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CATALYTIC HYDROGEN TRANSFER REACTION ON THE POLYNAPHTHOQUINONE

----- SYNTHESIS OF ANILINE AND DECOMPOSITION OF HYDROGEN SULFIDE

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Catalytic hydrogen transfers on the polynaphthoquinone are reported. Both the dehydrogenated and the hydrogenated products were simultaneously gained. Nitrobenzene was catalytically reduced to aniline by the hydrogen transfer from substrates in the temperature range 285°-330°C. Hydrogen sulfide chosen as a simple sulfur-containing compound was rapidly decomposed on the polynaphthoquinone in the range 30°-100°C.

The thermostable organic polymers containing quinone groups[1)] or nitrogen atoms[2)] have been shown to promote dehydrogenations. Polynaphthoquinone was found to markedly catalyze various dehydrogenations in the previous papers.[3a)~3d)] It was demonstrated in these studies that the dehydrogenation reactions on the quinone polymers like polynaphthoquinone were recognized to be the stoichiometric hydrogen transfer from the reactant to the quinone groups in the polymer. Hydrogen subtracted from the substrates is trapped on the quinone groups in the polymer, forming hydroquinone groups. The hydroquinone groups are rapidly reoxidized by oxygen to produce the quinones, by which the catalytic activity is completely restored. In other words, the dehydrogenations on the polynaphthoquinone catalytically proceed in the successive steps by way of the formation of hydroquinone groups. It is accordingly interesting to investigate the reducing power of the trapped hydrogen(hydroquinones) on the surface of the polynaphthoquinone as well as to extensively study the high catalytic activity of the polynaphthoquinone having the characteristic reactivity.

In the present study various catalytic hydrogen transfers on the polynaphthoquinone are reported, where the hydrogen atoms of the substrates, followed by trapping on the quinone groups in the polymer, were effectively utilized in the synthesis of aniline from nitrobenzene. The catalytic decomposition of hydrogen sulfide on the polynaphthoquinone was also investigated in connection with the removal of sulfur-containing compounds in waste gases[4)],[5)] the hydrogen of hydrogen sulfide being rapidly transferred to oxygen on the quinone groups in the polymer.

The catalytic synthesis of aniline from nitrobenzene on 1g of the polynaphthoquinone was carried out in the range of temperature from 285° to 330°C in an ordinary flow system using helium as a carrier gas. Hydrogen sulfide was decomposed in the temperature range of 30° to 100°C in flow of air. The decomposition of hydrogen sulfide in a closed circulating system(185 cm^3) was also investigated in the presence of oxygen using 0.3g of the polynaphthoquinone. The reaction products were quantitatively determined by gas chromatography using a Carbowax 1500 column, while hydrogen sulfide, water, sulfur dioxide, and carbon dioxide were analyzed by a dioctyl phthalate column or deactigel column. The gas products were also checked by IR spectroscopy. All of chemicals used were special grade and purified by distillation when necessary. Hydrogen sulfide with 99.5% purity was used without further purification. Polynaphthoquinone employed as a catalyst was obtained by a similar procedure to that previously described$^{3)}$ except for slight modifications. The polynaphthoquinone thus obtained was indicated to be a planar molecule by means of an electron microscopy. Those planar polymers are tightly aggregated to form the porous insoluble catalyst (the surface area:$70m^2/g$). The polynaphthoquinone was heated at 350°C for 4 hours in flow of helium or treated at 340°C for 12 hours in vacuum before use as a catalyst.

Hydrogen sulfide was employed as a simple sulfur-containing compound. The decomposition of hydrogen sulfide over 1g of the polynaphthoquinone was run in a flow system using a mixture of air and nitrogen as a carrier gas in the range from 30° to 100°C. All of the hydrogen sulfide passed onto the catalyst were decomposed under the present reaction conditions. The typical result at 60°C in the initial stage of the reaction is shown in Table. No evolution of sulfur dioxide was observed in the course of the reaction. The amounts of hydrogen sulfide decomposed within 12 minutes were correspond to 8 times of the effective quinone groups by mole. This means that the decomposition catalytically proceeds on the polynaphthoquinone. Sulfur was deposited on the catalyst through the reaction. The deposited sulfur was shown to be amorphous according to the X-ray diffraction pattern and uniformly dispersed on the surface of the polynaphthoquinone by electron microscopy. It was consequently found that the polynaphthoquinone had a high activity for the catalytic decomposition of hydrogen sulfide in the presence of oxygen. Two moles of hydrogen sulfide stoichiometrically reacted with one mole of oxygen on the catalyst. The adsorption of hydrogen sulfide on the polynaphthoquinone was expressed in the following Langmuir equation : $V_{ad}= bKP/(1+KP)$. The heat of adsorption was 8.1 kcal/mol; the value corresponding to the energy of hydrogen bond. The initial rate of the decomposition on the polynaphthoquinone in a closed circulating system was found to be proportional to the amount of hydrogen sulfide adsorbed. The rate was independent of the partial pressure of oxygen. Consequently, the hydrogen transfer from hydrogen sulfide to the quinone group of the polymer is the rate-determining step in the reaction sequence. Thus the decomposition of hydrogen sulfide on the polynaphthoquinone was explained to proceed in the hydrogen transfer process on the quinone groups in the polymer.

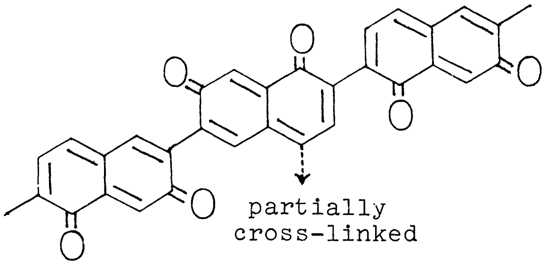

Fig.1. Polynaphthoquinone.

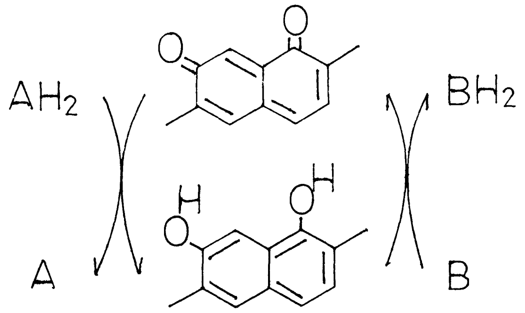

Fig.2. Hydrogen transfer process.

The catalytic hydrogen transfer in a flow system was acomplished, replacing oxygen by nitrobenzene(B), where various substrates(hydrogen donors : AH$_2$), such as ethylbenzene, n-propylbenzene, cumene, cyclohexanol, cyclopentanol, and cyclohexene, were employed. The dehydrogenations of the substrates on the polynaphthoquinone proceeded even in the absence of oxidizing agents until all of the effective quinone groups on the surface of the polymer were saturated with hydrogen, forming hydroquinone groups. When nitrobenzene was passed onto the reduced polynaphthoquinone in flow of helium in the temperature range from 285^o to 330^{o}C, the hydroquinone groups in the catalyst were reoxidized to quinones accompanied with the formation of aniline. The hydrogen transfer on the polynaphthoquinone was accordingly confirmed to proceed in two successive steps. The catalytic process of the hydrogen transfer is shown in Fig.2.

Table. The catalytic hydrogen transfer on the polynaphthoquinone(1g)

	AH$_2$-B a)	A-BH$_2$	conv.% b) (AH$_2$-B)	rate(x10^5) (mol/g·hr) (A-BH$_2$)	selec. c) %	T^{o}C	total s.v. (cc/g·hr)	E$_a$ (kcal/mol)
1	ethylbenzene	styrene	9.24	17.8	100	330	441	14.5
	nitrobenzene	aniline	61.7	5.6	95			
2	n-propylbenzene	β-methylstyrene	4.80	8.15	100	330	442	14.0
	nitrobenzene	aniline	28.3	2.7	99			
3	cumene	α-methylstyrene	7.50	12.76	100	330	436	13.6
	nitrobenzene	aniline	44.6	4.1	96			
4	cumene	α-methylstyrene	4.3	8.3	100	315	436	—
	nitrosobenzene	aniline	100	4.13	99			
5	cyclohexanol	cyclohexanone	8.1	4.7	25.5 e)	300	455	15.0 f)
	nitrobenzene	aniline	80.7	6.8	87			
6	hydrogen sulfide d)	sulfur	100	401.8	100	60	1980	13.0 g)
	oxygen	water	100	200.9	100			

a) the ratio against AH$_2$; nitrobenzene(4 vol%), nitrosobenzene(2.12 mol%), the partial pressure of AH$_2$; 0.086~0.11 atm.

b) the conversion is defined as the ratio of the consumed AH$_2$ or B to the supplied AH$_2$ or B .

c) (the yield of A or BH$_2$)/(the conversion)

d) the molar ratio of H$_2$S to O$_2$ is 2 : 1.

e) the approximate value; (benzene+cyclohexene)=37.5%, an unidentified oxidation product=37.0%

f) the value, obtained from the rate of the formation of aniline.

g) the value, in a closed circulating system.

When both a hydrogen donor and nitrobenzene were simultaneously passed through the polynaphthoquinone in the temperature range from 285° to 330°C, the catalytic hydrogen transfer between them took place, in which the corresponding dehydrogenated product and aniline as the hydrogenated product were simultaneously obtained. A part of the results are given in Table. The dehydrogenated product(A) and aniline were produced in the ratio of approximately 3 : 1, showing that the hydrogen transfer reaction is stoichiometrically expressed as follows:

$$3\ AH_2 + \text{nitrobenzene} \longrightarrow 3\ A + \text{aniline} + 2\ H_2O.$$

No evolution of hydrogen was observed in the course of the reaction. These results show that the hydrogen atoms of hydrogen donors were completely transferred to nitrobenzene. Though such an intermediate product as nitrosobenzene could not be observed, nitrobenzene may consecutively reduced to aniline on the polynaphthoquinone as is well known. In fact, when nitrosobenzene was used as an oxidizing agent, it was easily converted to aniline under a similar reaction condition as is shown in Table. Thus nitrobenzene was catalytically reduced to aniline by the reducing power of the trapped hydrogen (the hydroquinone group) on the polynaphthoquinone. The polynaphthoquinone, consequently, provides a catalytic hydrogen transfer reaction in a flow system as is shown in Fig.2, by which the dehydrogenated and the hydrogenated products could simultaneously be gained.

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