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Communications to the Editor

Heteronuclear Triatomic Transition-Metal Cluster Ions in the Gas Phase. Activation of C–H Bonds in Alkanes by $FeCo_2^+$

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The first-row group 8 atomic transition-metal ions are highly reactive toward alkanes in the gas phase with both C–H and C–C bond cleavages observed.[1-6] The reaction of bare transition-metal cluster ions with alkanes is a natural extension of the above studies and may serve as a bridge to surface chemistry.

In this report we describe the first studies involving a heteronuclear triatomic transition-metal cluster, $FeCo_2^+$, in the gas phase using a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer[7,8] equipped with laser ionization.[9] The above cluster ion is generated in situ by a two-step process previously described in detail for $FeCo^+$.[10] This technique promises to greatly extend the variety and size of metal clusters now accessible by electron impact[1b,11] and multiphoton ionization.[12] The first step involves a gas-phase ion–molecule reaction between a monatomic ion and a transition-metal carbonyl complex in which one or more carbonyls are displaced.[13] Next, collision-induced dissociation (CID)[8,14,15] of the resulting ion strips the remaining carbonyls from the complex producing the bare metal cluster ion. $FeCo_2^+$ is produced by CID on $FeCo_2(CO)_5^+$ (formed in reaction 2) ac-

$$Fe^+ + Co_2(CO)_8 \xrightarrow{20\%} FeCo_2(CO)_6^+ + 2CO \qquad (1)$$

$$Fe^+ + Co_2(CO)_8 \xrightarrow{80\%} FeCo_2(CO)_5^+ + 3CO \qquad (2)$$

celerated to 49-eV kinetic energy and isolated by swept double-resonance ejection pulses.[8] This undoubtedly results in formation of $FeCo_2^+$ with a distribution of internal energies. The CID collision gas pressure was kept high ($\sim 5 \times 10^{-6}$ torr) relative to the reagent gas pressure ($\sim 1 \times 10^{-7}$ torr), therefore, in order to allow the excess energy to be dissipated by thermalizing collisions with argon prior to reaction.

Table I. Distribution of Neutral(s) Lost in the Reactions of $FeCo_2^+$ with Aliphatic Alkanes[a,b]

	neutral(s) lost						
alkane	H_2	$2H_2$	$3H_2$	$4H_2$	C_2H_4 + H_2	C_2H_6 + H_2	C_2H_4 + $2H_2$
methane[c]							
ethane[c]							
propane	100						
butane	69	31					
2-methylpropane	100						
pentane	58	32	10			trace	
2-methylbutane	55	45					
2,2-dimethylpropane[c]							
hexane		56	20	7	10		7

[a] Argon present as collision gas at 5×10^{-6} torr of total pressure. [b] Product distributions are reproducible to ±10%. [c] No reaction is observed.

Both $FeCo^+$ and Co_2^+[1b] are unreactive toward alkanes in the gas phase in contrast to Fe^+ and Co^+, which are highly reactive. Interestingly, a recent study has shown that Co_2CO^+ does react with alkanes by C–H bond insertion.[16] This reverse trend has also been observed in matrix-isolation studies where iron dimers[17] and small nickel crystallites[18] were found to be more reactive toward alkanes than the corresponding metal atoms. Contrary to the above dimer ions, $FeCo_2^+$ is reactive with aliphatic alkanes (Table I.). No reaction is observed with methane, ethane, and neopentane. Propane, butane, isobutane, and 2-methylbutane react exclusively by dehydrogenation, as opposed to the bare metal ions, Fe^+ and Co^+, which react predominantly by C–C bond cleavage.[1-6] Pentane and hexane yield predominantly dehydrogenation products with a small amount of C–C bond cleavage products also observed.

Decomposition of metal–ligand complexes by collisional activation yields both structural as well as fundamental information on fragmentation pathways.[5] CID of $FeCo_2C_3H_6^+$ produced from propane yields predominantly elimination of C_3H_6 in high efficiency with a small amount of C_2H_4 and CH_4 elimination also observed. Elimination of C_2H_4 to generate $FeCo_2CH_2^+$ may involve a metallacyclic intermediate in analogy to olefin metathesis.[19,20] $FeCo_2C_4H_6^+$ formed from butane generates $FeCo_2C_4H_4^+$, $FeCo_2C_4H_2^+$, and $FeCo_2C_2H_2^+$ upon collisional activation in low efficiency with $FeCo_2^+$ observed at high kinetic energy. This is in stark contrast to $FeC_4H_6^+$ and $CoC_4H_6^+$, which

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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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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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