BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN	VOL. 39	551—555 (1966)

Vulcanized Aniline Black. Its Electrical Conductivity and Catalysis upon the Decomposition of Hydrogen Peroxide[*1,*2]

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(Received July 5, 1965)

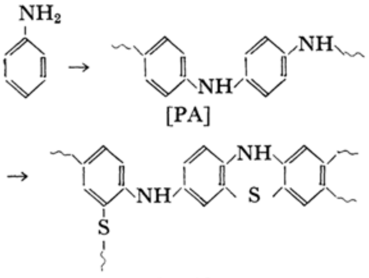
New semiconductive polymers have been prepared by the vulcanization of the oxidative condensation products of aniline. The polymers vulcanized are infusible black or black-violet powders insoluble in any organic solvent. The spin concentrations of the polymer vulcanized are about 1.5—2.5×10^{19} spins/g., about ten as much as those of the oxidative condensation products of aniline. The electrical conductivity increases with the increase in the sulfur content; the electrical resistivity at 20°C is 10^6—10^9 ohm-cm., and the activation energy is 0.68—1.18 eV. The polymers vulcanized have catalytic effects on the decomposition of hydrogen peroxide at 30°C. The catalytic effects of phenothiazine and the oxidative condensation products of aniline are, however, extremely slight. The catalytic ability depends not only on the structure of the polymer vulcanized, but also to some extent on its electrical conductivity.

[*1] Part II of a series of studies of organic catalysts. The previous paper, also presented in This Bulletin (**37**, 326 (1964)), will be referred to as Part I of this series.

[*2] Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

The catalytic action of organic semiconductors on chemical reactions has received little attention. In a previous paper,[1] however, we have shown that some organic dyes catalyze the photo-oxidation of isopropyl alcohol in the liquid phase, and that the dyes classified as *p*-type organic semiconductors are more effective in catalytic activity than those classified as *n*-type organic semiconductors. Dawans, Gallard, Jeyssie and Traynard[2] have recently reported that the semiconductive polymers containing free radicals have catalytic activities on the decomposition of nitrous oxide, the dehydration of cyclohexanol and the isomerization of 1-butene.

In this paper we will describe how a new semiconductive polymer (shown as PAS in Fig. 1) synthesized by the vulcanization of the oxidative condensation product of aniline (shown as PA in Fig. 1) catalyses the decomposition of hydrogen peroxide at room temperature; the correlation between the catalytic activities of the polymer and their semiconductive properties will also be discussed.



[PA]

[PAS]

Fig. 1

Experimental

The Preparation of the Semiconductive Polymers.—*a) The Oxidative Condensation Product of Aniline (PA).*—A mixture of 50 ml. of 7.5% hydrogen peroxide and 0.25 g. of ferrous sulfate was gradually added to 5 g. of aniline at 60°C; the mixture was then allowed to stand overnight. The black precipitate obtained by filtration was poured into 100 ml. of 2 N sulfuric acid at 50°C. After the mixture had been filtered, the precipitate was washed with a boiling aqueous solution of ammonium hydroxide and then with water. When the washed precipitate was dried over calcium chloride at room temperature under the reduced pressure of 1 mmHg for a day, about 1.3 g. of black powder was obtained, m. p. 115—137°C.

Found: N, 13.68%.

b) The Oxidative Condensation Product of Aniline Hydrochloride (PA-Cl).—A mixture of 13.5 g. of concentrated hydrochloric acid, 38 ml. of 5% hydrogen peroxide and 0.9 g. of ferrous sulfate was gradually added to 4.66 g. of aniline dispersed in 200 ml. of water at 0°C; the mixture was stirred at 0°C for an hour, and then at room temperature for 44 hr. To this mixture 20 ml. of ammonium hydroxide was added, and the precipitate obtained was washed thoroughly with water and then dried over calcium chloride in the same way as has been described in the case of a). The yield of the product was 2.5 g.

c) The Vulcanized Product (PAS).—The vulcanization of PA or PA-Cl was carried out under the various conditions shown in Table I. Here the synthetic procedure of PAS, in which the molar ratio of sulfur to aniline unit was 2.1, will be described in detail as an example. A mixture of 0.56 g. of PA, 1.18 g. of sulfur and 0.08 g. of iodine was heated at 200—210°C for about 10 hr. under a nitrogen stream. During the course of the reaction, the evolution of hydrogen sulfide was observed. The solidified product was pulverized, and then extracted with carbon disulfide using a Soxhlet apparatus for a day in order to remove excess sulfur and low-molecular-weight compounds. With this extraction process, 0.91 g. of a mixture of sulfur and the black powder consisting of low-molecular-weight compounds was obtained. The traces of sulfur and iodine which remained in the extracted residue were removed by sublimation at about 120°C under the reduced pressure of 1—2 mmHg for 8 hr. About 0.78 g. of the infusible black powders was obtained. The results of the elementary analysis of nitrogen or sulfur for the black powders are shown in Table I.

TABLE I. THE CONTENTS OF NITROGEN AND SULFUR IN PAS

Starting material	$S/\text{-}NHC_6H_4\text{-}$*	PAS		
		N%	S%	r_s
PA	0	15.56	0	0
PA	1/2	11.16	16.61	0.65
PA	2	10.08	29.05	1.46
PA	6	7.81	37.05	2.08
PA	6**	5.44	46.72	3.74
PA	8	8.35	35.05	1.84
PA	20	6.90	37.74	2.39
PA-Cl	0	—	—	—
PA-Cl	6	—	32.98	—

* $S/\text{-}NHC_6H_4\text{-}$ is the molar ratio of sulfur to aniline unit for the starting material.

** PA was vulcanized at 300°C.

Electrical Conductivities.—The d. c. resistivities of the polymers obtained were measured under a pressure of 1.0×10^3 kg./cm² at an applied electric field of 100—200 V./cm. according to the methods described in the preceding papers.[3] The current-voltage relationship was shown to be ohmic up to 10^4—10^5 V./cm. The electrical resistivity (ρ) at an ascending temperature was identical with that at a descending temperature, and a linear relationship between log ρ and $1/T$ was observed. The resistivity of all the polymers obtained fit the following equation, as does a typical organic semiconductor:

$$\rho = \rho_0 \exp(\Delta\varepsilon/2\boldsymbol{k}T)$$

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[1] H. Inoue, S. Hayashi and E. Imoto, This Bulletin, **37**, 326 (1964).

[2] F. Dawans, J. Gallard, PH. Jeyssie and PH. Traynard, *J. Polymer Sci.*, **Part c**, 1385 (1964).

[3] H. Inoue, S. Hayashi and E. Imoto, This Bulletin, **37**, 336 (1964).

TABLE II. RATE CONSTANTS FOR THE DECOMPOSITION OF HYDROGEN PEROXIDE, AND THE VALUES OF SPIN CONCENTRATIONS, RESISTIVITY AT 20°C (ρ_{20}) AND $\Delta\varepsilon$

Compound	r_s	g-Value	Half width gauss	Spin concn. spins/g.	ρ_{20}, Ω·cm.	$\Delta\varepsilon$, eV.	k, min^{-1}
PA	0	2.0034	18.9	2.2×10^{18}	$>10^{13}$	—	very small
PAS	0.65	2.0045	15.7	2.1×10^{19}	2.7×10^{9}	1.05	1.2×10^{-3}
PAS	1.46	2.0047	15.0	1.7×10^{19}	2.4×10^{6}	0.95	2.5×10^{-3}
PAS	2.08	2.0045	16.4	2.4×10^{19}	2.3×10^{8}	0.97	5.5×10^{-3}
PAS	3.74	2.0049	15.0	1.5×10^{19}	3.8×10^{6}	0.68	1.2×10^{-4}
PAS	1.84	2.0043	13.2	2.0×10^{19}	2.2×10^{9}	1.18	6.1×10^{-3}
PAS	2.39	2.0054	17.7	2.2×10^{19}	3.5×10^{8}	0.98	5.5×10^{-3}
PA-Cl	—	—	—	—	2.8×10^{9}	1.28	very small
PAS-Cl	—	—	—	—	1.7×10^{5}	0.5	3.3×10^{-4}

The Decomposition of Hydrogen Peroxide.—The rate of the decomposition of 7.3% hydrogen peroxide was determined by measuring the amounts of oxygen generated. A weighed amount of a catalyst was dispersed in 5 ml. of distilled water in a reaction vessel placed in a thermostat. After the thermal equilibrium had been reached, 5 ml. of 7.3% hydrogen peroxide was added to the dispersed solution. The amounts of oxygen generated were measured at appropriate time intervals by a gas burette connected with the reaction vessel. In order to stop the reaction after a certain time, 2 N sulfuric acid was added to the above dispersed solution. The rest of the hydrogen peroxide was titrated with potassium permanganate. The amount of oxygen generated coincided with that of hydrogen peroxide calculated by the following equation:

$$2\,H_2O_2 = 2H_2O + O_2$$

Results and Discussion

The Properties of the Semiconductive Polymers.—PA was a black-brown powder and was partially soluble in dimethylformamide. However, when the powders were placed in a solution of concentrated sulfuric acid, the solution showed a red-brown color. The infrared spectra of PA showed the absorptions of the –NH– band at 3200—3300 cm^{-1} and the out-of-plane deformation band of two adjacent free hydrogen atoms at 825—840 cm^{-1}. The ESR spectrum of PA showed the existence of unpaired electrons, and the spin concentration was about 2.2×10^{18} spins/g. PA-Cl was infusible black powders and was insoluble in any organic solvent; it showed a blue-green color in concentrated sulfuric acid. The PAS obtained by the cross-linking of PA or PA-Cl with various amounts of sulfur was an infusible black powder, most of which was insoluble even in concentrated sulfuric acid. The molar ratio of sulfur to aniline unit in PAS (r_s) was calculated by the following equation:

$$\text{Molar ratio } (r_s) = \frac{\text{S\%} \times 14}{\text{N\%} \times 32}$$

As is shown in Table I, several polymers with different sulfur contents were obtained.

The infrared spectrum of PAS was similar to that of PA. The absorption bands of PAS at 825—840 cm^{-1} and 1450—1500 cm^{-1} were shifted toward a lower-wave-number side by 10—15 cm^{-1} as compared with those of PA.

The spin concentration of PAS calculated from the ESR spectra was about 1.5—2.5×10^{19} spins/g., about ten times as much as that of PA. No remarkable difference in the spin concentration was, however, observed among the different sorts of PAS polymers. The g-value for PAS was close to that of a free electron, i. e., $g\simeq2.0023$. The half width of both PA and PAS was about 13.2—19.2 gauss, as narrow as that of the lattice polymer reported in preceding papers.[4]

Electrical Conductivities.—As can be seen in Table II, the ρ_{20} value of PA-Cl was low in comparison with that of PA ($>10^{13}$ ohm-cm.). The ρ_{20} value of PAS or PAS-Cl decreased with the increase in the sulfur contents; that is, the electrical conductivity increased with the increase in the degree of the vulcanization. This would imply that the degree of the conjugation of π

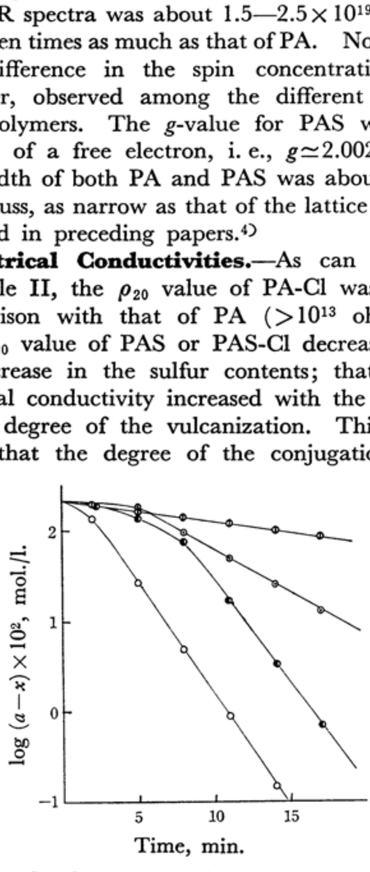

Fig. 2. Catalytic action of PAS on the decomposition of hydrogen peroxide: PAS of r_s, 1.84; a, 1.055 mol./l. and temp. 30°C.
○ PAS (r_s, 1.84), ◐ PAS (r_s, 2.39), ⊙ PAS (r_s, 1.49), ⦶ PAS-Cl

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[4] H. Inoue, T. Takiuchi and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 1291 (1962); H. Inoue and E. Imoto, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **83**, 1052 (1962).

electrons in PAS increases.

The Effects of the Semiconductive Polymers on the Decomposition of Hydrogen Peroxide.—As can be seen in Fig. 2, phenothiazine showed no catalytic action on the decomposition of hydrogen peroxide, but PA, PA-Cl or PAS-Cl showed a slight catalytic action. On the other hand, PAS accelerated the decomposition of hydrogen peroxide to oxygen and water, and the catalytic activity of PAS depended on the sort of PAS. The logarithmic value of the concentration of hydrogen peroxide, log $(a-x)$. decreased linearly with the reaction time after a certain induction period. The first order rate constant, k, was calculated from the straight line in Fig. 2 by the following equation:

$$k = \frac{1}{t} \log \frac{a}{a-x}$$

where a and x are the initial and the decomposed concentrations of hydrogen peroxide respectively, and where t is the reaction time. The results calculated are shown in Table II. The relationships between the spin concentration, $\Delta\varepsilon$, $\log \sigma_0$, or $\log k$ and r_s are shown in Fig. 3. No parallel relationship between the catalytic activity of PAS and the spin concentration or $\Delta\varepsilon$ was observed.

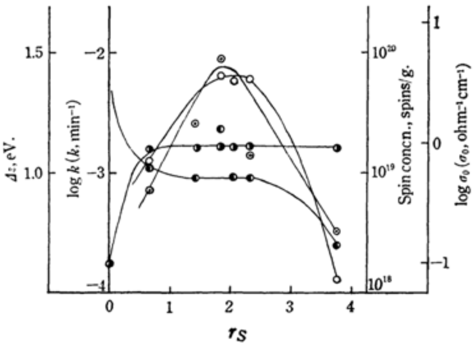

Fig. 3. Relationships between the spin concentration, $\Delta\varepsilon$, $\log \sigma_0$, or $\log k$ and r_s.
◑ Spin concn., ◐ $\Delta\varepsilon$, ⊙ $\log \sigma_0$, ○ $\log k$

However, it is interesting to note that the spin concentration of PAS, which showed a catalytic activity was ten times larger than that of PA, which showed only a slight catalytic activity. The $\Delta\varepsilon$ value of PAS which shows the best catalytic activity was about 1 eV. Surprisingly, a parallel relationship was found between the variations in $\log \sigma_0$ and $\log k$ for r_s. This seems to show that the catalytic activity is affected by the arrangement of the molecule, because $\log \sigma_0$ is related more or less to the molecular arrangement.

The Effect of pH on the Catalytic Action.—Dokukina et al.[5] have reported that the nitrogen atoms contained in a catalyst acted as the active center on the decomposition of formic acid. In this connection, the fact that the catalytic activity of PAS decreases when $\Delta\varepsilon$ becomes smaller than 1 eV. may be caused by the decrease in the relative density of nitrogen atoms on the surface of a PAS solid. Therefore, we investigated the problem of whether the catalytic activity of PAS is affected by the variation of the pH in the solution of hydrogen peroxide. Here, the PAS with a r_s value of 1.8 was used as the catalyst, and the reaction was carried out at pH 3, 4, 5.2, 7.5, 9.8 and 11.2 respectively, in which Sörensen's buffer solutions for the 3—8 pH range, and Britton-Robinson's buffer solutions for the range of more than pH 9, were used. To 0.05 g. of PAS dispersed in 5 ml. of the buffer solution there was added 5 ml. of 7.3% hydrogen peroxide; then the amount of oxygen generated was measured at appropriate time intervals. In the solution of more than pH 9, oxygen was generated even with no addition of PAS, and so this amount was subtracted from the total amount of oxygen generated. As can be seen in Fig. 4, the catalytic effect in the acidic solution with pH values less than 4 was extremely slight. However, the PAS in neutral or alkaline solutions showed catalytic activity. This seems to show that the basicity of PAS plays an important role in the catalytic ability.

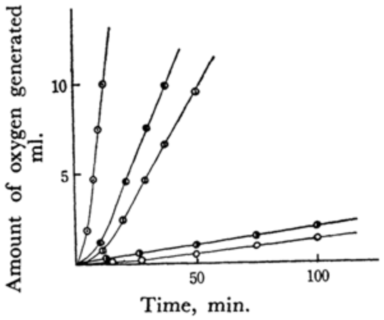

Fig. 4. Effect of pH on the catalytic action: PAS; r_s, 1.84.
○ pH 3, ◑ pH 4, ⦶ pH 5.2, ◐ pH 9.8, ⊙ pH 11.2

The Effect of the Acceptor on the Catalytic Action.—The catalytic ability of PAS is considered also to be related to its nature as an electron donor. If so, the catalytic activity of PAS treated with an electron acceptor, for instance, iodine, 1, 3, 5 - trinitrobenzene or 7, 7, 8, 8 - tetracyanoquinodimethane, must decrease as compared with that of the untreated PAS. The treatment of PAS with the electron acceptor was carried out by dispersing PAS for 12 hr. in a solution of the electron acceptor in benzene or ethanol. As is shown in Fig. 5, the catalytic activity of the treated PAS was lower than that of the untreated PAS. Therefore, the nature of PAS as an electron donor

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[5] E. S. Dokukina, S. Z. Roginskii, M. M. Sakkarov, A. V. Topchiev, M. A. Geiderikh, B. E. Davydov and B. A. Krentsel, *Doklady Akad. Nauk. S. S. S. R.*, **137**, 893 (1961).

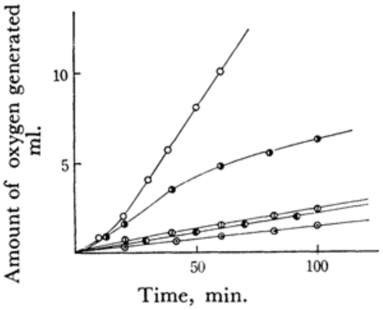

Fig. 5. Effect of the acceptor on the catalytic action: PAS; r_s, 1.84.
◑ Iodine, ⦶ 1, 3, 5-trinitrobenzene, ◐ sulfuric acid, ⊙ 7, 7, 8, 8-tetracyanoquinodimethane, ○ untreated PAS

seems to be important in the catalytic ability.

An Assumed Mechanism for the Catalytic Action of PAS.—As has been described above, it was assumed that the catalytic effect of the semiconductive polymers on the decomposition of hydrogen peroxide depends not only on the $\Delta\varepsilon$ value and their natures as electron donors, but also on the arrangement of the molecules and on the relative density of the nitrogen atom on the surface of the polymer solid. Though the details of the mechanism of the decomposition of hydrogen peroxide are not clear, it seems that hydrogen peroxide trapped on the nitrogen atoms on the catalyst is reduced by the conductive electron, decomposing to H_2O and O^-, and that O^- gives an electron to the hole on the catalyst, thus converting it to O_2, for example, by the following processes:

$$\mathrm{PAS} + H_2O_2 \rightarrow \mathrm{PAS}\cdots H_2O_2$$
$$\rightarrow \mathrm{PAS}^+ + H_2O + O^-$$
$$\mathrm{PAS}^+ + O^- \rightarrow \mathrm{PAS} + O\cdot \rightarrow O_2 + \mathrm{PAS}$$

Here, the catalytic ability must depend on the density and the arrangement of the active center such as the nitrogen atoms.