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Carbon Black as an Electron-transfer Catalyst. The Two-phase Dehydrogenation of Hydrazo Nitriles by an Aqueous Solution of Potassium Hexacyanoferrate(III), Using Carbon Black as the Catalyst

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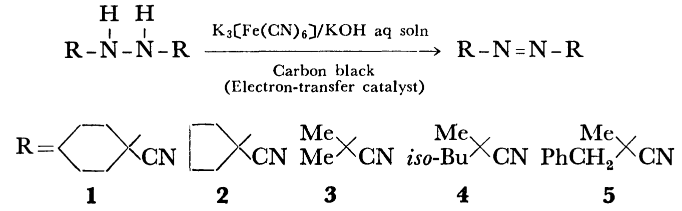
The two-phase(aqueous and organic phase) dehydrogenation of hydrazo nitriles by an aqueous solution of potassium hexacyanoferrate(III), using carbon black as the catalyst, was carried out at 40 °C with shaking. In the presence of carbon black, the two-phase dehydrogenation of hydrazo nitriles was accelerated, and the corresponding azo nitriles were obtained in good yields. The catalytic activity of channel blacks was larger than that of furnace blacks. Moreover, the increasing content of phenolic hydroxyl groups tended to increase the catalytic activity of carbon blacks. It became apparent that phenolic hydroxyl groups on the surface of carbon black act as an electron-transfer catalyst in the two-phase dehydrogenation. The reaction scheme was considered to be as follows. In the aqueous phase, phenolic hydroxyl groups on the surface are oxidized by an aqueous solution of $K_3[Fe(CN)_6]$ to give phenoxyl radicals, and then the carbon black with phenoxyl radicals is transferred into the organic phase, which contains hydrazo nitriles. Subsequently, in the organic phase, the phenoxyl radicals oxidize the hydrazo nitriles to give the corresponding azo nitriles, by which phenolic hydroxyl groups are regenerated. Thus, it was concluded that phenolic hydroxyl groups on the surface are recycled and that carbon black mediates the redox reaction occurring between aqueous and organic phases.

Recently, oxidation-reduction polymers containing 1,4-dihydronicotinamide(NAH), 2,4,5,6(1*H*,3*H*)-pyrimidinetetrone (alloxan), and 1,1′-dialkyl-4,4′-bipyridinium(viologen) moieties have been prepared, and their behavior as polymeric electron carriers has been investigated.[1] For instance, it has been reported that a polymer containing alloxan moieties mediates the redox reaction occurring between aqueous and organic phases (two-phase reaction).[1] Furthermore, it has been proved that the redox reaction between insoluble solids—two polymer beads, one containing NAH moieties and the other containing *p*-benzoquinone, was feasibly mediated by alloxan as an electron-transfer catalyst.[1,2]

On the other hand, using hindered phenols (*e.g.*, 2,4,6-triphenylphenol) as electron-transfer catalysts, the two-phase dehydrogenation of 1,2-disubstituted hydrazines in an organic solvent by means of an aqueous solution of potassium hexacyanoferrate(III) has been reported by Dimroth and Tüncher.[3]

The presence of phenolic hydroxyl groups on the surface of carbon black has been supported in the literature.[4,5] It is well known that phenolic hydroxyl groups are easily oxidized to quinonic oxygen groups or phenoxyl radicals (so-called "quinone radicals").[5,6]

In the present paper, we wish to report that, as well as hindered phenols, phenolic hydroxyl groups on the surface of carbon black act as electron-transfer catalysts in the two-phase dehydrogenation of hydrazo nitriles by means of an aqueous solution of $K_3[Fe(CN)_6]$:



Experimental

Materials and Reagents. The carbon black used was of two types: furnace black and color-channel black. The furnace blacks, Philblack O (BET specific surface area; 79.6 $m^2 g^{-1}$) and Philblack I (116.8 $m^2 g^{-1}$), were dried *in vacuo* after Soxhlet extraction with benzene to remove the resinous substances present on the surface. The color-channel blacks, Carbolac 1 (839.2 $m^2 g^{-1}$), FW 200 (460 $m^2 g^{-1}$), and Neospectra II (906 $m^2 g^{-1}$), were dried *in vacuo* without extraction, because it was known that channel blacks contain no resinous substances.

The hydrazo nitriles (**1**, **2**, **3**, **4**, and **5**) were prepared by the reaction of the corresponding ketones with sodium cyanide and hydrazine sulfate according to the method of Overberger *et al.*[7–9] All of these compounds were identified by means of mp, IR, NMR, and elemental analysis.

The benzene and dichloromethane used as solvents were purified and distilled by a general method.

Guaranteed-reagent-grade $K_3[Fe(CN)_6]$ from the Tokyo Kasei Kogyo Co., Ltd., was used without further purification.

Procedure of Two-phase Dehydrogenation. A typical example was as follows.[10] A solution of 2.0 g (6.0 mmol) of $K_3[Fe(CN)_6]$ in 10.0 cm^3 of aqueous potassium hydroxide (2.0 mol dm^3) was added to a mixture of 0.5 g of carbon black and 0.5 g (2.0 mmol) of **1** in 10.0 cm^3 of benzene. The reaction mixture was then shaken at 40 °C for 6 h. After the reaction, the carbon black was filtered with suction and washed with benzene. The benzene layer was separated from the filtrate, washed with 5 times with water, and dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol. The yield of the corresponding azo nitriles was determined by measuring the absorbance of the adsorption maximum at 350 nm (95% ethanol) due to the azo nitriles.

Treatment of Carbon Black with Sodium Tetrahydroborate. The treatment of carbon black with $NaBH_4$ was carried out according to the method of Studebaker.[11] For instance, 2.0 g of carbon black was stirred into 50 cm^3 of an aqueous solution containing 0.2 g of $NaBH_4$ and 0.6 g of sodium hydroxide under a nitrogen atmosphere. After reacting for 2 h at room temperature, the solution was made acidic with dilute sulfuric acid. The carbon black was subsequently filtered, washed with degassed hot water until the filtrate was neutral, and then dried *in vacuo.*

Treatment of Carbon Black with Hydrogen Peroxide. Into a mixture of 5.0 cm^3 of concentrated sulfuric acid, 50 cm^3 of glacial acetic acid, and 2.0 g of carbon black, 50 cm^3 of H_2O_2 (*ca.* 35%) was stirred drop by drop.[12,13] After the reaction for 24 h at room temperature, the carbon black was filtered, washed with water until the filtrate was neutral, and then dried *in vacuo.*

Treatment of Carbon Black with Benzoyl Peroxide. The treatment of carbon black with benzoyl peroxide (BPO) was carried out according to the method previously reported.[14] Two grams of BPO were added to a mixture of 2.0 g of carbon black and 150 cm^3 of carbon tetrachloride. In order to accelerate the oxidation of the surface of carbon black, oxygen gas was gradually bubbled into the mixture during the reaction. After a reaction for 50 h at 45 °C with stirring, the carbon black was separated by centrifugation at 10^4 rpm for 2 h. Subsequently, it was extracted with carbon tetrachloride, using a Soxhlet apparatus, for 100 h and then dried *in vacuo.*

Treatment of Carbon Black with Diazomethane. The treatment of carbon black with CH_2N_2 was carried out by a method similar to that described by Studebaker *et al.*[15] A typical example was as follows. Two grams of carbon black were stirred into 150 cm^3 of a diethyl ether solution of CH_2N_2 (*ca.* 2 wt%) at 0 °C. After a reaction for 48 h, the carbon black was filtered, washed with an absolute diethyl ether, and then dried *in vacuo.*

Results and Discussion

*Two-phase Dehydrogenation of **1** in the Presence of Carbon Black.* The two-phase dehydrogenation of **1** by an aqueous solution of $K_3[Fe(CN)_6]$ was carried out; the results are shown in Table 1. When the reaction was carried out in the absence of carbon black, 90.5% of the **1** remained unchanged (Run No. 1). Carbon black itself had no ability to dehydrogenate **1** in the absence of $K_3[Fe(CN)_6]$ (Run No. 2). However, in the presence of carbon black, **1** was dehydrogenated to the corresponding azo nitrile, 1,1′-azobis(cyclohexane-1-carbonitrile) in a good yield. Therefore, the results suggest that carbon black has a catalytic activity in the two-phase dehydrogenation of **1**.

Table 1. Two-phase dehydrogenation of **1** in the presence of carbon black

Run No.	Carbon black	(g)	$K_3[Fe(CN)_6]$ soln (cm^3)	**1** (mmol)	Azo nitrile yield %$^{a)}$
1	—	—	10	2.0	9.5
2	Carbolac 1	0.50	—	2.0	0.5
3	Carbolac 1	0.10	10	2.0	46.9
4	Carbolac 1	0.50	10	2.0	99.0$^{b)}$
5	Philblack O	0.50	10	2.0	24.5
6	Philblack O	1.00	10	2.0	49.6
7	Philblack O	1.00	10	2.0	64.5

a) A 10 cm^3 portion of benzene was used as the solvent; 40 °C, 6 h. b) Isolated yield after recrystallization: 90%.

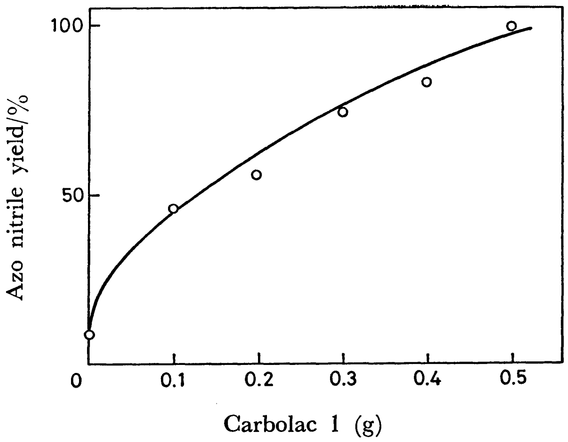


Fig. 1. The effect of the amount of Carbolac 1 on the two-phase dehydrogenation of **1**.
1 2.0 mmol, benzene 10.0 cm^3, $K_3[Fe(CN)_6]$ aq soln 10.0 cm^3; 40 °C, 6 h.

Using 2.0 mmol of **1** and various amounts of Carbolac 1, the effect of the amount of carbon black on the reaction was investigated. The results obtained are shown in Fig. 1. As is shown in Fig. 1, the reaction was accelerated with an increase in the amount of Carbolac 1.

From the above results, it may be concluded that carbon black acts as a catalyst in the two-phase dehydrogenation of **1** by an aqueous solution of $K_3[Fe(CN)_6]$.

Two-phase Dehydrogenation of Hydrazo Nitriles Using Carbolac 1 as a Catalyst. The results of the two-phase dehydrogenation of **2**, **3**, **4**, and **5** are shown in Table 2. It is found that the two-phase dehydrogenation of **2** to the corresponding azo nitrile is catalyzed by Carbolac 1 as well as that of **1**. Although **3**, **4**, and **5** were considerably oxidized to the corresponding azo nitriles by an aqueous solution of $K_3[Fe(CN)_6]$, even in the absence of carbon black, it became apparent that the two-phase dehydrogenation of these hydrazo nitriles was accelerated by Carbolac 1 and that the corresponding azo nitriles were obtained in good yields.

The azo nitriles obtained from the reaction were identified by the measurement of the mp and the IR and NMR spectra; no by-products were observed to be formed.

The preparation of azo nitriles is usually carried out by the oxidation of the corresponding hydrazo nitriles with Br_2 or nitrous acid.[7] In contrast to such oxidation, the two-phase dehydrogenation of hydrazo nitriles by an aqueous solution of $K_3[Fe(CN)_6]$, using carbon black as a catalyst, is a effective and convenient method for the preparation of azo nitriles, which are useful radical-chain initiators.

Ability of Various Kinds of Carbon Black as a Catalyst for the Two-phase Dehydrogenation. Using various kinds of carbon black, the effect of functional groups on the surface of carbon black on the two-phase dehydrogenation of **1** was studied. The results are shown in Table 3. The carbon black used was of two types:

Table 2. Two-phase dehydrogenation of hydrazo nitriles by the use of Carbolac 1 as the catalyst

Hydrazo nitrile	Carbolac 1 (g)	Temp/°C	Azo nitriles		
			Yield/%[c]	Mp θ_m/°C	Lit Mp θ_m/°C
1[a]	—	40	9.5	113—114	114—115[7]
	0.5		99.0		
2[a]	—	40	18.1	83.5—84	83—84[8]
	0.5		99.5		
3[b]	—	40	80.0	102—103.5	103—104[7]
	0.5		99.5		
4[a]	—	30	68.6	73—76	74—76[7]
	0.5		100		
5[a]	—	30	50.2	81.5—83	82—84[9]
	0.5		99.0		

a) A 10 cm^3 portion of benzene was used as the solvent. b) A 10 cm^3 portion of dichloromethane was used as the solvent. c) Reaction time; 6 h.

Table 3. Two-phase dehydrogenation of **1** by the use of various kinds of carbon black as catalysts (**1** 2.0 mmol, benzene 10.0 cm^3, $K_3[Fe(CN)_6]$ aq soln 10.0 cm^3; 40 °C, 6 h.)

Carbon black	(g)	Phenolic hydroxyl groups(mequiv. g^{-1})	Quinonic oxygen groups(mequiv. g^{-1})	Azo nitrile yield/%
FW 200[a]	0.1	0.10	1.42	45.4
Carbolac 1[a]	0.1	0.16	1.14	46.9
Neospectra II[a]	0.1	0.24	0.92	54.5
Philblack O[b]	0.5	0.02	0.18	24.5
Philblack I[b]	0.5	0.05	0.23	28.4

a) Color-channel black. b) Furnace black.

color-channel black and furnace black. The content of the phenolic hydroxyl groups was determined using 2,2-diphenyl-1-picrylhydrazyl according to the method previously reported by us.[13] The analysis of the quinonic oxygen groups was carried out by the determination of the hydrogen uptake from a $NaBH_4$ solution according to the method of Studebaker.[11] In general, color-channel blacks contain a number of phenolic hydroxyl and quinonic oxygen groups in comparison with furnace blacks.

From the results shown in Table 3, the ability of channel blacks as catalysts for the two-phase dehydrogenation was found to be larger than that of furnace blacks. Moreover, the increasing content of phenolic hydroxyl groups tends to increase the catalytic activity of channel blacks. In addition, Dimroth *et al.* have reported that hindered phenols act as electron-transfer catalysts in the two-phase dehydrogenation of 1,2-disubstituted hydrazines.[3]

Accordingly, it is suggested that phenolic hydroxyl groups on the surface of carbon black play an important role as catalysts in the two-phase dehydrogenation.

Two-phase Dehydrogenation Catalyzed by Various Treated Carbon Blacks. In order to clarify the reaction sites on the surface of carbon black, the two-phase dehydrogenation of **1** catalyzed by carbon black treated with $NaBH_4$, H_2O_2, or BPO was compared with that catalyzed by the untreated one. The results are shown in Table 4.

Table 4. Two-phase dehydrogenation of **1** by the use of treated Philblack O as the catalyst (Treated carbon black 1.00 g, **1** 2.0 mmol, benzene 10.0 cm^3, $K_3[Fe(CN)_6]$aq soln 10.0 cm^3; 40°C, 6h.)

Philblack O	$K_3[Fe(CN)_6]$ soln (cm^3)	Azo nitrile yield/%
Untreated	—	0.6
	10	49.6
Treated with $NaBH_4$	—	0.5
	10	63.0
Treated with H_2O_2	—	10.0
	10	100
Treated with BPO	—	25.8
	10	100
Treated with BPO and then $NaBH_4$	—	1.5
	10	99.5

It has been reported that quinonic oxygen groups on the surface of carbon black are reduced by $NaBH_4$ to give phenolic hydroxyl groups.[11] The content of phenolic hydroxyl groups on the surface of such treated Philblack O is 0.07 mequiv. g^{-1}.

The results shown in Table 4 indicate that the yield of the 1,1′-azobis(cyclohexane-1-carbonitrile) is increased by the use of $NaBH_4$-treated Philblack O as a catalyst. The result suggests that the catalytic activity of carbon black in the two-phase dehydrogenation is responsible for the phenolic hydroxyl groups on the surface.

Furthermore, the catalytic activity of carbon black in the two-phase dehydrogenation was extremely enhanced by the treatment with H_2O_2 and BPO. It is interesting to note that both H_2O_2- and BPO-treated Philblack O have the ability to oxidize **1** even in the absence of an aqueous solution of $K_3[Fe(CN)_6]$.

It has been confirmed that the pH of an aqueous slurry of furnace black changes from the basic to the acidic side and that the content of phenolic hydroxyl groups is increased by the treatment with H_2O_2.[12,13] The content of phenolic hydroxyl groups of such treated Philblack O is 0.11 mequiv. g^{-1}. Moreover, the surface of carbon black is also oxidized with H_2O_2 to give quinone radicals.

On the other hand, it has previously been reported that quinonic oxygen groups and phenoxyl radicals were easily introduced to the carbon black surface by treatment with BPO in the presence of oxygen.[14,16] In addition, it is well known that the number of unpaired electrons present on the surface of carbon black increases about 10 times when the carbon black is treated with BPO.[17] Therefore, BPO-treated Philblack O has a number of phenoxyl radicals, because it is believed that a large portion of the unpaired electrons on the surface of carbon black exists in quinone-radical forms.[6,14,16]

On the basis of the foregoing facts, it is considered that the high catalytic activity of both H_2O_2- and BPO-treated Philblack O may be due to the phenoxyl radicals formed on the surface of carbon black by the treatment. That is, phenoxyl radicals present on the surface of H_2O_2- and BPO-treated carbon black oxidize the hydrazo nitriles, by which means phenolic hydroxyl groups with the catalytic activity in the two-phase dehydrogenation are newly formed.

To confirm this, the catalytic activity of carbon black treated with BPO and then $NaBH_4$ was investigated. As is shown in Table 4, although BPO–$NaBH_4$-treated carbon black lost the ability to oxidize **1** in the absence of $K_3[Fe(CN)_6]$, the treated carbon black kept a high catalytic activity in the two-phase dehydrogenation. From these results, it is concluded that both phenolic hydroxyl groups and phenoxyl radicals on the surface catalyze the two-phase dehydrogenation.

On the other hand, using CH_2N_2-treated carbon black, the two-phase dehydrogenation of **1** was also studied; the results are shown in Table 5.

It is well known that phenolic hydroxyl groups on the surface are blocked by methylation with CH_2N_2.[14] As is shown in Table 5, the catalytic activity of the carbon black completely disappeared upon the treatment with CH_2N_2. The results also clearly show the role of phenolic hydroxyl groups as a catalyst in the two-phase dehydrogenation.

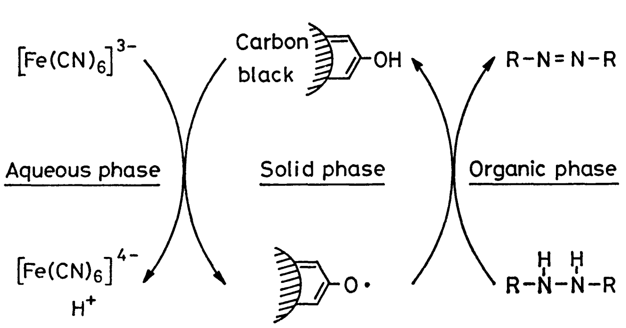
Table 5. Two-phase dehydrogenation of **1** by the use of CH_2N_2-treated carbon black as the catalyst (**1** 2.0 mmol, benzene 10.0 cm^3, $K_3[Fe(CN_6]$aq soln 10.0 cm^3; 40 °C, 6 h.)

Carbon black	(g)	Azo nitrile yield/%
CH_2N_2-treated Philblack O	1.00	0.7(49.6)[a]
CH_2N_2-treated Carbolac 1	0.50	1.0(99.0)[a]

a) The values in parentheses indicate the results in the presence of untreated carbon black.

Reaction Scheme of the Two-phase Dehydrogenation Catalyzed by Carbon Black. As has been mentioned above, it becomes apparent that the phenolic hydroxyl groups on the surface play an important role in the two-phase dehydrogenation. On the other hand, it is well known that phenolic hydroxyl groups on the surface are easily oxidized to quinonic oxygen groups or phenoxyl radicals("quinone radicals").[5,6,18] The phenoxyl radical formed on the surface will be stabilized by polycondensed aromatic rings of carbon black[13,16] and will have the ability to oxidize some compounds as well as 2,4,6-trisubstituted phenoxyl radicals.[3]

Therefore, the reaction scheme of the two-phase dehydrogenation using carbon black as a catalyst was considered to be as follows:



In the aqueous phase, the phenolic hydroxyl groups on the surface of carbon black will be oxidized by an aqueous solution of $K_3[Fe(CN)_6]$ to give phenoxyl radicals, and then the phenoxyl radicals will be transferred into the organic phase, where they will abstract hydrogen atoms from the hydrazo nitriles to give the corresponding azo nitriles and phenolic hydroxyl groups regenerated. That is, during the reaction, phenolic hydroxyl groups on the surface of carbon black are recycled and the carbon black mediates the electron transfer(*i.e.*, redox reaction) between aqueous and organic phases. For example, in the case of Run No. 4 in Table 1, the carbon black was recycled *ca.* 45 times.

In conclusion, it is considered that carbon black acts as an electron-transfer catalyst in the two-phase dehydrogenation.

Two-phase Dehydrogenation of 1,2-Disubstituted Hydrazines by an Aqueous Solution of $K_3[Fe(CN)_6]$ *Using Carbon Black as a Catalyst.* The two-phase dehydrogenation of 1,2-disubstituted hydrazines, such as hydrazobenzene and *N*-phenyl-*N'*-triphenylmethylhydrazine, was also carried out. However, the effect of carbon black as a catalyst could not be confirmed, because these hydrazines were easily dehydrogenated to the corresponding azo compounds by the use of an aqueous solution of $K_3[Fe(CN)_6]$, even in the absence of carbon black.

In addition, the two-phase dehydrogenation of 9,10-dihydroanthracene and 1,2-diphenylethane by an aqueous solution of $K_3[Fe(CN)_6]$, using carbon black as a catalyst, was investigated at 40—90 °C. The dehydrogenation of these compounds was unsuccessful under these conditions, and the starting material was recovered unchanged.

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