Table I. Intensity of Fluorescence of Methylviologen Dication with Different Concentrations of Clays

concn, g/L	% cec[a]	fluorescence[b] intensity
	Montmorillonite	
0.20	5.6	40
0.15	7.5	42
0.10	11	41
0.05	22	36
0.02	56	25
0.01	112	14
	Hectorite	
0.50	2.8	82
0.25	5.6	64
0.05	28	40

[a] % cec is the fraction of the clay-exchangeable cations which have been replaced by MV^{2+}. % cec was calculated by using the previously determined cation-exchange capacity of the clay (0.89 mequiv/g for montmorillonite and 0.72 mequiv/g for hectorite).[6] $[MV^{2+}] = 5.0 \times 10^{-6}$ M. [b] Given in arbitrary units. The intensity scales for the two clays were not identical. The quantum yields were 0.070 for hectorite and 0.014 for montmorillonite.

structure for intercalation. On the basis of above evidence, it may be reasonable to attribute the observation of fluorescence of MV^{2+} to a reduction of nonradiative deactivation processes when it is in such a planar configuration. We note that fluorescence from a strained MV derivative, 1,1′-ethylene-2,2′-dipyridinium dichloride (diquat dichloride), has been reported previously ($\phi_F = 0.04$).[18] Similar steric arguments have been put forward to explain the strong increase of fluorescence of 2-*p*-toluidinyl-6-naphthalenesulfonate (TNS) when bound to proteins.[19] Clearly when MV^{2+} is intercalated into clays any external quenching by the chloride anion will be reduced. However, the iron content of the clays may act as possible quencher of MV^{2+} fluorescence.[12] We therefore measured the fluorescence of MV^{2+} in different clays having different iron content.[20] The measured intensities were 5 times larger in hectorite compared to montmorillonite whereas no fluorescence could be detected in samples with nontronite. The fluorescence spectral maximum was 328 nm in hectorite and 330 nm in montmorillonite. Quantum yields were 0.070 and 0.014 in the two clays, respectively. The relative iron content of these three swelling clays provides a satisfactory rational for the observed differences in fluorescence efficiency.

The effect of the ratio of MV^{2+}/clay on the fluorescence intensity was also investigated (Table I). In the case of hectorite there was a decrease in fluorescence intensity as the fraction of the clay-exchangeable cations replaced by MV^{2+} (percent cec; see Table I) increased (decreasing clay concentration). The same trend was observed for montmorillonite. The fluorescence enhancement with increasing clay concentration (up to 0.2 g/L) cannot be the result of stacking of MV^{2+} on the clay surface as has been shown to be the case for the radical cation $MV^{+\bullet}$.[21,22] Rather, it may be explained by one or both of two possibilities since there was no free MV^{2+} for cec < 90%.[23] There may be more than one binding site for MV^{2+} with the colloidal particles. A weak binding to the surface of the clay may be a site in which the MV^{2+} retains some internal flexibility and which is exposed to external quenchers. In such a location the MV^{2+} fluorescence would be reduced. The second site would be a preferential intercalation into the interlayer region of the clay where the MV^{2+} dication was rigidly bound. A similar interpretation has been proposed by Schoonheydt et al.[24] to explain the fluorescence behavior of $Ru(bpy)_3{}^{2+}$ adsorbed onto clay particles. Alternately self-quenching of fluorescence of MV^{2+} may be occurring at the higher percent cec as the sites become saturated with MV^{2+}.

Time resolved fluorescence measurements provide additional information on the binding processes.[25] The fluorescence decay of MV^{2+} in hectorite (0.05 g/L) obeyed double exponential kinetics with decay times of 3.51 and 1.57 ns. The fluorescence contribution of each component to the total spectrum was 0.72 and 0.28, respectively.[25] In the case of MV^{2+} and montmorillonite (0.5 g/L) the decay times were 1.13 and 0.37 ns with fractional fluorescences of 0.37 and 0.63, respectively. These results support the model of two different binding sites for MV^{2+} in the clays. The lower values in montmorillonite may be due to quenching by bound iron.

Experiments are under way to verify our interpretation, to further characterize the fluorescence of the adsorbed MV^{2+} into clays, and to exploit these observations to provide a better understanding of the structure and function of the system.

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Dehydrogenation of Isobutane by Oxygen-Deficient Cobalt/Oxygen Cluster Ions

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We report the gas-phase reactions of coordinated cobalt/oxygen cluster ions with isobutane using chemical ionization/fast-atom bombardment (CI/FAB) mass spectrometry.[1-3] In particular, the activation of hydrocarbon bonds in the alkane by metal/oxygen cluster ions of certain stoichiometries is reported, and the reactivity is discussed in terms of the structure of the reactive metal/oxygen cluster ions.

Metal cluster ions were formed by the bombardment of a metal foil with an energetic (8 keV) primary beam of fast xenon atoms. The sputtered metal cluster ions react with O_2 in the high-pressure (0.1–0.2 torr) ion source,[3] and the metal cluster product ions were analyzed in a reverse-geometry, double-focusing mass spectrometer[4] by collision techniques.[5] Three types of coordinated co-

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Table I. Collision-Induced Neutral Fragments of Cobalt/Oxygen/Isobutane Cluster Ions

	% relative abundances[a]								
parent ion	H	H_2	O	H_2O	CH_4	C_2H_4	C_3H_4	C_4H_8	C_4H_{10}
$[Co_2OC_4H_8]^+$	3	3	12	11		3	5	100	
$[(Co_2O)HC_4H_8]^+$		7	31					100	
$[Co_2OC_4H_{10}]^+$		90	10						100
$[Co_3O_2C_4H_8]^{+b}$	<1	2		2		6	29	100	
$[(Co_3O_2)HC_4H_8]^+$	3	1	8	3			100	83	
$[Co_2O_2C_4H_{10}]^+$	5	2		2					100
$[Co_3O_3C_4H_{10}]^+$	2	<1							100
$[CoC_4H_8]^{+c}$	3	15			22			100	
$[CoC_4H_{10}]^+$	2	33			100				55
$[Co_2C_4H_{10}]^+$									100
$[Co_3C_4H_{10}]^+$		10							88

[a] Relative to 100% for the most abundant fragmentation. No correction has been made for unicluster dissociations. Fragmentations corresponding to cobalt-containing moieties are not shown. [b] The loss of CH_3 was observed also (relative abundance = 6). [c] The loss of C_3H_7 was observed also (relative abundance = 8).

balt/oxygen cluster product ions were observed: oxygen-deficient clusters $[Co_xO_{x-1}]^+$, oxygen-equivalent clusters $[Co_xO_x]^+$, and cobalt-deficient clusters $[Co_xO_{x+1}]^+$ (in low abundance). These metal/oxygen cluster ions are similar to those produced by beam techniques and by ion cyclotron resonance mass spectrometry.[6]

The reaction of the cobalt/oxygen cluster ions with isobutane produces novel cluster product ions, for example, $[Co_xC_4H_{10}]^+$ (x = 1–5), $[Co_xO_xC_4H_{10}]^+$ (x = 1–4), $[Co_xO_{x-1}C_4H_{10}]^+$ (x = 1–4), and $[Co_xO_{x-1}(C_4H_{10})_2]^+$ (x = 1–2) clusters. These cluster ions correspond to the attachment of an isobutane molecule(s). At the pressures employed, it is probable that the cobalt/oxygen/isobutane cluster ions are collisionally stabilized association complexes.[2,3] Products containing the $[Co_xO_{x+1}]^+$ moieties were not observed presumably because of the low precursor cluster ion abundance.

Other ions observed include $[CoCH_3]^+$, $[CoC_3H_6]^+$, and $[CoC_4H_8]^+$, formed by gas-phase reactions[3] of sputtered Co^+ with isobutane. The $[CoC_3H_6]^+$ and $[CoC_4H_8]^+$ species correspond to exothermic reactions of Co^+ with i-C_4H_{10}.[7,8] The observation of the endothermic reaction product $[CoCH_3]^{+}$[8] indicates that the cobalt ions are sputtered with excess kinetic energy or in excited states. In fact, the energy distributions of sputtered metal ions have been shown to be broad, extending beyond 20 eV.[9]

Table I presents the relative abundances of pertinent fragmentations observed in the collision-induced dissociation of the more abundant cluster product ions. The oxygen-equivalent $[Co_xO_xC_4H_{10}]^+$ (x = 2,3) clusters dissociate primarily by the loss of isobutane. Fragments were not observed that correspond to the dissociation of hydrocarbon bonds. This indicates that isobutane is bound weakly in the cluster ion and that there is no significant interaction between Co_xO_x moieties with isobutane bonds. Similar results were observed for the dissociation of the $[Co_2C_4H_{10}]^+$ cluster. (It is known that the Co_2^+ dimer does not react with isobutane (exothermically) to cleave C–C or C–H bonds.[7,10])

Cluster products $[Co_xO_{x-1}C_4H_8]^+$ (x = 2–4) were observed in the CI/FAB mass spectrum corresponding to the dehydrogenation of isobutane on the oxygen-deficient metal cluster ion. Analogous cluster products $[(Co_xO_{x-1}H)C_4H_8]^+$ (x = 2,3) also were observed. The core of these clusters apparently corresponds to a hydroxylated cobalt/oxygen cluster ion.[11] The $[Co_2OC_4H_8]^+$, $[Co_3O_2C_4H_8]^+$, and $[(Co_3O_2H)C_4H_8]^+$ clusters also dissociate to lose C_3H_4. By comparison, $[CoC_4H_8]^+$ dissociates to form a $[CoC_3H_4]^+$ fragment (Table I), and Co^+ reacts with isobutene at translational energies greater than 0.5 eV to form $[CoC_3H_4]^{+}$.[12] A reasonable assumption is that the clusters are π-bonded complexes because of the moderate bonding interaction between C_4H_8 and the cobalt/oxygen cluster core.

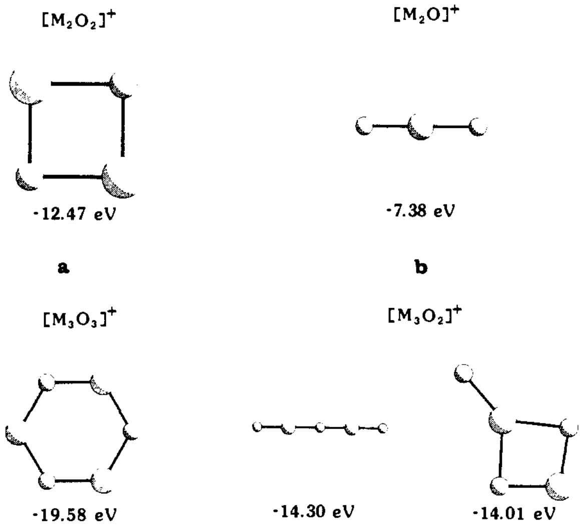

Figure 1. Low-energy structures of metal/oxygen clusters obtained by energy optimization through an electrostatic model.[13,14] (a) The low-energy structures of the oxygen-equivalent $[Co_2O_2]^+$ and $[Co_3O_3]^+$ clusters. The cobalt atoms in the ring structures of the oxygen-equivalent cluster ions may not be sterically accessible for reaction. The corresponding linear structures were found to lie 0.9 and 1.39 eV above the respective closed structures. (b) The low-energy structures of the oxygen-deficient $[Co_2O]^+$ and $[Co_3O_2]^+$ clusters. The structures of the oxygen-deficient clusters possess terminal cobalt atoms available for reaction by insertion into isobutane bonds.

The predominant fragmentations of the oxygen-deficient $[Co_2OC_4H_{10}]^+$ clusters correspond to the loss of C_4H_{10} and the loss of H_2 (to produce a $[Co_2OC_4H_8]^+$ fragment). Also, the $[Co_3O_2C_4H_{10}]^+$ cluster unimolecularly dissociates by loss of H_2. We conclude that the $[Co_xO_{x-1}C_4H_8]^+$ clusters are formed by the rapid dissociation (dehydrogenation) of the $[Co_xO_{x-1}C_4H_{10}]^+$ clusters. Analogous products and fragments are observed from/as diadduct species $[Co_2O(C_4H_n)(C_4H_m)]^+$, where ($n$,$m$) = (10,10), (9,10), (8,10), and (8,8). The dehydrogenations reported here are suggestive of structurally related reactivity, and they may be analogous to the gas-phase reaction of $[Co_2CO]^+$ with isobutane that is proposed to occur by insertion of the polarized, bare-metal end of (CO)–Co–Co^+ into C–H bonds.[10]

The difference in reactivity of the cobalt/oxygen cluster ions may be due to a structural difference between the oxygen-deficient and the oxygen-equivalent cobalt cluster ions. We have inves-

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tigated structures of the cobalt/oxygen cluster ions by geometry optimization[11,13] based on an ionic model.[14] The low-energy structures (Figure 1a) of the unreactive oxygen-equivalent $[Co_xO_x]^+$ clusters consist of closed structures: rings, ladders, and cages.[1] The low-energy structures (Figure 1b) of the reactive oxygen-deficient $[Co_xO_{x-1}]^+$ clusters consist of chains and structures with terminal cobalt atoms.[11] The terminal cobalt atom in these reactive clusters is sterically accessible or on an edge of the cluster ion, which reacts by insertion into hydrocarbon bonds. The oxygen-equivalent cluster ions do not react because there are no cobalt atoms accessible for reaction. These arguments are analogous to the perception that catalysis occurs on steps or defects of metal surfaces.[15]

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Proton-Catalyzed Cis–Trans Stereomutation of *cis*-1,2-Diarylcyclobutanes

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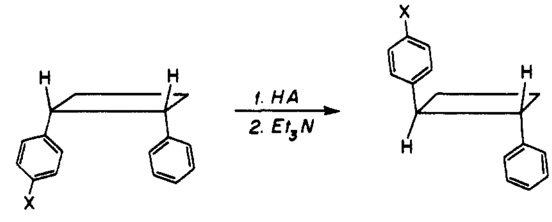
When cyclopropanes that possess vicinal aryl substituents are treated with trifluoroacetic acid they often undergo cis–trans stereomutation much more rapidly than they ring open.[2,3] Several studies of this unusual reaction have shown that (1) aryl substituents with electron-donating groups in the ortho or para position enhance the rate of stereomutation[2,3] and (2) when the reaction is catalyzed with deuterated acid the isolated products show no evidence of significant deuterium incorporation after short reaction times.[3] The mechanism of this reaction is not yet settled; however, we have suggested that it may proceed via a cyclization-induced rearrangement that requires acid catalysis.[3] An intriguing corollary of this hypothesis is that 1,2-diarylcycloalkanes other than cyclopropanes should also be susceptible to catalytic cis–trans stereomutation by Brønsted acids. In this paper we report that two new examples of facile, acid-catalyzed cis–trans stereomutation of *cis*-1,2-diarylcycloalkanes have been found.

Our initial work in this area focused on the reactions of *cis*-1,2-diphenylcyclobutane (**1a**) in Brønsted acids. Cyclobutane **1a** and an authentic sample of the corresponding trans diastereomer, **2a**, were prepared by the methods of Dodson and Zielske.[4] Cyclobutane **1a** was recovered unchanged after standing in trifluoroacetic acid at 25 °C for 20 h; however, when **1a** was allowed to react in 19:1 methylene chloride–trifluoromethanesulfonic acid at 0 °C for 5 min, followed by a triethylamine quench, we isolated analytically pure *trans*-1,2-diphenylcyclobutane (**2a**) in 95% yield (Figure 1).



1a: X = H; A = CF_3SO_3
1b: X = CH_3O; A = CF_3CO_2

2a: X = H
2b: X = CH_3O

Figure 1.

The stereomutation of **1a** was also carried out with 9:1 methylene chloride–trifluoromethanesulfonic acid-*d* at 0 °C and the reaction was quenched after 2 min. The crude product from this reaction consisted of a clean, 1:1 mixture of *cis*- and *trans*-1,2-diphenylcyclobutanes. Mass spectrometric analysis of the individual diastereomers isolated from the mixture confirmed extensive deuteration in both.[5] In fact, both diastereomers incorporated up to 10 deuterium atoms, approximately equal amounts of d_4 and d_5 species predominating in each. There was less than 2 mol % of d_0 material in either of the isolated products. ^{2}H NMR spectra of these products demonstated that deuterium exchange occurred exclusively in the phenyl rings.[6]

Unfortunately, even 19:1 methylene chloride–trifluoromethanesulfonic acid is partially heterogeneous at 0 °C. We desired to study the stereomutation reaction under homogeneous conditions; however, **1a** proved to be unreactive in trifluoroacetic acid and in chlorosulfonic acid over 0–25 °C. Reactions of **1a** in solvent systems containing fluorosulfonic acid or sulfuric acid produced varying amounts of intractable side products.

cis-1-(4-Methoxyphenyl)-2-phenylcyclobutane (**1b**)[7] proved to be conveniently soluble in a variety of Brønsted acids and much more reactive toward acid-catalyzed stereomutation than **1a** (Figure 1). Thus, when **1b** was allowed to react in trifluoroacetic acid at 25 °C for 3 h a 2:1 mixture of **1b** and *trans*-1-(4-methoxyphenyl)-2-phenylcyclobutane (**2b**), respectively, was obtained in 83% yield. When cyclobutane **1b** was allowed to react in trifluoroacetic acid-*d* at 25 °C for 5.25 h a 1:1 mixture of cis and trans diastereomers was isolated in 97% yield. Mass spectrometric analysis of the separate diastereomers from this reaction showed that both contained newly incorporated deuterium; however, the maximum amount of deuterium uptake in this case was only two atoms in each.[8] ^{2}H NMR analysis of the cis and trans products unambiguously demonstrated that deuterium incorporation occurred exclusively in the activated ring, ortho to the methoxy group in both.[9]

Our results can be rationalized by a cyclization-induced rearrangement mechanism (Scheme I).[10] Thus, protonation of an aromatic ring[11] of cyclobutane **1** may be followed by rearrange-

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