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DEHYDROGENATION OF HYDRAZOBISCYCLOHEXANENITRILE AND HYDRAZOBISISOBUTYRONITRILE BY POTASSIUM FERRICYANIDE IN THE PRESENCE OF CARBON BLACK

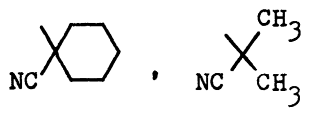
Norio TSUBOKAWA and Naoki TAKEDA
Faculty of Engineering, Niigata University, 2-8050 Ikarashi,
Niigata 950-21

In the presence of carbon black, the two-phase dehydrogenation of hydrazobiscyclohexanenitrile and hydrazobisisobutyronitrile in organic solvent by an aqueous solution of potassium ferricyanide gave the corresponding azo-compound in a good yield. It became apparent that the two-phase dehydrogenation of the hydrazines was catalyzed by phenolic hydroxyl groups on the carbon black surface.

By use of hindered phenols such as 2,4,6-tris(4-t-butylphenyl)phenol as a catalyst, the two-phase dehydrogenation of 1,2-substituted hydrazines in organic solvent by an aqueous solution of potassium ferricyanide has been reported by K. Dimroth et al. (1). On the other hand, the presence of phenolic hydroxyl groups on the surface of carbon black has been supported in the literatures (2,3). In this communication, we wish to report that as well as the hindered phenols, the phenolic hydroxyl groups on the carbon black surface catalyze the two-phase dehydrogenation of 1,2-substituted hydrazines such as hydrazobiscyclohexanenitrile (<u>I</u>) and hydrazobisisobutyronitrile (<u>II</u>).

$$\mathrm{R-\overset{H}{N}-\overset{H}{N}-R} \xrightarrow[\text{Carbon black}]{K_3Fe(CN)_6/KOH} \mathrm{R-N=N-R}$$

R=



<u>I</u> <u>II</u>

Carbon blacks used were Philblack O (HAF, Specific surface area; 79.6 m^2/g) and Carbolac 1 (HCC, 839.2 m^2/g) dried at 110°C in vacuo. To remove the resinous substances present on the surface, Philblack O was extracted with benzene by use of Soxhlet apparatus. The content of phenolic hydroxyl groups on the surface of Philblack O and Carbolac 1 is 0.02 meq/g and 0.17 meq/g, respectively (4).

In a sealed tube, I (2.0 mmol) was dissolved in benzene (10 ml) and shaken with carbon black (0.1-1.0g) and a saturated solution of potassium ferricyanide (10 ml) in 2N aqueous potassium hydroxide. The reaction was carried out at 40°C. After the reaction, carbon black was removed by filtration. The benzene layer was separated, washed 3 times with water and dried. Benzene was removed in vacuo and the yield of the corresponding azo-compound was determined by uv spectroscopic method.

Table 1. Two-phase dehydrogenation of I in benzene by aqueous solution of $K_3Fe(CN)_6$ in the presence of carbon black

Run	Carbon black	(g)	$K_3Fe(CN)_6$ aq. soln. (ml)	I (mmol)	Azo-compound 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

a: The reaction was carried out for 6 hr at 40°C.

b: Isolated yield after recrystallization, 90.0%.

The results of the dehydrogenation of I are shown in Table 1. When the reaction was carried out in the absence of carbon black, 90.5% of I remained unchanged. Carbon black scarcely reacted with I in the absence of potassium ferricyanide. However, in the presence of carbon black, especially in the presence of Carbolac 1, I was dehydrogenated to the corresponding azo-compound in a good yield. The yield of the azo-compound in the presence of Carbolac 1 was higher than that of Philblack O, in which the effect of the phenolic hydroxyl groups on the surface as a catalyst was suggested.

In addition, the results of the dehydrogenation of II are also shown in Table 2. Although II was dehydrogenated in the absence of carbon black, the dehydrogenation was also accelerated by carbon black.

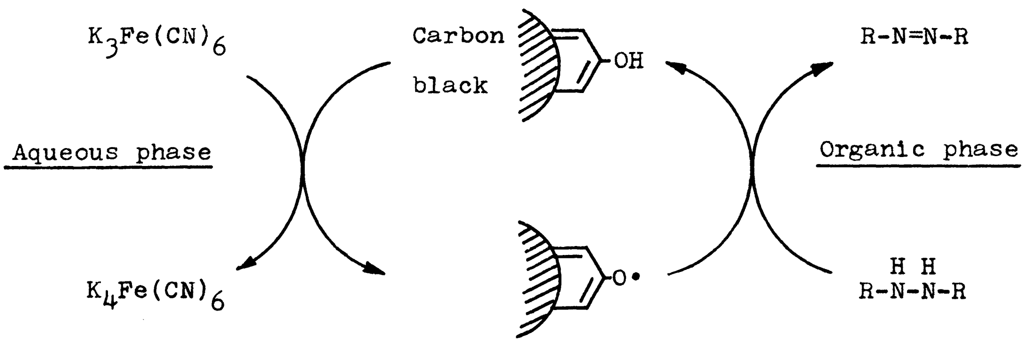
From these results, it was found that carbon black catalyzes the two-phase

Table 2. Two-phase dehydrogenation of II in dichloromethane by aqueous solution of $K_3Fe(CN)_6$ in the presence of carbon black

Run	Carbon black	(g)	$K_3Fe(CN)_6$ aq. soln. (ml)	II[a] (mmol)	Azo-compound yield (%)[b]
7	-	-	10	2.0	80.0
8	Philblack O	1.00	10	2.0	94.2
9	Carbolac 1	0.50	10	2.0	99.5

a: Ten ml of dichloromethane was used as solvent.

b: The reaction was carried out for 6 hr at 40 °C.



Scheme 1.

dehydrogenation of the hydrazines. The reaction mechanism was considered as follows (Scheme 1). In the aqueous phase, the phenolic hydroxyl groups on the carbon black surface will be oxidized by potassium ferricyanide to give phenoxy radicals (5) and then the carbon black having phenoxy radicals will be transfered into the organic phase containing the hydrazines. In the organic phase, the phenoxy radicals will abstract hydrogen atoms of the hydrazines to give the corresponding azo-compound whereby phenolic hydroxyl groups will be regenerated.

In order to ensure the above mechanism, by use of hydrogen peroxide (H_2O_2)-treated carbon black and sodium borohydride ($NaBH_4$)-treated carbon black the dehydrogenation of I was compared with that of untreated one. The results are shown in Table 3.

It has been well known that quinonic oxygen groups present on the surface of carbon black are reduced by $NaBH_4$ to give phenolic hydroxyl groups (6). On the other hand, it has been reported that the content of phenolic hydroxyl groups on the surface is increased by treatment with H_2O_2 (4,7).

Table 3. Two-phase dehydrogenation of I by $K_3Fe(CN)_6$ in the presence of treated carbon black

Run	Carbon black	(g)	$K_3Fe(CN)_6$ aq. soln. (ml)	I (mmol)	Azo-compound yield (%)[a]
10	H_2O_2-treated Philblack O[b]	1.0	10	2.0	100 (49.6)
11	$NaBH_4$-treated Philblack O[c]	1.0	10	2.0	63.0 (49.6)
12	$NaBH_4$-treated Carbolac 1[d]	0.1	10	2.0	66.0 (46.9)

a: Under the same condition with the case of Table 1. The values in parentheses indicate the results in the presence of untreated carbon black. The content of phenolic hydroxyl groups (4,6); b: 0.11 meq/g, c: 0.07 meq/g, d: 0.28 meq/g.

The results shown in Table 3 indicate that in the presence of the treated-carbon black the yield of the azo-compound increases with an increase in the content of the phenolic hydroxyl groups on the surface. In other words, the catalytic activity of the carbon black was enhanced by the treatment with H_2O_2 and $NaBH_4$.

Accordingly, it was concluded that the phenolic hydroxyl groups catalyze the two-phase dehydrogenation of the hydrazines by potassium ferricyanide. Further application to dehydrogenate activated $-CH_2-CH_2-$ group is now under investigation.

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