$$
\begin{aligned}
-d[Mo_3O_4(H_2O)_9{}^{4+}]/dt &= k_{obsd}\,[Mo_3O_4(H_2O)_9{}^{4+}] \qquad (2)\\
&= \{k_o + k_h[H^+]\}\,[VO_2^+][Mo_3O_4(H_2O)_9{}^{4+}]
\end{aligned}
$$

tercept and slope of Figure 1 were $7.5\times10^{-3}sec^{-1}$ and $4.82\times10^{-3}M^{-1}sec^{-1}$, respectively. Rate equation shows two terms involving $[H^+]$-dependent and -independent rates. The $[H^+]$-independent term indicates substitution of a coordinated water of $Mo_3O_4^{4+}$. This makes bridge bond with OH^- of VO_2^+. The increase in the rate of oxidation with increasing hydrogen-ion concentration implies that the protonation of $Mo_3O_4^{4+}$ produces $Mo_3O_3(OH)^{5+}$ containing the OH^- group which is more strongly coordinated than water. It is not observed that the molybdenum(IV)-hydroxide species were formed by dissociation of proton from a coordinated water under the condition of this experiment.

Ratios of the rate constants for a series of oxidants reduced by two different reductants are often used as a diagnostic criterion for assigning redox reactions as proceeding by outer-sphere mechanisms or inner-sphere mechanisms.[3] Ratios (k_F/k_{Ir}) of the rate constants for the reactions of $Mo_2O_{4(aq)}{}^{2+}$ and $[Mo_2O_4(edta)]^{2-}$ with $[Fe(phen)_3]^{3+}$ and $[IrCl_6]^{2-}$ are 281,[4] while ratios of k/k_{Ir} for VO_2^+ oxidation of $Mo_2O_{4(aq)}{}^{2+}$ and $Mo_3O_{4(aq)}{}^{4+}$ are 6.3 and 3.0, respectively.[5] These ratios are not in agreement with that observed for the outer-sphere reactions of $[Fe(phen)_3]^{3+}$ and $[IrCl_6]^{2-}$ with $[Mo_3O_4(H_2O)_9]^{4+}$.[2] This fact indicates that the aquaoxomolybdenum(IV) trimer reacts rapidly via an inner-sphere mechanism with VO_2^+. This aquaoxomolybdenum(IV) complex allows for complexation by the inner-sphere oxidant. We assume that rate determining step of the reaction(1) is the process which the coordination number of vanadium in aqueous solution is increased from four or five in V(V) to six in V(IV) since redox step accompanying structural change seems energetically prohibitive.[6]

The mechanisms for the oxidation of the aquaoxomolybdenum(IV) trimer by VO_2^+ may be described by the steps (a) and (b).

$$
\left.
\begin{aligned}
&Mo_3O_{4(aq)}{}^{4+} + VO^+_{2(aq)} \xrightarrow{k_1} \underset{(I)}{O_4Mo_3\text{-}OH\text{-}VO(OH)_{(aq)}{}^{5+}}\\
&(I)\ \textit{fast}\ \text{products}
\end{aligned}
\right\}(a)
$$

$$
\left.
\begin{aligned}
&Mo_3O_{4(aq)}{}^{4+} + H^+ \underset{}{\overset{K_h}{\rightleftharpoons}} Mo_3O_3(OH)_{(aq)}{}^{5+}\\
&Mo_3O_3(OH)_{(aq)}{}^{5+} + VO^+_{2(aq)} \xrightarrow{k_2} O_3Mo_3\text{-}OH\text{-}VO^{6+}_{2(aq)}\\
&O_3Mo_3\text{-}OH\text{-}VO^{6+}_{2(aq)} \xrightarrow{fast} \text{products}
\end{aligned}
\right\}(b)
$$

From this equations $k_{obsd} = \{k_1 + K_hk_2[H^+]\}\,[VO_2^+]$, $k_1 = k_o$, and $K_hk_2 = k_h$. These results are consistent with the empirical

From mechanisms (a) and (b) we obtain

$$
-d[Mo_3O_4(H_2O)_9{}^{4+}]/dt = \{k_1 + K_hk_2[H^+]\}\,[VO_2^+]\,[Mo_3O_4(H_2O)_9{}^{4+}] \qquad (3)
$$

rate equation. It is considered that the rate determining step for the reaction is the formation of the bridging complex between two reactants, Mo(IV) and V(V). The bridging ligand of an intermediate is donated by the reducing agent, $[Mo_3O_4(H_2O)_9]^{4+}$, as in the reactions of VO_2^+ with $[Fe(CN)_6]^{4-}$ and chromium(VI) with $[Fe(CN)_6]^{4-}$, $[Fe(bipy)(CN)_4]^{2-}$, and $[Fe(bipy)_2(CN)_2]$.[6,7]

Detailed mechanisms of the reaction should be the subject of further investigations.

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The Reductive N-Benzylation of Alkanolamines using Tetracarbonylhydridoferrate, $HFe(CO)_4^-$, as a Selective Reducing Agent

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The combination of two functionalities of alkanolamines having amino and hydroxyl group makes them versatile intermediates for countless industrial applications: they are of particular interest to the textile, pharmaceutical and household products industries[1]. Secondary alkylalkanolamines are generally prepared by the ring opening of an epoxides with an alkylamines[2]. The addition of imidoosmium reagents to alkenes[3] and methods for the alkylation of primary amines with 2-bromoalcohols[4] are also well established procedures for the preparation of N-alkyl-1, 2-alkanolamines. Cope et al[5] suc-

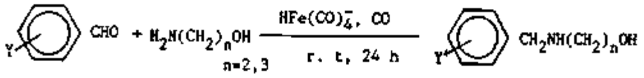
Table 1. The Reductive N-Benzylation of Alkanolamines using HFe(CO$_4^-$[a]

Exp. No.	Benzaldehyde (YPhCHO)	Alkanolamine ($H_2N(CH_2)_nOH$)	Product ($YPhCH_2NH(CH_2)_nOH$	Yield (%)[b]
1	Y; -H	n=2, $H_2N(CH_2)_2OH$	$PhCH_2NH(CH_2)_2OH$	80
2	p-Cl	$H_2N(CH_2)_2OH$	p-$ClPhCH_2NH(CH_2)_2OH$	92
3	o-Cl	$H_2N(CH_2)_2OH$	o-$ClPhCH_2NH(CH_2)_2OH$	67
4	p-OCH_3	$H_2N(CH_2)_2OH$	p-$CH_3OPhCH_2NH(CH_2)_2OH$	74
5	o-OCH_3	$H_2N(CH_2)_2OH$	o-$CH_3OPhCH_2NH(CH_2)_2OH$	70
6	-H	n=3, $H_2N(CH_2)_3OH$	$PhCH_2NH(CH_2)_3OH$	73
7	p-Cl	$H_2N(CH_2)_3OH$	p-$ClPhCH_2NH(CH_2)_3OH$	74
8	Y; o-Cl	$H_2N(CH_2)_3OH$	o-$ClPhCH_2NH(CH_2)_3OH$	60
9	p-OCH3	$H_2N(CH_2)_3OH$	p-$CH_3OPhCH_2NH(CH_2)_3OH$	64
10	o-OCH_3	$H_2N(CH_2)_3OH$	o-$CH_3OPhCH_2NH(CH_2)_3OH$	61

[a] At room temperature for 24 h under carbon monoxide. [b] Isolated yields.

cessfully developed the catalytic reduction of ethanolamine and 2-aminopropanol with various aldehydes and ketones over platinium oxide-platinium catalyst in 1 or 2 atmosphere of hydrogen to give the corresponding 2-alkylalkanolamine. Little attention, however, has been paid to the normal reductive alkylation of alkanolamines using reducing reagents. Most recently, Saavedra[6] reported the reductive alkylation of 2-alkanolamines with carbonyl compounds and sodium borohydride.

We have demonstrated that the tetracarbonylhydridoferrate, HFe(CO)$_4^-$, is effective for the reductive alkylation of amines[7], heterocyclization[8], ester synthesis[9], and the reductive amination of azides[10]. We herein wish to report the reductive N-benzylation of 2- or 3-aminoalkanols with benzaldehyde derivatives using tetracarbonylhydridoferrate as a selective reducing agent. A preliminary report of this work was published elsewhere[11].



Alkanolamines such as ethanolamine and propanolamine reacted with benzaldehyde derivatives in the presence of tetracarbonylhydridoferrate solution at room temperature for 24 h under an atmosphere of carbon monoxide to give the corresponding N-benzylaminolakanol derivatives in good yields. The reaction proceeds smoothly at room temperature with an absorption of carbon monoxide after some induction period and with color change of ethanolamine with benzaldehydes is more reactive thn that of propanolamine with benzaldehydes. Accordingly, the yield of N-benzylaminoethanol is higher than that of N—benzylaminopropanol. The gas absorbed amounts to 1.4—1.8 mol/mol-ferrate, and this amount absorbed affords sufficient yield of products[7].

In the cases of substituted benzaldehydes, such substituents as the chloro and methoxy groups have almost no effect on the formation of N-benzylation when located at the para position, but they have some inhibitory effect when located at the ortho position. Such influence of the substituents seems to be due to steric hindrance and inductive effect. The mechanism of the reaction is not clear, but the reaction seems to proceed via Schiff bases and include the reduction of carbon-nitorgen bonds.

The following is a typical experimental procedure. The tetracarbonylhydridoferrate was prepared according to the method described in a previous paper[12]. To a mixture of the ferrate (11 mmol) and ethanolamine (0.68g, 11 mmol) was added drop by drop, p-chlorobenzaldehyde (1.59g, 11 mmol) for 3-5 min; the mixture was then stirred for 24 h at room temperature under an atmosphere of carbon monoxide. The reaction was stopped and the potassium carbonate formed in the reaction was filtered off. The filtrate was concentrated to 3-5 ml on a rotary evaporator. N-(p-Chlorobenzyl) ethanolamine(1.88g, 92%) was purified by careful vacuum distillation and then analyzed by boiling point, IR, NMR, and elemental analyses. N-(p-Chlorobenzyl) ethanolamine (Exp. No. 3): Bp 96°C/0.43 mmHg; ^1H-NMR(60 MHz) (CCl_4): δ(ppm) 1.43(2H, m, CH_2-), 1.70(2H, m, N-CH_2-), 2,73(2H, t, CH_2-O), 4.47(H, s, OH), 7.22(4H, s, Ar). IR(neat): νN-H; 3400 cm^{-1}, νO-H; 3600 cm^{-1}. (Found; C, 58.19; H, 6.53; N, 7.50; Cl, 19.16. Calcd for $C_9H_{12}NOCl$; C, 58.21; H, 6.51; N, 7.54; Cl, 19.12%).

The synthesis of aziridine and azetidine from these products obtained is in progress.

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