Tetrahedron Letters No. 37, pp 3541 - 3542.
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0040-4039/79/0908-3541$02.00/0

THE REACTION OF o-PHENYLENEDIAMINE AND SOME AROMATIC AMINES WITH SUPEROXIDE ANION RADICAL AND MOLECULAR OXYGEN

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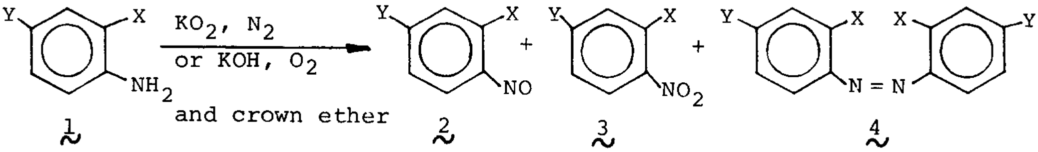
The superoxide anion has been suggested as a probably intermediate in several oxidation processes.[1] It can act as a base, a nucleophile or an oxidant or reductant in redox reactions.[2] Coordinated to different metals it forms superoxo complexes, which were assumed as the primary products of reactions between metal complexes and dioxygen and as the key intermediate in the case of some oxygenases[3] and dismutase.[4]

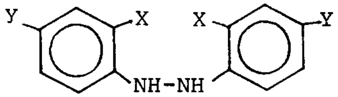
In copper(I) chloride catalyzed oxygenations of aromatic amines to azobenzenes[5] and o-phenylenediamine to cis,cis-mucononitrile[6] coordinated superoxide anion may be involved and in connection to that we wanted to see what course the reactions take when "naked" O_2^- reacts with these compounds.

In a typical experiment 2.84 g (40 mmol) KO_2 and 1.06 g (4 mmol) 18-crown-6 ether were suspended in 40 ml dry benzene and stirred with 1.08 g (10 mmol) o-phenylenediamine or 20 mmol aromatic amine under nitrogen for 5 hr. The mixture was poured on 40 ml water, the organic part separated and the water extracted with an other 40 ml benzene. The joined extracts were concentrated and separated by TLC (silica gel, CH_2Cl_2). The results we obtained according to the reaction (1) are summarized in the Table.



(1)

	X	Y
a)	X = NH_2,	Y = H
b)	H	H
c)	CH_3	H
d)	H	CH_3
e)	H	OMe



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It is noteworthy that no cis,cis-mucononitrile was formed under our conditions. KO_2 oxidizes o-phenylenediamine (**1a**) however to **2a**, **3a** and **4a** in a constant molar ratio whatever excess of KO_2 was applied and the starting **1a**

Table

Starting amines[a] [mmol]	KO_2 [mmol]	Crown ether [mmol]	Time [hr]	Products (yield) [%][b]
1b (2.6)	5.2	0.5	2	4b (82)
5b (2.0)	5.0	0.5	2	4b (~100)
1c (2.0)	5.0	0.5	4	4c (34)
1d (2.0)	5.0	0.5	4	4d (42)
1e (2.5)	5.0	0.5	4	4e (84)
1a (10)	40	4.0	10	2a (38); 3a (28); 4a (26)
1a (2.0)	20	1.0	10	2a (36); 3a (28); 4a (26)
1a (5.0)	20[c]	2.0	6	2a (10); 3a (8); 4a (8)
1a[d] (5.0)	20[c]	-	40	2a (12); 3a (9); 4a (8)
1b (2.0)	5.0[c]	0.5	15	4b (65)
5b (2.0)	5.0[c]	0.5	2	4b (~100)
1c (2.0)	5.0[c]	0.5	15	4c (38)
1d (2.0)	5.0[c]	0.5	15	4d (42)
1e (2.0)	5.0[c]	0.5	8	4e (44)

a) reactions were run at 25°; b) all compounds had the expected analytical and spectroscopic properties known from the literature; c) KOH instead of KO_2; d) in 50 % MeOH

was totally consumed. This suggests the parallel formation of the products 2a, 3a and 4a. Surprisingly the oxidation of 1a by molecular oxygen in benzene catalyzed by "naked" OH^-, generated from KOH and 18-crown-6 ether, yielded the same products in identical molar ratios but in a much slower reaction. Similar results were obtained in base-catalyzed oxygenation of 1a in 50% methanol.[7]

1b and 5b were oxidized almost quantitatively to 4b indicating that 5b may be a coupled intermediate for the formation of 4b following hydrogen abstraction by O_2^- or by OH^- and O_2. The ortho and para substituted anilines 1c, 1d and 1e gave the corresponding azobenzenes 4c, 4d and 4e but in much lower yields.

Acknowledgement: We are grateful to Prof.L.Markó for support throughout this work.

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(Received in UK 3 July 1979)