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Modifying Effect of Selenium on Catalytic Reactivity of Transition Metals

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Sodium selenite increased the catalytic reactivity of the metal salts ($MoCl_5$, $FeCl_2$, $SnCl_2$, $HgCl_2$, $CuCl_2$, $PbCl_2$, and $AsCl_3$) and decreased that of the metal salts ($NaAuCl_4$, AgCl, $BiCl_3$, $CoCl_2$, $NiCl_2$, $PdCl_2$, and Na_2PtCl_6) in the reduction of nitrobenzene to N-phenylhydroxylamine and/or aniline with sodium borohydride in water.

Modifying effects of selenium on the toxicities of a number of heavy metals are of current interest in the field of selenium biology. There have been many reports on the toxicological effects based on the interaction between metals and selenium.[1] For example, simultaneous administration of either $HgCl_2$ or $CdCl_2$ and sodium selenite (Na_2SeO_3) mutually masks the individual toxicities.[2] This detoxification is ascribed to the formation of metal-selenium complexes.[3] In the field of organic chemistry, the interaction between selenium and metal has not been clarified. Here we report that Na_2SeO_3 affects the catalytic reactivity of the transition metal salts during the reduction of nitrobenzene with sodium borohydride ($NaBH_4$).

Typically, the reaction was carried out as follows. Nitrobenzene (10 mmol) was added to a mixture of 1 mol% Na_2SeO_3, 2 mol% $FeCl_2 \cdot 4H_2O$, and $NaBH_4$ (50 mmol) in water (50 ml). The mixture was stirred for 16 h at 37 °C. After a black solid was removed by filtration, the ether extract from the filtrate was analyzed by HPLC.

The results are summarized in Table 1. Na_2SeO_3 increased the nitrobenzene

Table 1. Modifying effect of sodium selenite

$$PhNO_2 \xrightarrow[NaBH_4,\ H_2O]{\text{Metal chloride, } Na_2SeO_3} PhNHOH + PhNH_2$$

Entry	Metal chloride	Na_2SeO_3 a)	Reaction time/h	Recovered $PhNO_2$/%	Products/%	
					PhNHOH	$PhNH_2$
1	-	+	16	98	1	1
2a	$MoCl_5$	+	1	0	0	100
b		-	1	92	4	1
3a	$FeCl_2 \cdot 4H_2O$	+	16	0	0	100
b		-	16	91	2	3
4a	$SnCl_2 \cdot 2H_2O$	+	1	0	85	0
b		-	1	91	5	1
5a	$HgCl_2$	+	16	0	93	0
b		-	16	83	13	0
6a	$CuCl_2 \cdot 2H_2O$	+	1	0	91	2
b		-	1	45	0	55
7a	$PbCl_2$	+	1	46	22	0
b		-	1	97	2	0
8a	$AsCl_3$	+	16	77	6	14
b		-	16	98	1	0
9a	$NaAuCl_4 \cdot 2H_2O$	+	1	63	35	0
b		-	1	0	69	24
10a	AgCl	+	16	49	43	0
b		-	16	1	32	60
11a	$BiCl_3$	+	1	77	20	1
b		-	1	40	47	0
12a	$CoCl_2 \cdot 6H_2O$	+	0.5	7	52b)	40
b		-	0.5	0	0	100
13a	$NiCl_2 \cdot 6H_2O$	+	0.5	0	61b)	36
b		-	0.5	0	0	99
14a	$PdCl_2$	+	1	0	94	0
b		-	1	0	1	99
15a	$Na_2PtCl_6 \cdot 4H_2O$	+	0.5	1	96	0
b		-	0.5	1	4	93
16a	$CdCl_2 \cdot 1/2H_2O$	+	16	98	0	0
b		-	16	99	0	0
17	pptc)		16	7	84	0
18	$CuCl_2 \cdot 2H_2O$	Selenided)	1	0	94	0

a) +:present, -:absent. b) After 1 h, PhNHOH was not detected by TLC and $PhNH_2$ was the main product. c) The precipitate (ca. 38 mg) produced in the experiment (entry 5a) was used as a catalyst. d) In place of Na_2SeO_3, the selenide (0.1 mmol) prepared by the method described in ref. 6 was used as the selenium source.

consumption in the reaction catalyzed by the metal and metalloid salts ($MoCl_5$, $FeCl_2$, $SnCl_2$, $HgCl_2$, $CuCl_2$, $PbCl_2$, and $AsCl_3$) (entries 2-8). Na_2SeO_3 alone scarcely catalyzed the reduction of nitrobenzene under the conditions used (entry 1).⁴⁾ It is noteworthy that the catalytic reaction with $CuCl_2$-Na_2SeO_3 (entry 6a) gives N-phenylhydroxylamine (PhNHOH), the partial reduction product to aniline. It shows that Na_2SeO_3 inhibits the reduction of PhNHOH to aniline, which is produced in the blank experiment (entry 6b). On the other hand, Na_2SeO_3 decreased the reduction rate of nitrobenzene and/or PhNHOH in the reaction catalyzed by the metal salts ($NaAuCl_4$, AgCl, $BiCl_3$, $CoCl_2$, $NiCl_2$, $PdCl_2$, and Na_2PtCl_6) (entries 9-15). In particular, when $PdCl_2$ or Na_2PtCl_6 was used, the product was changed completely from aniline to PhNHOH (entries 14 and 15). In the case of $CdCl_2$, no reaction occurred with or without Na_2SeO_3 (entry 16).

A black, gray, or brown precipitate appeared in all the runs performed with the metal salt-Na_2SeO_3 and the metal salt catalysts. In order to examine the participation of the precipitate in the former runs, it was isolated after 1 h from the reaction mixture using $HgCl_2$-Na_2SeO_3 (entry 5a). When the precipitate, in place of $HgCl_2$-Na_2SeO_3, was reused as a catalyst under the same reduction conditions, its behaviour was similar to that of $HgCl_2$-Na_2SeO_3, although minor deterioration in catalyst performance was observed (entry 17). This finding indicates that the precipitates (presumably metal-selenium complexes⁵⁾) play a crucial role in the reduction catalyzed by metal salt-Na_2SeO_3.

It is known that Na_2SeO_3 is reduced by $NaBH_4$ in water to give the selenides (NaHSe and Na_2Se) in situ.⁶⁾ The catalytic use of the selenides with $CuCl_2$ led to a product distribution similar to that obtained in the reduction catalyzed by $CuCl_2$-Na_2SeO_3 (entry 18). From this result, we presume that Na_2SeO_3 interacts with each metal in the form of selenide.

In conclusion, it was found that Na_2SeO_3 increased or decreased the catalytic reactivity of the metal salts in the reduction of nitrobenzene with $NaBH_4$. The organic reaction with the metal salt-Na_2SeO_3-$NaBH_4$ system is without precedent, and the extension to various substrates is now under investigation.

References

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