in Fig. 1. The kinetic curve becomes well linearized in the 1/I vs t coordinates, which indicates the preferential consumption of  $O_2^{-1}$  due to disproportionation. The rate constant of this reaction (k), determined from the data in Fig. 1c at  $25^{\circ}$ C, has the value of  $(4.7 \pm 0.5) \cdot 10^{-3}$  M<sup>-1</sup>·sec<sup>-1</sup>, and was later taken into account in the calculation of rates of reaction of  $O_2^{-1}$  with olefins.





Fig. 1. EPR spectrum of  $O_2^{-1}$  in acetonitrile (t = 77 K) (a), the kinetic curve of the spontaneous consumption of  $O_2^{-1}$  (b) (where I is integral intensity) and its anamorphosis (c) in the 1/I vs t coordinates.

Fig. 2. Kinetic curves of change in the relative intensity of the EPR signal of  $O_2^{\cdot}$  (where  $I_0$  and  $I = I_1 - I_2$  are the initial and current intensities of the signal;  $I_1$  in the presence,  $I_2$  in the absence of styrene) (a) and their semilogarithmic anamorphoses (b).  $[C_6H_5C_2H_4] = 4.35 \cdot 10^{-2}$ ,  $[O_2^{\cdot}] = 4.7 \cdot 10^{-3}$  mole/liter (1);  $[C_6H_5C_2H_4] = 2.16 \cdot 10^{-3}$ ,  $[O_2^{\cdot}] = 4.7 \cdot 10^{-3}$  mole/liter (2).

Fig. 3. Dependence of the rate constant of the first-order reaction of  $O_2$ , with styrene on the concentration of styrene.

Comparison of the data on the consumption kinetics of  $O_2$ , with perfluorooctene, styrene, and cyclohexene shows that the olefins studied can be arranged in the following series: cyclohexene < styrene < perfluorooctene. Thus, the reactivity of the olefins increases with increase in the electrophilicity of the substituents at the double bond.

In aprotic media,  $0_2$ , may react with alkyl halides by the nucleophilic substitution mechanism [3, 4]. Our evaluation of the rates of reaction of  $0_2$ , with perfluorooctene and perfluorooctane showed that under the conditions used, perfluorooctane is completely inert toward  $0_2$ . Thus, the possibility of the reaction of perfluorooctene with  $0_2$ , by the nucleophilic substitution mechanism can be excluded, and the high rates of consumption of  $0_2$  in the presence of perfluorooctene can be regarded as being due only to its reaction with the activated double bond of the olefin.

The reaction of  $O_2$  with perfluorooctene (PFO) at the  $O_2$  /olefin ratios of 0.3-10, at room temperature, proceeds virtually at the moment of mixing the solutions. The conventional products of the oxidation of PFO by oxygen (oxides, fluorophosgene, HF, acid fluorides) are not present in the reaction mixture. By means of gas-liquid chromatography, and also using spectrophotometry ( $\lambda$  276, 272, 263, and 252 nm) it was possible to note the appearance of unidentified transformation products of perfluorooctene, in the formation of which background

m/z	Relative intensity, I, %	Ion	m/z	Relative intensity, I, %	Ion
222	1,45	COOC <sub>2</sub> H <sub>5</sub> ] <sup>+.</sup>			0 "
177	27	Cooc,H, C≡0+ C,H, Cooc,H,	149	100	C <sub>6</sub> H₄ O H C O H
150	8,1	C₅H₃C=O l <sup>++</sup> <sup>↓</sup> OC₂H₅	122 105 104 93	5,1 11,7 10,2	$\begin{bmatrix} \\ C_{6}H_{3}-C \\ C_{6}H_{6}\end{bmatrix}^{+}$ $C_{6}H_{6}\end{bmatrix}^{+}$
			55 77 65	8,8 8,8	$C_6H_5^+$ $C_5H_5^+$

TABLE 1. Mass Spectrum of the Main Product of the Reaction of  $O_2^{-1}$  with Styrene, 70 eV

electrolyte clearly also takes part. Cyclohexene is inert toward  $O_2^{\cdot}$ , and its introduction into the solution virtually does not change the rate of consumption of  $O_2^{\cdot}$ , in this case equal to the rate of disproportionation of  $O_2^{\cdot}$ .

It was found from the investigation of the reaction of  $O_2$ , with styrene that the halfconversion time of  $O_2$ , in this reaction is 100 or more minutes, which enables its consumption kinetics during the course of the reaction to be followed with fair accuracy by the EPR method. The main characteristics of the EPR spectrum of  $O_2$ , when styrene is introduced into the solution, and also in the course of the reaction, practically do not change.

Figure 2 shows the kinetic curves of the change in the relative intensity of the EPR signal of the superoxide-ion in the reaction of  $O_2$  with styrene (curves la and 2a). The kinetic curves become well linearized in the log I/I<sub>0</sub> vs t coordinates (lines 1b and 2b).

The order of the reaction with respect to styrene changes from 1 to 0 with increase in the styrene concentration (Fig. 3). In the concentration range of  $(0.515-4.35)\cdot 10^{-2}$  mole/ liter, the first-order rate constant of the consumption of  $O_2$ ' is independent of the styrene concentration. The observed dependence indicates that the reaction of  $O_2$ ' with styrene proceeds through the stage of an intermediate ion-radical adduct with its subsequent dissociation to the reaction end products in the limiting stage of the process.

The transformation products of styrene were analyzed by gas-liquid chromato-mass spectrometry. The main reaction product, the mass spectrum of which is given in Table 1, was identified through automatic comparison with a spectra bank as diethyl o-phthalate. The other product, in the mass spectrum of which characteristic ions were found with mass numbers 150, 122, 105, and 77 (Table 1), was identified as ethyl benzoate. Unlike [8], we did not detect ethylbenzene and 1,4-diphenylbutane in the products of the reaction of  $O_2$ ' with styrene.

The formation of the o-phthalate ester as the main product indicates a complex reaction mechanism. At the first stage the formation of a peroxide takes place:

$$\bigcirc -CH = CH_2 + O_2^{-} \longrightarrow \bigcirc -\bar{C}H - CH_2 - O - O^{-}$$

The dissociation of peroxide particle with the cleavage of the C-C bond and migration of the  $CH_2$  group to the o-position of the benzene ring can occur synchronously with an intramolecular rearrangement:



followed by oxidation of the aldehyde and alcohol groups to carboxylic groups and esterification of the acid with the participation of the background electrolyte. Because of the presence of considerable amounts of benzoic acid in the reaction products, the possibility cannot be excluded of the occurrence of a process with the fragmentation of the peroxide with the intermediate formation of formaldehyde and a ketyl anion-radical of benzaldehyde (BKR):

 $\bigcirc -\bar{C}H-CH_2-O-O \longrightarrow \bigcirc -\bar{C}HO + CH_2O$ 

The fragments of the splitting of the anion-radical may either react together, or undergo independent transformations. The reversed condensation of the fragments, which because of the  $\sigma$ ,  $\pi$ -conjugation in the ketyl group may proceed with transfer of the reaction center, should lead to the formation of a disubstituted product



Direct reaction of the BKR with oxygen may also lead to the formation of benzoic acid.

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