$$W(CO)(CS)(DPE)_2 + HgX_2 \longrightarrow (DPE)_2(CO)WC{\equiv}SHgX_2 \quad (3)$$

tion. The complexes are poor conductors in nitrobenzene[10] and each displays a single ν(CO) band in its ir spectrum, shifted to higher frequency. The thiocarbonyl absorption is not shifted to higher frequency, but again appears overlapped with a ligand absorption band near 1095 cm^{-1}, lower than the original CS band by approximately 65 cm^{-1}. These reactions with mercuric halides are in contrast to those reported[11] for *cis*-$W(CO)_2(DPE)_2$ in which ionic products of the type $[W(CO)_2(DPE)_2HgX]HgX_3$ are formed by oxidative addition to the metal.

An ionic,[12] diamagnetic complex is formed in yields above 80% when **1** is stirred with 0.5 equiv of $AgBF_4$ in CH_2Cl_2 or acetone. The thiocarbonyl ν(CS) band can be definitely located in the ir spectrum of this complex and is lowered as compared with that of **1** by about 55 cm^{-1}, while the CO band is raised (Table I). Elemental analyses, molar conductivity, and the stoichiometry of the reaction indicate that two thiocarbonyl molecules are associated with one silver ion, as in eq 4. The carbonyl complex, $W(CO)_2(DPE)_2$,

$$2W(CO)(CS)(DPE)_2 + AgBF_4 \longrightarrow [(DPE)_2(CO)WCSAgSCW(CO)(DPE)_2]BF_4 \quad (4)$$

in contrast, was found to react with $AgBF_4$ in an oxidation–reduction process with formation of silver metal. The resulting paramagnetic $[W(CO)_2(DPE)_2]BF_4$ was isolated from this reaction, and its identity was confirmed by preparation of the identical complex in a metathesis reaction of the reported triiodide salt[13] $[W(CO)_2(DPE)_2]I_3$ and $AgBF_4$.

Like $(DPE)_2(CO)WCSW(CO)_5$, the mercuric halide and silver ion complexes of **1** are rapidly converted to **1** in CH_2Cl_2 solution in the presence of PPh_3. However, all of these complexes may be recrystallized with very little decomposition occurring in solution.

It is apparent from these studies that in complexes where the electron density on the metal is sufficiently high and the ν(CS) frequency is sufficiently low, the sulfur atom of a thiocarbonyl ligand may act as a donor toward other metals. It is also clear that the sulfur of the CS group in $W(CO)(CS)(DPE)_2$ is a better donor than is the oxygen of the CO. These results indicate that it will be possible to synthesize other complexes containing end-to-end bridging thiocarbonyls.

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(9) $W(CO)(DPE)_2(CS)HgI_2$ crystallizes as the methylene chloride adduct. *Anal.* Calcd for $W(CO)(DPE)_2(CS)HgI_2{\cdot}CH_2Cl_2$: C, 41.45; H, 3.14; S, 2.05. Found: C, 40.98; H, 2.99; S, 1.91.
(10) The molar conductivities of $W(CO)(DPE)_2(CS)HgCl_2$ and $W(CO)(DPE)_2(CS)HgI_2{\cdot}CH_2Cl_2$, *ca.* 10^{-3} *M* in nitrobenzene, are 5.5 and 5.4 ohm^{-1} cm^2 mol^{-1}, respectively.
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On the Coupling of Adenosine Triphosphate Hydrolysis to a Simple Inorganic Redox System: $VO^{2+} + H_2O_2$

Sir:

The enzyme-catalyzed hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and inorganic phosphate (P_i) provides the main source of energy for many biological processes. Nonenzymatic hydrolysis of ATP has been investigated by many workers[1-4] in an effort to learn more about the mechanism of catalysis by enzymatic systems. In many biological cases, it appears that ATP hydrolysis occurs simultaneously with some electron transfer reaction. The present work is largely an effort to study catalysis of ATP hydrolysis by a simple inorganic redox reaction (H_2O_2 oxidation of VO^{2+}) in a nonenzymatic system to test a theory that redox reactions mediated by polyphosphates labilize phosphorus to substitution.

Hydrolysis rates of ATP were followed by monitoring the amount of P_i produced, using the molybdenum blue method for phosphate determination as modified by Baginski, *et al.*,[5] for use in the presence of nucleoside phosphates. Standard orthophosphate solutions (with and without added ATP) showed a linear dependence of A_{700} (absorbance of phosphomolybdenum blue complex at 700 nm) with $[P_i]$ giving a slope of $(1.55 \pm 1.07) \times 10^4\ M^{-1}$.

All runs were made using solutions of reagent grade $VOSO_4$, $Na_2H_2ATP \cdot 4H_2O$ (Sigma Chemical Co.), and H_2O_2. Phosphate present buffered the solution to pH ~2.5 in all runs. Only P_i formation was monitored in this preliminary study, but as mentioned below any $P_2O_7^{4-}$ formed would probably be hydrolyzed to P_i by a process similar to that for ATP hydrolysis.

Our initial findings summarized in Table I show comparative rates of hydrolysis of ATP, revealing moderate enhancement by VO^{2+} and dramatic enhancement by coupling with H_2O_2 oxidation of VO^{2+}. Hulett[2] gives a value of $\sim 8 \times 10^{-8}$ sec^{-1} for the first-order rate constant of the uncatalyzed hydrolysis of ATP (at pH 4, 25°). Enhancement of phosphate ester hydrolysis by VO^{2+} alone has also been observed by Hofstetter, *et al.*, in the case of salicylphosphate.[6]

The last two runs in the table indicate that H_2O_2 concentration is an important factor in the enhancement of ATP

Table I. Summary of Catalytic Effects

$[VO^{2+}]_0$, *M*	$[H_2O_2]_0$, *M*	$[ATP]_0$, *M*	Time required for complete hydrolysis (at 25°)
0	0	10^{-2}	>3 months[a]
10^{-2}	0	9×10^{-3}	~8 weeks[a]
0	10^{-2}	10^{-2}	(No enhancement)
10^{-2}	1.2×10^{-2}	9×10^{-3}	1 day
1.3×10^{-2}	1.2×10^{-1}	1.4×10^{-2}	3 hr

[a] Hydrolysis is too slow for accurate measurement of rates.

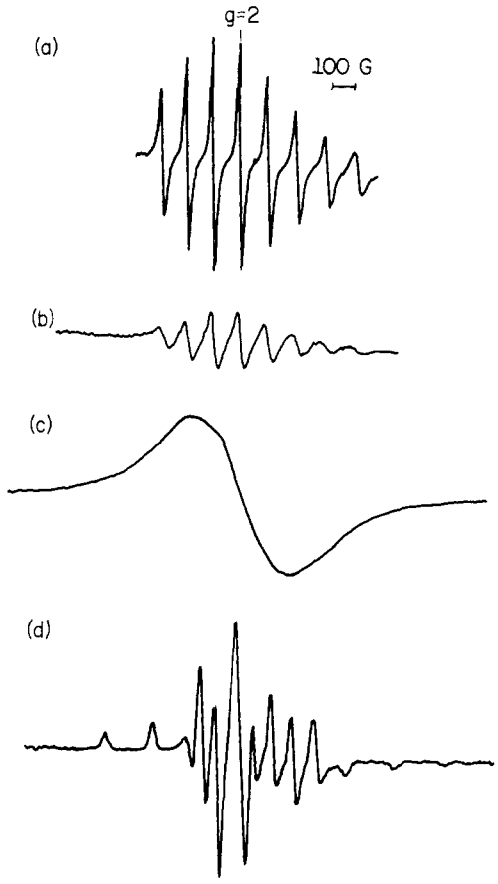

Figure 1. Esr spectra of VO^{2+} and VO^{2+}-ATP in aqueous solution. Concentrations are all $\sim 10^{-2}$ *M*. Room temperature spectra are at ~9.5 GHz; spectra at 77°K are at ~9.1 GHz: (a) VO^{2+} at room temperature, A = 116 G; (b) VO^{2+} and ATP at room temperature, A = 114 G; (c) VO^{2+} at 77°K; (d) VO^{2+} and ATP at 77°K, $A_{\parallel}$ = 200 G, $A_{\perp}$ = 76 G.

hydrolysis. When H_2O_2 is present in a limited amount ($[H_2O_2] = 10^{-3}$ *M*, $[VO^{2+}] = [ATP] = 10^{-2}$ *M*) the production of P_i slows after 2×10^{-3} *M* P_i is produced, and reverts to the rate of hydrolysis observed in runs without H_2O_2 present. *This indicates that oxidation of* $VO^{2+} \rightarrow V(V)$ *is the important factor in enhancement of ATP hydrolysis.*

Replacement of H_2O_2 with MnO_4^- also yields enhancement of ATP hydrolysis. Replacement of ATP with $P_2O_7^{4-}$ also inhibits oxidation of VO^{2+} by H_2O_2 with hydrolysis of $P_2O_7^{4-}$ to P_i.

Esr spectra of VO^{2+} (with and without ATP) are shown in Figure 1. No ^{31}P superhyperfine structure is observed. At room temperature, the normal eight-line ^{51}V signal (a) is broadened upon addition of ATP (b). At 77°K, the line broadening present for ATP-free VO^{2+} (c) is diminished and the g-anisotropy of the ^{51}V hyperfine structure is revealed (d). All these facts clearly indicate that binding occurs between VO^{2+} and ATP in aqueous solution.

When H_2O_2 and VO^{2+} are added in equimolar concentrations (without ATP), the solution becomes amber and then exhibits the bright yellow of the decavanadate ion ($H_2V_{10}O_{28}^{4-}$) permanently.[8]

When ATP is present, addition of equimolar quantities of VO^{2+} and H_2O_2 results in a solution which is initially amber in color, and then reverts to the blue VO^{2+} color. Thus, when ATP is present, VO^{2+} is not immediately oxidized as it is without ATP. Esr monitoring shows that VO^{2+} is being oxidized slowly. Thus, ATP protects the VO^{2+} from oxidation by H_2O_2. Only after about 1 week does the solution exhibit the yellow decavanadate color. At this point, the hydrolysis of ATP is essentially complete. Gas evolution is observed and becomes more prevalent as the $[VO^{2+}]_0/[ATP]_0$ ratio is increased above 1/1 and as $[H_2O_2]_0$ is increased.

A large excess of H_2O_2 added to a VO^{2+}-ATP solution causes it to turn amber, then pale yellow-green. Esr spectra indicate that some VO^{2+} is still present, so that ATP is still protecting the VO^{2+} to some extent.

In runs in which $[VO^{2+}] = [H_2O_2]$, and in which ATP was present, only ~50% of the VO^{2+} was oxidized, as shown by the intensity of the esr spectrum. Brooks and Sicilio[7] observed similar behavior and explained it by saying that some of the H_2O_2 undergoes catalytic decomposition to O_2 and H_2O.

They also report that the rate of oxidation is slowed 100-fold by the introduction of chelating agents like $EDTA^{4-}$. ATP chelation in the present study slows the rate of oxidation by a factor of $\sim 10^3$ or more. $P_2O_7^{4-}$ exhibits a similar but smaller inhibition.

The structure of the VO^{2+}-ATP complex probably involves phosphate O's bound to three of the five available coordination positions with the adenosine moiety folded over and probably bound to one or both of the other available sites, resulting in shielding of the VO^{2+} ion from attack by H_2O_2.

If direct H_2O_2 oxidation of VO^{2+} is prevented by the chelated ATP, it is possible that H_2O_2 attacks at the phosphate linkage of the ATP ligand (bound to VO^{2+}), followed by electron transfer from the VO^{2+} ion through the phosphate to the H_2O_2. This would explain the large catalytic effect the redox process has on the hydrolysis of ATP.

Detailed kinetic studies on this and other redox systems are now under way to determine the mechanistic pathways involved in the enhancement of ATP hydrolysis by electron transfer reactions. It is hoped that such studies will provide insights concerning the enzymatic catalysis of ATP hydrolysis in biological systems.

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Crossed Molecular Beam Synthesis of a New Compound, CH_3IF

Sir:

The crossed molecular beam technique, while primarily confined to elucidating the dynamics of reactions for which the products are readily predicted, offers a method for the