This rationale is similar to those invoked by others to explain the photo and thermal decarboxylation of acids in the presence of Ce(IV)[10] and Pb(IV),[11] and it is consistent with Adamson's radical-pair hypothesis[2] and with the mechanism invoked by Haim and Taube[12] to explain the photolysis of $Co(NH_3)_5I^{2+}$ ion.

Reactions 5 and 6 readily account for the doubling of $\varphi_{Co^{2+}}$ in degassed 5 *M* isopropyl alcohol. Thus, the primary quantum yield for Co^{2+} production is not changed by the addition of isopropyl alcohol. Ketyl radicals,[13] as well as simple alkyl radicals,[14] are known to be efficient reducing agents for many metal ions. Oxidized ketyl radicals (in reaction 6) would deprotonate to form acetone. The ketyl radical is probably also formed in the nondegassed isopropyl alcohol system, but it is efficiently trapped by dissolved oxygen, thus effectively preventing the doubling of $\varphi_{Co^{2+}}$ according to reaction 6.

Furthermore, we would predict, using our scheme, the constancy in $\varphi_{Co^{2+}}$ and the increase in CH_4/C_2H_6 which were observed by Kantrowitz,[5] *et al.*, as [isopropyl alcohol] was increased. Above 1 *M* *i*-PrOH, CH_4 was the only hydrocarbon product, with $\varphi_{CH_4} = {}^1/_2\varphi_{Co^{2+}}$(degassed) = $\varphi_{Co^{2+}}$(nondegassed).

Thus, it is unnecessary to postulate two different excited states. The *apparent* quantum yield is changed by solvent, as found by Kantrowitz,[5] *et al.*, but there is no evidence to support their claim that the primary quantum yield is affected. The overall photoreduction is explained by a two-step sequence involving a primary photoreduction and a secondary thermal reduction of the substrate.

However, it should be noted that for complex **1** the product analysis requires the intermediacy of acetoxy radcal, and this strongly suggests that **1*** is either a radical pair or a charge-transfer excited state with radical character (which ultimately undergoes facile homolytic cleavage). Therefore, we maintain that until unambiguous evidence to the contrary is obtained, the radical-pair mechanism serves as an adequate model to explain the known behavior of Co(III) complexes.

One should also note that this reaction provides a convenient preparation of ketyl radicals from alcohols in aqueous medium.

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Robert D. Lindholm*
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

Thomas K. Hall
Department of Chemistry, Rochester Institute of Technology
Rochester, New York 14623

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Transition Metal Promoted Organic Reactions as Models for Nitrogenase Behavior

Sir:

In both enzymic and nonenzymic reactions of nitrogen (N_2), a central role is ascribed to transition metal species.[1] The principal property of the enzyme nitrogenase, which contains iron and molybdenum, is its remarkable reductive action on not only N_2, but also substitute, organic substrates, including acetylenes, cyanide ion, nitriles, and isonitriles. We report herein the simulation of such enzymic organic reactions by various reducing agent–transition metal combinations *also* recognized for their pronounced nonenzymic N_2-fixing properties, thus supporting the assigned role of transition metals in biological N_2 fixation reactions, permitting comprehension of the chemical behavior described, and helping pave the way for further understanding of the enzymic phenomena.

Past efforts have demonstrated that nitrogenase brings about the reduction of: (1) alkyl cyanides to the corresponding hydrocarbons,[2,3] (2) hydrogen cyanide or cyanide ion to primarily methane and ammonia,[4,5] in addition to some methylamine and traces of ethane and ethylene,[6] and (3) isonitriles to methane, the major hydrocarbon product, and the corresponding amine, accompanied by higher hydrocarbons (*e.g.*, ethane and ethylene in the methylisonitrile or ethylisonitrile case[1a,2,6]), findings that reveal a marked propensity for complete reductive cleavage of triple bonds, as in the N_2 case. In addition, alkynes are converted to alkenes.[2,4,7] In relation to these biological reactions, our studies have involved (Table I) three transition metals, molybdenum, iron, and—as an example of a nonbiological element—titanium,[8] all of which fix nitrogen under mild, abiological conditions. By comparison, methane and various amounts of ethane and ethylene are formed from potassium cyanide through the action of Fe(III)– and Ti(IV)–naphthalenide combinations.[9] In the case of cyclohexylisonitrile, $FeCl_3$–Mg and $TiCl_3$–Mg produced methane, cyclohexane, and trace amounts of ethane, and ethylene, with no detectable amounts of cyclohexylamine, while $Mo(acac)_3$– and $Fe(acac)_3$–naphthalenide promoted formation of cyclohexane alone. The combinations $MoCl_5$–Mg[10] and $FeCl_3$–Mg[9] effected formation of hexene-1 from hexyne-1, although further reduction to hexane was also involved. The laboratory, transition metal

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(10) For conversion of alkynes to alkenes by Mo complexes and borohydride or dithionite, see G. N. Schrauzer and G. Schlesinger, *ibid.*, **92**, 1808 (1970); G. N. Schrauzer and P. A. Doemeny, *ibid.*, **93**, 1608 (1971). Ammonia yields $\leq 0.1\%$ from N_2 (2000 psi) were observed after 5 days reaction at room temperature.

Table I. Reduction Products (% Yields)[a] Formed by Action of Transition Metal–Reducing Agent Combinations on N_2, KCN, $C_6H_{11}NC$, and n-$C_4H_9C{\equiv}CH$

Transition metal (0.01 mol) –reducing agent	N_2	KCN[b]		n-$C_4H_9C{\equiv}CH$[b]
$Mo(acac)_3$–NaNp (1:6)		NoCH$_4$	C_6H_{12} (22)	
$MoCl_5$–Mg[c,d]	NH_3			$CH_3(CH_2)_3CH{=}CH_2$ (10), n-C_6H_{14} (13)
$Fe(acac)_3$–NaNp (1:6)		CH_4 (5)	C_6H_{12} (13)	
$FeCl_3$–Mg[c,d]	NH_3	No CH_4; C_2H_{4-6}	CH_4 (2.6), C_6H_{12}, C_2H_{4-6} (trace)	$CH_3(CH_2)_3CH{=}CH_2$ (33), n-C_6H_{14} (5)
$TiCl_3$–Mg[e]	NH_3	No CH_4; C_2H_{4-6} (trace)	CH_4 (6.4), C_6H_{12}, C_2H_{4-6} (trace)	
Cp_2TiCl_2–NaNp (1:6)[f]	NH_3	CH_4 (0.7); C_2H_6 (12)		
(Nitrogenase)	NH_3	CH_4 (major prod); CH_3NH_2; C_2H_{4-6} (trace)	CH_4, C_2H_{4-6} (trace) (from CH_3NC and C_2H_5NC)	$RCH{=}CH_2$

[a] Yields based on metal derivatives. [b] THF solution (20–40 ml) for 2–5 days at room temperature with 1 mol of reactant. [c] M. E. Vol'pin, A. A. Belyi, and V. B. Shur, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2225 (1965). [d] M. E. Vol'pin and V. B. Shur, *Nature (London)*, **209**, 1236 (1966). [e] For $TiCl_4$–Mg fixation results, see *c* and *d* above. [f] E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Amer. Chem. Soc.*, **89**, 5707 (1967).

induced reduction of acetonitrile, although principally involving cyanide loss,[11] did lead to formation of small amounts (0.2–2%) of ethane, the product of the enzyme reaction; in addition some ammonia and primary amine were detected.

As in nitrogenase reactions,[1] all organic substrate studies herein inhibit the fixation of N_2 by the transition metals employed. Acetylene reductions were restricted to the use of transition metal–Mg combinations, since it was noted that sodium metal or sodium naphthalenide alone caused conversion to ethylene.[12] Because the transition metals herein are in themselves effective hydrogenation catalysts, "overreduction" of an acetylene to alkane is not surprising. In preliminary runs, compounds of cobalt and chromium were found to give, under the conditions described herein, results similar to those found with iron, molybdenum, and/or titanium.

Although no one transition metal–reducing agent combination mimics all the nitrogenase phenomena, all of the latter can be simulated by the group as a whole. The entire body of results demonstrates that the characteristic reactions of nitrogenase carried out on organic substrates are not so unusual that they cannot be realized nonenzymically by a representative group of specific transition metal compounds. It seems likely that in the enzyme system particular transition metal derivatives are utilized, not so much for their chemical novelty as for their compatibility with other cellular constituents. The rate of the complete reductive cleavage of the N_2 triple bond may be greatly accelerated so as to preclude other, undesirable reaction courses—evidently possible as indicated by the behavior of substrates other than N_2—with such selectivity conceivably a result of the combined effect of molybdenum and iron. Also, it is apparent from this study that, in an overall sense, closer simulation of nitrogenase behavior is achieved with iron than with molybdenum, in accordance with the view expressed by some[1] that iron is the coordinating species in the enzymic process.[13]

(11) C. Bjorklund and H. Rudler, unpublished observations to be reported more fully elsewhere.
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Although it is true that the titanium based, abiological catalytic fixation of N_2 is operated in aprotic media, the very site of the biological process also might be water free, by virtue of protection offered by the enzyme structure. Also, strong reducing agents (*e.g.*, naphthalene radical anion or Mg) are employed in the laboratory fixations; but the utilization of probably 12–15 mol of ATP[1] for reduction of each mole of N_2 to ammonia would allow a high reduction potential for the enzymic reaction. Finally, in the enzymic N_2 fixation process, *molybdenum* may be substituted by *vanadium*,[14,15] an elemental neighbor of *titanium*. In view of the foregoing, we believe that the Ti(II)–based room temperature–atmospheric pressure catalytic N_2 fixation process[16] represents an instructive transition metal model for the biochemical phenomenon. However, further elucidation of the obscure and probably complicated enzymic and nonenzymic transformations described herein must await more detailed and incisive experimentation.

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E. E. van Tamelen,* H. Rudler, C. Bjorklund
Department of Chemistry, Stanford University
Stanford, California 94305
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Alkali Sensitivity of 3-Methylpyrimidine Nucleosides

Sir:

After the first and only successful isolation of 3-methyluridine from an *enzymatic hydrolysate of soluble*