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Abstract

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CATALYTIC PROPERTIES OF ORGANIC POLYMERS WITH A SYSTEM OF CONJUGATED BONDS

FORMATION OF HYDROPEROXIDES BY OXIDATION OF ALKYLAROMATIC HYDROCARBONS AND CYCLOHEXANE

All good solid inorganic catalysts for reactions of the oxidation–reduction class are metals or semiconductors. This regularity is often associated with electronic transitions accompanying the activating chemisorption of molecules. This point of view is confirmed by the correlation observed in many cases between the catalytic and physical electronic properties of inorganic solid catalysts (1). The question of the existence of similar relationships for organic compounds has so far remained unclear (2). For monomeric synthetic organic compounds forming molecular crystals, earlier studies gave negative results, while the electronic properties of biocatalysts have been studied too poorly for the establishment of such regularities. In this connection, the study of the catalytic properties of synthetic organic polymers with respect to oxidation–reduction reactions is of great interest—the oxidation of toluene in the presence of polymethyl-β-chlorovinyl ketone (3), and the decomposition of formic acid, as well as of hydrazine and hydrogen peroxide, on products of heat treatment of polyacrylonitrile (4). In these studies the semiconductor properties of the polymer were associated with the presence of conjugated bonds, purely carbon bonds in the first case and mixed carbon–carbon and carbon–nitrogen bonds in the second.

From the electronic point of view, catalytic activity may also be expected in less stable organic semiconductors, for example in monomeric charge-transfer complexes and the corresponding polymers. In this connection see the work (5).

Organic polymers with various types of conjugation are distinguished by increased thermal and chemical stability and include a great variety of functional groups. Therefore it seemed reasonable, first of all, to study systematically the catalytic properties of semiconductors of this type. The catalytic influence of monomeric phthalocyanines on the oxidation of cumene and other aromatic hydrocarbons was investigated (6,7). In both studies the electronic mechanism of catalysis did not interest the authors, and the catalytic properties of the organic semiconductor were not compared with its electron-physical properties.

The present work sets forth the results of an investigation of the effect of polymeric organic semiconductors with a system of conjugated bonds, both containing and not containing heteroatoms in the conjugation chain (^{8}), on the catalytic oxidation of alkylaromatic hydrocarbons and cyclanes.

Among the semiconductors the following were taken: polymeric copper phthalocyanines (^{9}), polymeric complexes of tetracyanoethylene (^{10}), and products of dehydrochlorination of perchlorovinyl (^{11}). Copper polyphthalocyanine II(k)H was obtained under the conditions of phthalocyanine synthesis from pyromellitic acid in the pres–

in the presence of ammonium molybdate; by an analogous route, but in the absence of a catalyst, copper II(b)H polyphthalocyanine was obtained. The synthesized polyphthalocyanines were first treated with weak solutions of hydrochloric acid and ammonia, then with concentrated sulfuric acid, with subsequent washing with water at each stage of treatment, after which extraction with organic solvents—dimethylformamide and pyridine—was carried out. The samples treated in this way were heated at 250° and 10^{-1} mm Hg until the release of subliming impurities ceased.

Table 1

Electrophysical characteristics of the polymeric semiconductors investigated

No.	Sample	Electrical conductivity at 300°K, $\Omega^{-1} \cdot$ cm^{-1}	Activation energy of conductivity, E_σ, kcal/mol	σ_0, $\Omega^{-1} \cdot$ cm^{-1}	Number of unpaired spins per 1 g	Specific surface area, S
1	Copper II(k)H polyphthalocyanine	$10^{-4.2}$	3.7	$10^{-1.6}$	$5.1 \cdot 10^{20}$	0.55
2	Copper II(b)H polyphthalocyanine	$10^{-5.2}$	5.1	$10^{-1.6}$	$6.7 \cdot 10^{20}$	4.1

No.	Sample	Electrical conductivity at 300°K, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$	Activation energy of conductivity, E_σ, kcal/mol	σ_0, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$	Number of unpaired spins per 1 g	Specific surface area, S
3	Polymeric complex of copper tetraazaannulene A-2	10^{-7}	7.4	$2 \cdot 10^{-2}$	–	–
4	Same, A-3	10^{-7}	7.3	$2 \cdot 10^{-2}$	–	–
5	Polyvinylene I	10^{-15}	13.6	10^{-5}	$3.6 \cdot 10^{19}$	0.30
6	Polyvinylene II	10^{-8}	6.7	10^{-3}	$7 \cdot 10^{19}$	0.35

The polymeric complexes of tetraazaannulene were obtained by the interaction of tetraazaannulene with copper acetylacetonate both in nitrobenzene medium (A-3) and in its absence (A-2). Polymer A-2 was obtained in the presence of a small amount of water. The reaction was carried out for 5 h at 160–180°. Polyvinylenes (products of the dehydrochlorination of perchlorovinyl) were obtained by thermal treatment of the polymer in an inert atmosphere at 500°C (polyvinylene I) or in air at 400°C (polyvinylene II) for 1 h.

The catalytic activity of the polymers listed in Table 1 was investigated with respect to the oxidation of cumene and other aromatic hydrocarbons, as well as cycloalkanes.

Experimental procedure and discussion of the experimental results

The rate of oxidation was studied volumetrically. The reaction apparatus was made in the form of a catalytic "duck" of double-walled molybdenum glass, between the walls of which hot water from a thermostat circulated. To eliminate diffusional complications, intensive shaking of the liquid being oxidized was carried out with the aid of a suitable device. In carrying out an experiment, 5 cm^3 of liquid (cumene, ethylbenzene, etc.) was poured into the reaction apparatus; its temperature was brought to the desired value within several minutes, and then a weighed portion of catalyst (most often 20 mg) was introduced and the apparatus was connected to a gas burette filled with oxygen. The shaking device

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

and stopwatch were then switched on. The oxidation rate was measured from the amount of oxygen absorbed. In the oxidation of cumene, isopropylbenzene hydroperoxide is formed. The amount of hydroperoxide formed was determined iodometrically. In all cases, within the accuracy of the experiment, the amount of oxygen absorbed corresponded to the amount of hydroperoxide formed. In the selected temperature range, neither without a catalyst nor in the presence of the organic catalysts studied did the hydroperoxides formed decompose appreciably. In this and other cases, the oxidation rate increased linearly with increasing amount of catalyst.

Figure 1 shows the kinetic curves for the oxidation of cumene, calculated per unit surface area of the sample P(k)H, at various temperatures. The activation energy of cumene oxidation, found from the slope of the straight lines of the initial oxidation rates, was 11 kcal/mol (Fig. 2). The oxidation of other hydrocarbons on the catalyst P(k)H is shown in Fig. 3. As is evident from the figure, oxygen is introduced at a tertiary carbon much more readily than at a secondary one, and practically does not react with a primary carbon. In cyclohexane the OOH group is formed approximately as readily as in ethylbenzene*. Cyclanes with a smaller number of atoms in the ring have not yet been studied.

Fig. 1. Kinetic curves for the oxidation of cumene on copper polyphthalocyanine P(k)H at various temperatures:
I –52°; *II* –67°; *III* –80°, *IV* –90° C

Fig. 2. Determination of the activation energy for copper polyphthalocyanine P(k)H

Figure 4 presents the kinetic curves (1-3) for the oxidation of cumene, calculated per 1 m^2 of catalyst, on samples P(k)H, P(b)H, and on monomeric copper phthalocyanine. It follows from the figure that the polymer of the P(k)H grade is catalytically the most active. This same sample has the lowest activation energy of electrical conductivity (see Table 1); its electrical conductivity is also higher than that of the P(b)H grade sample. Polyphthalocyanines, especially P(k)H, proved to be more active than monomeric phthalocyanine.

The two investigated samples of polymeric copper tetracyanoethylene complexes were practically identical in their electrophysical properties (see Table 1). The rate of cumene oxidation, calculated per 1 g of catalyst, also proved to be close (practically identical) for these samples (see Fig. 4, curves 4, 5). However, the situation may change when the calculation is made per 1 m^2 of surface, the value of which, because of the small amount of material, has not yet been determined.

From the electronic standpoint, the polyvinylene samples proved to be of interest. One of them—polyvinylene I—is practically an insulator

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

($\sigma_{300^\circ\ \mathrm{K}} = 10^{-15}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$), whereas the other—polyvinylene II ($\sigma_{300^\circ\ \mathrm{K}} = 10^{-8}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$)—is a semiconductor. From Fig. 4 (curves 6-7) it is evident that cumene oxidation on polymer I was completely absent. This may serve as an indication of a correlation between the physical semiconductor properties and the catalytic properties for the oxidative reaction studied.

Investigation of the above-mentioned polymeric materials showed that all of them (with the exception of polyvinylene I) possess catalytic activity with respect to the reaction of cumene oxidation to hydroperoxide. We compared catalytic activity within individual groups of polymers close in their chemical composition. The presence of ions the metal in the polymer proved unnecessary for the manifestation of catalytic activity. Thermal treatment of the polymers has a strong effect both on the electrical conductivity and its activation energy, and on the catalytic activity. In the samples studied, a decrease in the band gap and an increase in the electrical conductivity of the samples (measured before catalysis) was accompanied by an increase in the specific catalytic activity in the cumene oxidation reaction. However, the data are insufficient for categorical conclusions, since measurements of the electrical characteristics during and after catalysis have not yet been made.

Fig. 3. Kinetic curves for the oxidation of various hydrocarbons on copper polyphthalocyanine P(k)H: **1** –cyclohexane, $T = 71^\circ$; **2** –ethylbenzene, $T = 92.5^\circ$; **3** –cumene, $T = 89^\circ$; **4, 5** –toluene; benzene, $T = 71^\circ$C

Fig. 4. Kinetic curves for the oxidation of cumene on various polymers: **1** –phthalocyanine monomer, **2** –copper polyphthalocyanine P(b)H, **3** –copper polyphthalocyanine P(k)H, **4** –polymeric complexes of copper tetraacetonitrile A-2, **5** –the same, A-3, **6** –polyvinylene P, **7** –polyvinylene I

From the data presented, it may be suggested that the ability to catalyze the mild oxidation of alkylaromatic compounds with formation of hydroperoxide groups at a secondary or tertiary carbon atom of the alkyl radical is characteristic of many (possibly all) organic polymers with a system of conjugated carbon and carbon-nitrogen π- and σ-bonds, provided they exhibit semiconductivity under oxidation conditions. It may be supposed that cyclohexane is not the only cyclane whose mild oxidation is accelerated by these semiconductors. This type of oxidation requires the presence of oxygen on the surface of the organic

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* The difference in the slope of the straight lines is explained mainly by the difference of 21.5° in the experimental temperature.

semiconductor under the conditions of catalysis, which proceeds in an organic liquid, in the form of undissociated O_2 molecules or, more probably, in the form of O_2 ion radicals.

A. N. Frumkin recently arrived at a similar conclusion on the basis of electrochemical data.

The conclusions drawn, and the possibility of extending them to a wider range of systems, require further study.

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CITED LITERATURE

1. S. Z. Roginskii, *Problems of Kinetics and Catalysis*, **8**, 1955, p. 200; **10**, 1960, p. 5; *Kinetics and Catalysis*, **1**, 15 (1960).
2. S. Z. Roginskii, *Journal of the All-Union Chemical Society named after Mendeleev*, **5**, No. 5, 482 (1960).
3. A. N. Nesmeyanov, A. M. Rubinshtein et al., DAN, No. 3, 135, 609 (1960).
4. E. S. Dokukina, S. Z. Roginskii et al., DAN, **137**, No. 4, 893 (1961).
5. N. P. Keier, G. K. Boreskov et al., *Kinetics and Catalysis*, **2**, No. 4, 509 (1961).
6. A. Cook, *J. Chem. Soc.*, 1938, 1761.
7. H. Kropf, *Ann. Chem.*, **637**, 73 (1960).
8. A. A. Berlin, *Chemistry and Technology of Polymers*, No. 7–8, 139 (1960).
9. A. A. Berlin, L. G. Cherkashina, E. I. Balabanov, *High-Molecular Compounds*, **4**, No. 2 (1962).
10. A. A. Berlin, N. G. Matveeva et al., *High-Molecular Compounds*, **4**, No. 6 (1962).

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