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Indirect Electrolytic Reduction of Derivatives of Hydroxylamine

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Several derivatives of hydroxylamine have been reduced by electrolytically generated Ti(III) or Fe(II) in the presence of suitable complexing agents. The preparative use of the indirect reduction was demonstrated and dependence of the rate of the reaction on the structure of the hydroxylamine derivative was investigated by polarography.

The reduction of hydroxylamine to ammonia *via* the radical NH_2. (or NH_3^+) by Ti(III), V(III), Cu(I), and Fe(II) has been the subject of many investigations.[1–9] Among other methods the enhancement of the polarographic waves of Ti(IV),[1] V(IV),[7] and Fe(III)[2] in suitable media has been used to measure the rate of the reaction between the metals in their lower oxidation state and hydroxylamine.

From these investigations, especially through the work of Tomat and Rigo,[5–9] it appears that only the unprotonated hydroxylamine reacts and that hydroxylamine, in certain cases at least, has to form a complex with the metal ion before electron transfer from metal to hydroxylamine takes place.

The formation of the amino radical as an intermediate was shown by a competition between aromatic substrate and metal ion for the radical;[9] aniline derivatives as well as ammonia were formed. It is not yet clear, whether the electron transfer to the amino radical occurs between solvent separated entities or within a complex.

The purpose of the present work is to investigate the reduction of derivatives of hydroxylamine by means of metal ions brought in a suitable oxidation state by electrolytic reduction. The rate of the reduction of different substrates was measured from the enhancement of the polarographic waves of Ti(IV) and Fe(III) by the substrates. As substrates, *N*-mono- and disubstituted hydroxylamines, aliphatic amine oxides, and heteroaromatic *N*-oxides were used.

RESULTS

Polarographic investigation

In alkaline solution hydroxylamine oxidizes the triethanolamine (TEA) complex of Fe(II); the catalytic increase of the polarographic wave of the Fe(III) complex in the presence of hydroxylamine has been used to calculate the rate of the reaction.[2]

The reaction between the Fe-(II)-triethanolamine complex and some substituted hydroxylamines has been investigated similarly. In Table 1 are given the rate constants for the reaction in a medium containing 2×10^{-4} M Fe(III), 4×10^{-2} triethanolamine and 0.1 M sodium hydroxide. The rate constants have been obtained by the method of Koutecky;[10] it is assumed that the reduction of a substituted hydroxylamine molecule requires the oxidation of two Fe(II) and that the amine radical does not abstract a hydrogen atom from the solvent or react in other ways.

In a similar way the reaction between Ti(III) and hydroxylamine derivatives has been investigated in oxalic acid (Table 2) and in EDTA (Table 3).

The reduction involves presumably the reduction of the unprotonated hydroxylamine derivative as it does for the unsubstituted hydroxylamine;[5] pH and the pK of the hydroxylamine derivative are thus important for the reaction. However, also the stability constants of the complexes of the complexing agents (oxalic acid, EDTA, triethanolamine) and of

Table 1. Pseudo first-order rate constants k (l mol^{-1} s^{-1}) of the reaction between electrolytically produced Fe(II) (from 2×10^{-4} M Fe(III)) and hydroxylamine derivatives (1.1×10^{-2} M) in 0.1 M NaOH containing 4×10^{-2} triethanolamine (TEA).

Added hydroxylamine	$-E_{\frac{1}{2}}$(V *vs.* SCE) of Fe-complex	k (l mol^{-1} s^{-1})
None	1.00_8	–
Hydroxylamine	1.01_5	780
N-Methylhydroxylamine	0.99_4	380
N-Ethylhydroxylamine	0.97_5	290
N-Isopropylhydroxylamine	0.97	190
N-*t*-Butylhydroxylamine	0.98_5	220
N-Benzylhydroxylamine	0.95_5	200
N,*N*-Diethylhydroxylamine	0.99	120
N-Hydroxypiperidine	0.98	120
N-Hydroxypyrrolidine	0.99	28
Triethylamine oxide	1.00	39
Pyridine *N*-oxide	1.00	23

Table 2. Pseudo first-order rate constants k (l mol^{-1} s^{-1}) of the reaction between electrolytically generated Ti(III) (from 10^{-3} M Ti(IV)) and derivatives of hydroxylamine (5×10^{-2} M) in 0.2 M oxalic acid; pH = 1.2.

Added hydroxylamine	$-E_{\frac{1}{2}}$(V *vs.* SCE) of Ti-complex	k (l mol^{-1} s^{-1})
None	0.30_5	–
Hydroxylamine	0.31_5	51
N-Methylhydroxylamine	0.32	32
N-Ethylhydroxylamine	0.32_5	13
N-Isopropylhydroxylamine	0.33_5	10
N-*t*-Butylhydroxylamine	0.31	28
N-Benzylhydroxylamine	0.33_5	28
N-Hydroxypyrrolidine	0.33	3.3×10^2
N-Hydroxypiperidine	0.31_5	1.4×10^2
N,*N*-Diethylhydroxylamine	0.32_5	3×10^2
A – OH [a]	0.31	1.6×10^5
Triethylamine *N*-oxide	0.32	123

[a] Concentration of Ti(IV) 5×10^{-5} M and of A – OH 2×10^{-3} M.

Table 3. Pseudo first-order rate constants k (l mol^{-1} s^{-1}) of the reaction between electrolytically generated Ti(III) (from 2×10^{-4} M Ti(IV)) and derivatives of hydroxylamine (10^{-2} M) in an acetate buffer pH 5.5 containing 10^{-3} M EDTA.

Added hydroxylamine	$-E_{\frac{1}{2}}$(*vs.* SCE) of Ti-complex	k (l mol^{-1} s^{-1})
None	0.46_5	–
Hydroxylamine	0.54	2.8×10^2
N-Methylhydroxylamine	0.51_5	6.3×10^2
N-Ethylhydroxylamine	0.49_5	47
N-Isopropylhydroxylamine	0.47_5	9.5
N-*t*-Butylhydroxylamine	0.46_5	1.8×10^2
N-Benzylhydroxylamine	0.48_5	1.3
N-Hydroxypiperidine	0.49_5	5.4×10^4
N-Diethylhydroxylamine	0.45	7.3×10^2
Pyridine *N*-oxide	0.46_5	1.3
Triethylamine *N*-oxide	0.46	78
Acetoxime	0.47_5	15

the hydroxylamines with Ti(III)/Ti(IV) resp. Fe(II)/Fe(III) are probably of importance, and these are not known at present. A discussion of the results in the tables will be deferred until more data are known; only the striking difference between primary and secondary hydroxylamines in the reduction by Fe(II) and Ti(III) should be pointed out.

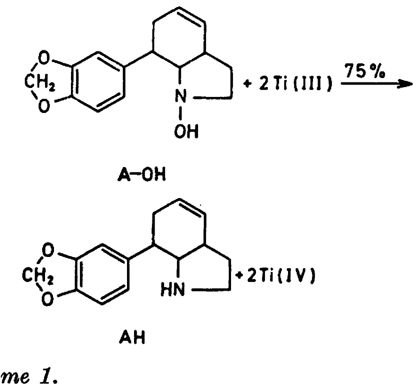
Preparative reduction

Hydroxylamine derivatives may be reduced chemically[11] by, a.o., zinc, iron or tin and acid, and presumably by Ti(III) under suitable conditions, *e.g.* in oxalic acid. Some aliphatic hydroxylamines are reducible electrolytically in slightly acid solution, but the reduction potential is quite near that of the reduction of hydrogen ions.

The reduction by electrolytircally egenerated Ti(III) or Fe(II) has certain advantages; it takes place at a less negative potential where hydrogen ions are not reduced and the low concentration of the metal salts facilitates the work-up compared to the reduction by chemical reagents where at least equivalent amounts of reagents must be used.

The conditions used in Tables 1, 2, and 3 have been chosen to show that reduction may be performed both in acid, nearly neutral, and alkaline solution. This may be of interest if stability or solubility of the substrate requires special considerations with respect to pH. Other conditions than those cited may work; generally, however, the rate decreases as pH decreases.

$$2\mathrm{Ti(IV)} + 2e^- \rightarrow 2\mathrm{Ti(III)}$$



Scheme 1.

The reduction in 0.2 M oxalic acid containing 10^{-2} M of 7-(1,3-benzodioxol-5-yl)-2,3,3a,6,7,7a-hexahydro-1-hydroxy-1*H*-indole (A – OH) may exemplify the reaction shown in Scheme 1. The indirect electrolytic reduction was in this case found to be preferable to chemical reduction.

Under similar conditions *N*-hydroxypiperidine yields 82 % piperidine determined polarographically through the *N*-nitrosamine.

EXPERIMENTAL

For the polarographic investigation a "multipurpose unit 563", AMEL, Milano, was used; a potentiostat from Tage Juul Electronics, Copenhagen, was employed for the preparative reductions.

The primary hydroxylamines were prepared by electrolytic reduction of the corresponding nitrocompounds in hydrochloric acid. The secondary hydroxylamines were gifts from Dr. P. E. Iversen and compound A – OH from Professor K. Torssell.[12]

Reduction of compound A – OH. A suspension of compound A – OH (1 g) in 0.2 M aqueous oxalic acid containing 20 % ethanol and 0.5 g of titanium tetrachloride was reduced at – 0.5 V (SCE), $n = 2$ F/mol. The reduction completed, the concentration of secondary amine (A) was determined by polarography after nitrosation,[13] yield 75 %. An excess of ammonia was added and the catholyte extracted twice with methylene chloride. A white precipitate, partly formed during the reduction, was filtered off, but was discarded, as an IR-spectrum did not indicate the presence of organic matter complexed with the mainly inorganic precipitate.

The methylene chloride was washed with water, dried and evaporated; the residue, 0.8 g, was dissolved in 10 ml of chloroform and dry hydrogenchloride added; on addition of ether the hydrochloride of A crystallized very slowly, m.p. 206 – 207 °C; after 4 days 0.48 g was obtained. (Found: C 64.27; H 6.74; N 4.70; Cl 12.56. Calc. for $C_{15}H_{18}ClNO_2$: C 64.40; H 6.51; N 5.01; Cl 12.67).

Reduction of N*-hydroxypiperidine. N*-Hydroxypiperidine (1 g) was reduced in 0.2 M aqueous oxalic acid containing 0.5 g of titanium tetrachloride, $n = 2$ F/mol. The reduction completed the content of the secondary amine, piperidine, was analyzed by polarography after nitrosation;[13] polarographically determined yield 82 %.

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