eliminate C_4H_6 as the only fragment.[14] $FeCo_2C_4H_8^+$ ions produced from either butane or isobutane yield similar CID spectra with elimination of H_2, $2H_2$, and C_4H_8 observed. Considerably more C_4H_8 elimination occurs for $FeCo_2C_4H_8^+$ produced from isobutane than from butane. This reduced dehydrogenation suggests that formation of $FeCo_2((CH_2)_3C)^+$ is difficult or that substantial rearrangement is required prior to dehydrogenation.

$FeCo_2C_5H_{10}^+$ generated from pentane yields predominantly dehydrogenations following collisional activation to form $FeCo_2C_5H_6^+$ in high efficiency with $FeCo_2C_5H_4^+$ formed at high energy. A small amount of C_2H_6 elimination to form $FeCo_2C_3H_4^+$ is also observed. CID of $FeCo_2C_5H_8^+$ formed from pentane yields exclusively H_2 elimination in high efficiency with no $FeCo_2C_3H_4^+$ formed. Only a trace of $FeCo_2^+$ is produced from CID of either $FeCo_2C_5H_{10}^+$ or $FeCo_2C_5H_8^+$. These results suggest that $FeCo_2^+$ initially dehydrogenates pentane forming $FeCo_2C_5H_{10}^+$, which subsequently eliminates C_2H_6. CID of $FeCo_2C_5H_{10}^+$ formed from 2-methylbutane yields elimination of H_2, $2H_2$, C_2H_6, and C_5H_{10} while $FeCo_2C_5H_8^+$ eliminates predominantly H_2 and $2H_2$. Some rearrangement between the ions produced from pentane and 2-methylbutane may take place. The facile formation of $FeCo_2C_5H_6^+$ from CID of the pentane ions may proceed through a dehydrocylization process[21,22] generating a cyclopentadiene or a hydrido–cyclopentadienyl complex. Both $FeC_5H_{10}^+$ and $CoC_5H_{10}^+$ species lose predominantly C_2H_4 and C_3H_6 upon collisional activation.[5a,b,14]

The dehydrogenation products formed from hexane, $FeCo_2C_6H_{10}^+$ and $FeCo_2C_6H_8^+$, eliminate hydrogen forming $FeCo_2C_6H_6^+$ in high efficiency upon collisional activation with a small amount of $FeCo_2^+$ observed at higher kinetic energies. This is in contrast to the ion–molecule reaction of $FeCo_2^+$ with hexane in which $FeCo_2C_4H_8^+$ and $FeCo_2C_4H_6^+$ are formed and suggests that they are produced by initial dehydrogenation forming $FeCo_2C_6H_{12}^+$ followed by rearrangement with elimination of C_2H_4 generating $FeCo_2C_4C_4H_8^+$. The $FeCo_2C_4H_8^+$ may retain sufficient internal energy for dehydrogenation forming $FeCo_2C_4H_6^+$. The facile formation of $FeCo_2C_6H_6^+$ may proceed via a dehydrocyclization[21,22] process resulting in benzene formation. The heteronuclear dimer complex $FeCoC_6H_6^+$ loses Fe forming $CoC_6H_6^+$ while $FeCo_2C_6H_6^+$ loses C_6H_6 exclusively upon collisional activation, indicating a change in relative bond energies going from the dimer to the trimer.[10]

In summary, $FeCo_2^+$ is more reactive than the dimer ions, $FeCo^+$ and Co_2^+, with aliphatic alkanes. It reacts predominantly via initial insertion across a C–H bond followed by elimination of hydrogen. This may then be followed by further dehydrogenations, rearrangements, or cleavage of the hydrocarbon framework. The CID results suggest that considerably more chemistry can take place on a trinuclear transition-metal cluster than on the corresponding atomic metal ions as exemplified by the dehydrogenations of $FeCo_2C_4H_6^+$. The trinuclear species Co_3^+ and $NiCo_2^+$ have also been synthesized from reactions of Co^+ and Ni^+ with $Co_2(CO)_8$, respectively, and are currently under investigation in our laboratory.

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Registry No. $FeCo_2^+$, 91295-13-5; $FeCo^+$, 91295-14-6; Co_2^+, 73145-42-3; Fe^+, 14067-02-8; $Co_2(CO)_8$, 10210-68-1; methane, 74-82-8; ethane, 74-84-0; neopentane, 463-82-1; propane, 74-98-6; butane, 106-97-8; isobutane, 75-28-5; 2-methylbutane, 78-78-4; pentane, 109-66-0; hexane, 110-54-3.

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(21) For a recent review on dehydrocyclization in the presence of metal-containing catalysts, see: Bragin, O. V.; Krasavin, S. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1983**, *52*, 625 and references therein.

(22) Dehydrocyclization is proposed for reactions of $CoFe^+$ with 1-pentane and 1-hexene. Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.*, submitted for publication.

Solar Light Induced Formation of Chiral 2-Butanol in an Enzyme-Catalyzed Chemical System

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Reduction of ketones to alcohols, chemically[1,2] or electrochemically,[3] in the presence of enzymes is of current interest as a means for the synthesis of optically active alcohols. In these systems, powerful reductive agents such as H_2[1] and glucose-6-sulfate[4] are used as the motive power for the reduction of the ketones. Substantial efforts are also directed in developing photosensitized electron-transfer reactions in particular as a means of solar energy conversion and storage.[5,6] Light induced reduction of a variety of electron acceptors in the presence of adequate electron donors has been accomplished.[7] Thus, the use of primary light induced electron-transfer reactions in driving the secondary enzyme-catalyzed reduction of ketones seems feasible. Here we wish to report on the photosensitized preparation of NADPH using a sensitizer and dimethyl-4,4′-bipyridinium (methylviologen, MV^{2+}) as primary electron acceptor. The formation of NADPH is mediated by $MV^{+\cdot}$ in the presence of ferredoxin-$NADP^+$ reductase. The ketone, 2-butanone is then reduced by NADPH in the presence of the enzyme alcohol dehydrogenase to (−)-2-butanol with an optical purity of 100%. This system can be visualized as an endoergic energy storage system as well as a useful synthetic apparatus for the preparation of optically active alcohols.

The system is composed of an aqueous 0.1 M tris/HCl buffer solution (p*H* 7.8) that includes ruthenium tris(bipyridine) ($Ru(bpy)_3^{2+}$ 7.5×10^{-5} M) as sensitizer, ammonium ethylenediamine tetraacetic acid ($(NH_4)_3EDTA$, 2×10^{-2} M) as electron donor, and dimethyl-4,4′-bipyridinium (methylviologen, MV^{2+}, 1×10^{-3} M) as primary electron acceptor. 2-Mercaptoethanol[8] (1×10^{-3} M), $NADP^+$ (1×10^{-3} M), the ketone 2-butanone (0.15 M), and the two enzymes ferredoxin-$NADP^+$ reductase (FDR, EC 1.18.1.2, 0.5 unit), and alcohol dehydrogenase from T. Brockii[9] (ALDH, EC 1.1.1.2, 10 units) are also included in the system.[10] The deaerated mixture (3 mL) was illuminated in a glass cuvette with a 1000-W halogen–quartz lamp (light filtered through a Kodak 2C filter, $\lambda > 400$ nm). The rate of 2-butanol formation was followed by gas chromatography at time intervals of illumination (Figure 1). After 40 h of illumination a 27% conversion of 2-butanone to 2-butanol was estimated. The alcohol produced is optically active, and the (−)-2-butanol enantiomer is formed with a 100% optical purity.

The system shows resistibility under the reaction conditions. After the prolonged illumination of 22 h renewal of the electron donor concentrations, $(NH_4)_3EDTA$, restores the activity of the system, and the rate of 2-butanone reduction is similar to that observed in the original system. The different components involved in the system are recycled during the production of (−)-2-butanol,

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(1) (a) Wong, C.-H.; Daniels, L.; Orme-Johnson, W. H.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 6227–6228. (b) Abril, O.; Whitesides, G. M. *Ibid.* **1982**, *104*, 1552–1554.

(2) Wong, C.-H.; Whitesides, G. M. *J. Org. Chem.* **1982**, *47*, 2816–2818.

(3) Discosimo, R.; Wong, C.-H.; Daniels, L.; Whitesides, G. M. *J. Org. Chem.* **1981**, *46*, 4622–4623.

(4) Wong, C.-H.; Gordon, J.; Cooney, C. L.; Whitesides, G. M. *J. Org. Chem.* **1981**, *46*, 4676–4679.

(5) (a) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83–90. (b) Gratzel, M. *Ibid.* **1981**, *14*, 376–384.

(6) (a) Bard, A. J. *Science* (*Washington, D.C.*) **1980**, *207*, 138–144. (b) Willner, I.; Laane, C.; Otvos, J. W.; Calvin, M. *Adv. Chem. Ser.* **1982**, *No. 177*, 71–95.

(7) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244.

(8) Mercaptoethanol is added as a stabilizing agent for alcohol dehydrogenase (cf. ref 9).

(9) Lamed, R. J.; Zeikus, G. *Biochem. J.* **1981**, *195*, 183–190.

(10) The enzyme alcohol dehydrogenase from T. Brockii is stable at the concentrations of EDTA employed in this study.

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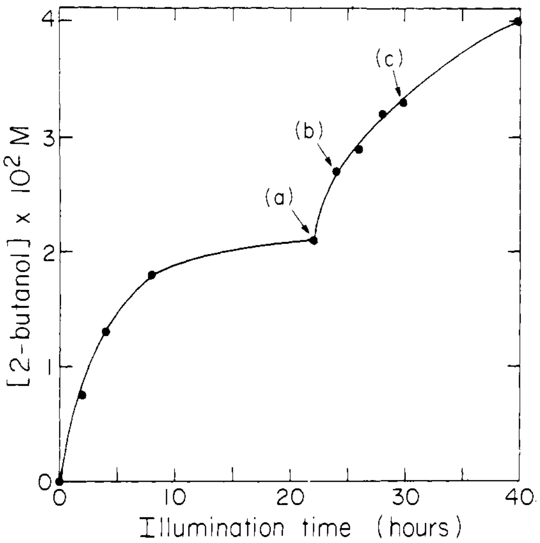

Figure 1. Rate of 2-butanol formation at different illumination time intervals. Initial $(NH_4)_3EDTA$ concentration 2 × 10^{-2} M. (a) Addition of $(NH_4)_3EDTA$, 2 × 10^{-2} M, (b) addition of $(NH_4)_3EDTA$, 1.7 × 10^{-2} M, (c) addition of $(NH_4)_3EDTA$, 1.7 × 10^{-2} M.

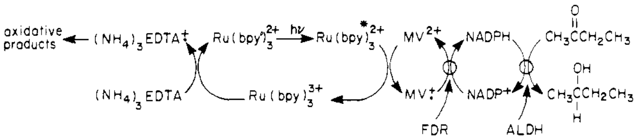

Figure 2. Cyclic scheme for the photosensitized reduction of 2-butanone by $(NH_4)_3EDTA$.

Table I. Turnover Numbers (TN) of Components Involved in the Photosensitized Reduction of 2-Butanone

	$Ru(bpy)_3^{2+}$	MV^{2+}	FDR[a]	$NADP^+$	ALDH[b]
TN	530	40	24 000	40	6000

[a] FW ≃ 40 000; cf.: Shin, M. *Methods Enzymol.* **1971**, *23*, 441. [b] FW ≃ 40 000.[9]

and their different turnover numbers after 40 h of illumination are summarized in Table I.

The different steps involved in the photoinduced reduction of 2-butanone have been confirmed by separate experiments. Illumination of the aqueous system that includes only the sensitizer, $(NH_4)_3EDTA$, MV^{2+}, $NADP^+$ and the enzyme ferredoxin reductase, results in the formation of NADPH (followed spectroscopically at λ = 340 nm). When either MV^{2+} or ferredoxin reductase are excluded from the system no photosensitized formation of NADPH is observed. These results imply that $MV^{+\cdot}$ formed upon illumination mediates the reduction of $NADP^+$ to NADPH in the presence of the enzyme.[11] Introduction of 2-butanone to the photochemically produced NADPH does not lead to the disappearance of NADPH, and no alcohol is formed. Yet, upon introduction of the enzyme alcohol dehydrogenase the NADPH disappears and 2-butanol is observed as product. These facts confirm that NADPH mediates the reduction of 2-butanone in the presence of the second enzyme.[9] In view of these results we suggest the scheme outlined in Figure 2 as the cyclic photoinduced process leading to the reduction of 2-butanone. This cycle involves a photosystem that produces $MV^{+\cdot}$ and two subunits of enzyme-catalyzed reactions. In the first unit NADPH is formed in a process catalyzed by ferredoxin-$NADP^+$ reductase. The subsequent unit utilizes NADPH in the reduction of 2-butanone in the presence of alcohol dehydrogenase.

The net reaction accomplished in this system corresponds to the reduction of 2-butanone by EDTA (eq 1).[12] The thermodynamic balance of this process is endoergic by ca. 33 kcal per mol of EDTA.

$$R{-}N(CH_2CO_2^-)_2 + CH_3C({=}O)CH_2CH_3 + 2H_2O \rightarrow R{-}NHCH_2CO_2^- + CH_2O + HCO_3^- + CH_3CHOHCH_2CH_3 \tag{1}$$

It should be noted that substitution of EDTA by other electron donors, i.e., cysteine and triethanolamine, similarly results in the photoinduced formation of $MV^{+\cdot}$ with the subsequent formation of NADPH. This demonstrates the wide applicability of various electron donors in the system.

In conclusion, we have demonstrated the feasibility of coupling enzymes as catalysts in artificial photosensitized electron-transfer reactions. This approach is useful as a synthetic tool for the light induced preparation of chiral alcohols, as well as a novel attitude for the development of energy conversion and storage systems. It is conceivable that under similar experimental conditions other NADPH-dependent enzymes, i.e., lactate dehydrogenase, glutamic dehydrogenase, and alanine dehydrogenase, would lead to the reduction of other prochiral ketones as well as to the preparation of optically active amino acids.

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $(NH_4)_3EDTA$, 15934-01-7; MV^{2+}, 4685-14-7; $NADP^+$, 53-59-8; FDR, 9029-33-8; ALDH, 9031-72-5; 2-butanone, 78-93-3; (-)-2-butanol, 14898-79-4.

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(11) Other chemical reductions mediated by viologen radicals have been recently reported; cf.: Goren, Z.; Willner, I. *J. Am. Chem. Soc.* **1983**, *105*, 7764.

(12) Willner, I., Ford, W. E.; Otvos, J. W.; Calvin, M. In "Bioelectrochemistry"; Keyzer, H., Gutmann, F., Eds.; Plenum: New York, 1980; pp 55-81.

Spin Trapping of a Cobalt-Dioxygen Complex

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The spin-pairing model for binding O_2 to transition-metal complexes describes the bound O_2 as a fragment into which anywhere from 0.1 to 0.8 of an electron is transferred upon binding to the metal.[1-3] As the ligand field strength of the ligands attached to the metal is increased more extensive electron transfer occurs. In all instances the unpaired electron in this system is localized mainly on O_2 making it difficult to determine the actual charge on this fragment. This charge transfer increases the basicity of a coordinated O_2 molecule over that of molecular oxygen. For example, it has been shown that trifluoroethanol can hydrogen bond to the terminal oxygen of the O_2 adduct of [bis(salicylidene-γ-iminopropyl)methylamine]cobalt(II) (CoSMDPT-O_2).[4] The magnitude of the shift in the O-H stretching frequency indicates[5] that the enthalpy of hydrogen bond formation is 6.6 kcal mol^{-1} making the terminal oxygen of the bound O_2 about as basic as the carboxyl oxygen in *N*,*N*-dimethylacetamide.

This work was extended to a study of the Co(II) complex catalyzed oxidation by O_2 of 2,6-disubstituted phenols to quinones.[6] The mechanism proposed for this reaction[6] suggests that coor-

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(1) Tovrog, B. S.; Kitko, D. J.; Drago, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 5144.

(2) Drago, R. S.; Corden, B. B. *Acc. Chem. Res.* **1980**, *13*, 353.

(3) Drago, R. S. In "The Coordination Chemistry of Metalloenzymes"; Drago, R. S., Bertini, I., Luchinat, C., Eds.; Reidel: Dordrecht, Holland, 1983; p 247.

(4) Drago, R. S.; Cannady, J. P.; Leslie, K. A. *J. Am. Chem. Soc.* **1980**, *102*, 6014.

(5) Drago, R. S.; O'Bryan, N.; Vogel, G. C. *J. Am. Chem. Soc.* **1970**, *92*, 3924.

(6) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580.

0002-7863/84/1506-5353$01.50/0