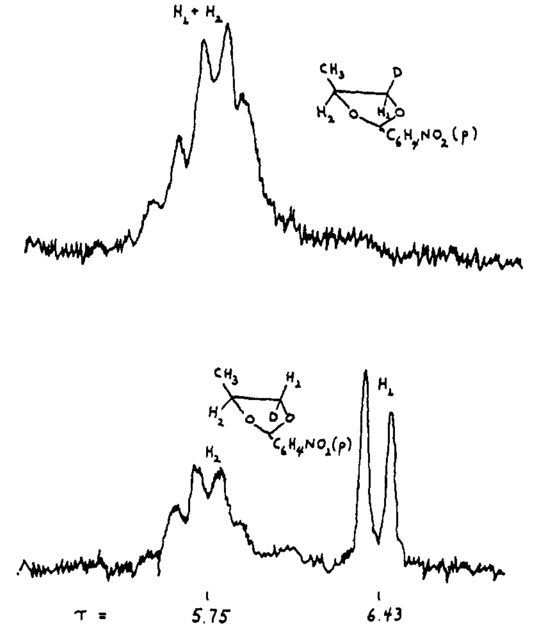
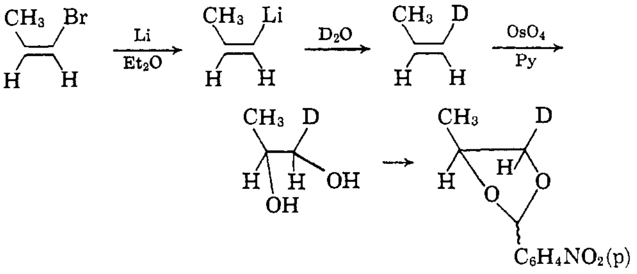
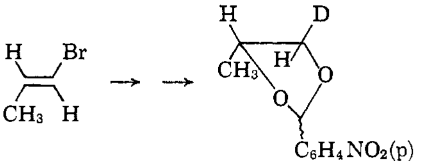


Figure 1.

same as that of VIII′[9] and that of XI as that of IX′, it follows that the absolute configuration at C-1 of VIII and IX is (*R*). As far as product stereospecificity is therefore concerned, lactaldehyde, either D or L, and acetaldehyde have the same substrate–coenzyme relationship (VII and II).



X



XI

The above results point out the need for further testing the importance of hydrophilic and hydrophobic regions in product stereospecificity control.

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Received December 23, 1965

A Novel Amination Reaction of Carboxylic Acid Derivatives with Tetrakis(dimethylamino)titanium

Sir:

We wish to report a new reaction in which tetrakis(dimethylamino)titanium (I) converts carboxylic acids and their common derivatives (esters, anhydrides, amides) into orthoamides and ketene N,N-acetals, conveniently and in good yields.

N,N-Dimethylformamide, for example, is converted to the previously unknown[1] tris(dimethylamino)methane ($HC[N(CH_3)_2]_3$, bp 70° (50 mm), $n^{25}D$ 1.4348), in 83% yield by I at room temperature in ethyl ether in several hours. The structural assignment of the triamine is based on its molecular weight, nmr spectra, and elemental analysis. *Anal.* Calcd for $C_7H_{19}N_3$: C, 57.9; H, 13.2; N, 28.9; mol wt, 145. Found: C, 57.9; H, 13.3; N, 29.3; mol wt (cryoscopy in benzene), 144. The nmr spectrum (benzene solution, TMS internal standard) exhibited sharp singlets at τ 6.98 and 7.69 in the expected ratio of 1:18.

N,N-Dimethylacetamide is converted to 1,1-bis(dimethylamino)ethylene ($CH_2{=}C[N(CH_3)_2]_2$, bp 115° (744 mm), $n^{25}D$ 1.4500, lit.[2] $n^{20}D$ 1.4518) in 87% yield under essentially the same conditions as above. *Anal.* Calcd for $C_6H_{14}N_2$: C, 63.1; H, 12.4; N, 24.5; mol wt, 114. Found: C, 62.7; H, 12.1; N, 24.3; mol wt (mass spectroscopy), 114. The nmr spectrum (benzene solvent, TMS internal standard) exhibited sharp singlets at τ 6.60 and 7.53 in the expected ratio of 1:6.

The titanium is converted in both examples to insoluble oxide.

Experiments are in progress to determine the generality of the reaction as a synthetic tool, and a detailed description of this and further work will be reported shortly.

(1) The first authentic member of this series, N,N′,N′′-triphenyl-N,N′,N′′-trimethyltriaminomethane, was reported by D. H. Clemens, E. Y. Shropshire, and W. D. Emmons, *J. Org. Chem.*, **27**, 3664 (1962).
(2) H. Bredereck, F. Effenberger, and H. P. Beyerlin, *Chem. Ber.*, **97**, 3081 (1964).

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Received January 4, 1966

The Oxidation of Water Coordinated to Cobalt(III)

Sir:

Until recently, there have been few systematic investigations of the oxidation of water by metal ion complexes. Some ideas on the mechanism of the oxidation taking account of existing kinetic and thermodynamic data were recently advanced,[1] but the data leave much latitude in the interpretations based on them. In this communication we report the results of some tracer experiments which prove that the water in the first coordination sphere of $(NH_3)_5CoOH_2^{3+}$ can be oxidized. The observations thus fix an important feature of the mechanism, at least in this case.

When, at 50°, a solution of $AgNO_3$ is added to an acidic solution of $K_2S_2O_8$ and $(NH_3)_5CoOH_2(ClO_4)_3$, a small percentage of the Co(III) complex is reduced to

(1) H. Taube, *J. Gen. Physiol.*, **49**, 29 (1965).

Table I. Yields of Co^{2+} in the Ag^+–$S_2O_8^{2-}$–$(NH_3)_5CoOH_2^{3+}$ Reaction[a]

No.	$AgNO_3$, *M*	$K_2S_2O_8$, *M*	$(NH_3)_5Co$-OH_2^{3+}, *M*	$(Co^{2+})_\infty/(SO_4^{2-})_\infty$
138	0.050	0.051	0.0064	0.0050
139	0.043	0.040	0.023	0.0140
146	0.046	0.039	0.023	0.0100[b]
141	0.100	0.041	0.078	0.0320

[a] At 50°; pH 2.0 ± 0.3; $\mu = 0.6 \pm 0.1$; $S_2O_8^{2-}$ taken to complete reduction. [b] $(Co(ClO_4)_2)_0 = 6.4 \times 10^{-4}$ *M*; $(Co^{2+})_\infty = 14.8 \times 10^{-4}$ *M*.

Co^{2+} (Table I). Most of the oxygen gas produced in the reaction results from the silver-catalyzed oxidation of solvent water by persulfate, but by using O^{18}-enriched $(NH_3)_5CoOH_2^{3+}$ we have found that 60–80% of the Co^{2+} is accompanied by the oxidation of the coordinated water molecule. The ratio of coordinated H_2O oxidized to Co^{2+} produced, O^*/Co^{2+}, is shown for some typical experiments in Table II.

Table II. Oxidation of Coordinated Water in the Ag^+–$S_2O_8^{2-}$–$(NH_3)_5CoO^*H_2^{3+}$ Reaction[a]

No.	$AgNO_3$, *M*	$K_2S_2O_8$, *M*	$(NH_3)_5CoOH_2^{3+}$,[b] *M*	*t*, min	$Co_t^{2+} \times 10^3$ *M*	O_2[c] $\times 10^3$	F_O[d]	O^*/Co^{2+}[e]
169	0.043	0.101	0.059	3.0	1.35	8.2_0	1.338	0.68
170	0.043	0.100	0.179	3.0	2.16	6.62_6	1.643	0.62
174	0.087	0.101	0.044	1.5	1.03	7.9_0	1.240	0.61
177[f]	0.080	0.094	0.041	2.3	3.05	12.5	1.059	0.79

[a] At 50°; pH 1.7 ± 0.2; $\mu = 0.6 \pm 0.1$. [b] 7.00 times more enriched than solvent H_2O ($F_{Co(III)} = 7.0$). [c] Moles of O_2 evolved per liter of reaction solution. [d] Enrichment of O_2 compared to solvent H_2O. [e] Number of moles of coordinated H_2O oxidized per number of moles of $(NH_3)_5CoOH_2^{3+}$ reduced, calculated from $O^*/Co^{2+} = 2[(F_O - 1)O_2]/[(F_{Co(III)} - 1)Co_t^{2+}]$. [f] $Co(ClO_4)_2 = 2.74 \times 10^{-3}$ *M* at $t = 0$ min.

The decomposition of $S_2O_8^{2-}$ at 50° in the absence of Ag^+ also leads to reduction of the Co(III) complex, but, as is shown in Table III, the gaseous product in this case is nitrogen rather than oxygen.

Table III. Production of N_2 in the $S_2O_8^{2-}$–$(NH_3)_5CoOH_2^{3+}$ Reaction at 50°

$S_2O_8^{2-}$, *M*	$(NH_3)_5CoOH_2^{3+}$, *M*	pH	$\Delta N/\Delta Co^{2+}$
0.15	0.0039	3.6	0.92
0.15	0.019	2.5	~0.94

In the silver-catalyzed reaction we believe that an intermediate in the reaction between Ag^+ and $S_2O_8^{2-}$ interacts with $(NH_3)_5CoOH_2^{3+}$ to give Co^{2+} and HOO^*H. It is quite reasonable to assume, as has been demonstrated for a variety of oxidizing agents,[2] that the hydrogen peroxide is then oxidized to oxygen with preservation of the O–O bond. Although OH, SO_4^-, Ag(II), Ag(III), and $Co(H_2O)_6^{3+}$ can all exist as intermediates in solutions of silver persulfate,[3,4] we have concluded that the effective intermediate is Ag(II) and/or Ag(III). Gas analysis and detailed kinetic studies[5] on the uncatalyzed reaction offer compelling evidence that OH radicals react with the complex to give exclusively nitrogen as the gaseous product. In addition, the absence of a significant pH effect on the composition of the gaseous product (Table III) suggests that if interconversion of OH to SO_4^- is occurring at lower pH values, the SO_4^- radical also produces nitrogen. It is unlikely that Co^{3+}(aq) (produced by the oxidation of Co^{2+}) is the responsible intermediate, since Co^{2+} actually inhibits the reduction of the complex (Table I, no. 146; Table II, no. 177) and has no marked effect on the O^{18} tracer results. This leaves as possibilities Ag(II), Ag(III), or some intermediate not yet considered. Direct experiments have shown that when Ag^{2+} is added to $(NH_3)_5CoOH_2^{3+}$ at 50°, Co^{2+} is in fact formed.

The possibility of a higher valence state of silver producing oxygen and Co^{2+} from $(NH_3)_5CoOH_2^{3+}$ is consistent with two quite different proposals for the oxidation of water. One mechanism envisions the production of hydrogen peroxide from two metal ions acting simultaneously as "one-electron" oxidizing agents,[1,6] *e.g.*

$$AgO^+ + H\overset{H}{O}Co^{III}(NH_3)_5 \rightarrow Ag^{2+} + HOOH + Co^{2+} + 5NH_3$$

The other suggestion is that a single metal ion may oxidize water to hydrogen peroxide in a "two-electron" step,[7,8] *e.g.*

$$2H^+ + AgO^+ + H\overset{H}{O}Co^{III}(NH_3)_5 \rightarrow Ag^{2+} + H\overset{H}{O}Co^{IV}(NH_3)_5$$

$$(NH_3)_5Co^{IV}OH_2 + OH_2 \rightarrow 5NH_3 + Co^{2+} + 2H^+ + HOOH$$

The problem of differentiating between the two mechanisms remains as does that of accounting for the Co^{2+} which is produced but not accompanied by oxidation of the coordinated water. Kinetic and tracer experiments in progress may provide answers to these questions.

Acknowledgments. Financial support by the Atomic Energy Commission and the National Institutes of Health is gratefully acknowledged. Funds for purchase of the Cary spectrophotometer were made available by the National Science Foundation under Grant G-22611.

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Received December 15, 1965

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(2) W. Schumb, C. Satterfield, and R. Wentworth, "Hydrogen Peroxide," American Chemical Society Monograph No. 128, Reinhold Publishing Corp., 1955, Table 2, p 386.

(3) W. Wilmarth and A. Haim, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers Inc., New York, N. Y., 1962, p 199.

(4) J. B. Kirwin, *et al.*, *J. Phys. Chem.*, **67**, 2288 (1963).

(5) H. Taube and D. Thusius, to be published.

(6) M. Calvin, *Rev. Pure Appl. Chem.*, **15**, 1 (1965).

(7) A. A. Noyes, *et al.*, *J. Am. Chem. Soc.*, **57**, 1221 (1935).

(8) J. B. Kirwin, *et al.*, *J. Phys. Chem.*, **67**, 1617 (1963).