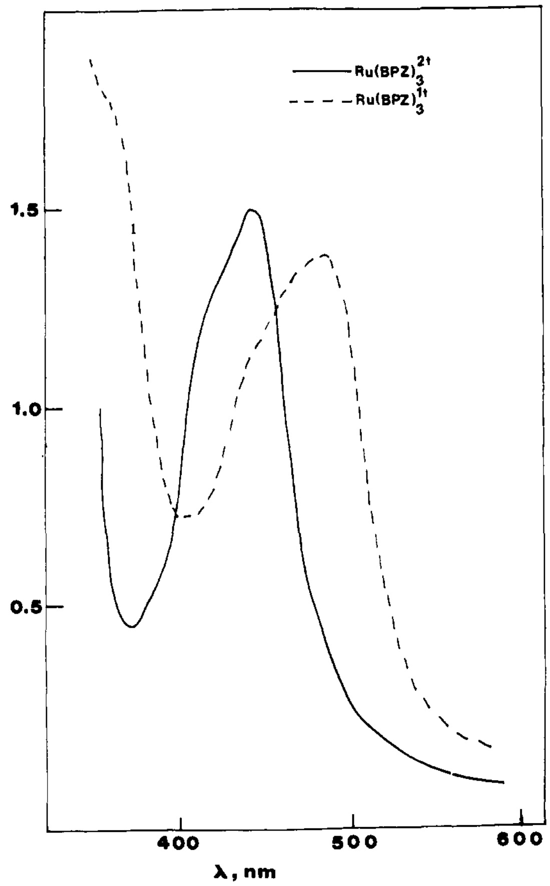

Figure 1. Visible spectrum of 9.0 × 10^{-5} M Ru(bpz)$_3^{2+}$ in ethanol in the presence of 0.2 M TEOA (—); after irradiation at λ = 435.8 ± 7 nm (---).

TEOA then scavenges Ru(bpy)$_3^{3+}$, re-forming Ru(bpy)$_3^{2+}$. On the other hand, Ru(bpz)$_3^{2+*}$ is reductively quenched by TEOA, forming Ru(bpz)$_3^+$ which in turn is oxidized by MV^{2+}. Figure 1 shows Ru(bpz)$_3^+$[19] as prepared by irradiating (λ 435.8 ± 7 nm) under nitrogen an ethanolic solution of Ru(bpz)$_3^{2+}$ and TEOA. When exposed to air Ru(bpz)$_3^+$ is oxidized to re-form Ru(bpz)$_3^{2+}$. The basic reaction mechanism for the above three-component system is thus

$$\mathrm{Ru(bpz)_3^{2+}} \xrightarrow{h\nu} \mathrm{Ru(bpz)_3^{2+*}} \tag{1}$$

$$\mathrm{Ru(bpz)_3^{2+*}} + \mathrm{TEOA} \rightarrow \mathrm{Ru(bpz)_3^{+}} + \mathrm{TEOA^+} \tag{2}$$

$$\mathrm{Ru(bpz)_3^{+}} + \mathrm{MV^{2+}} \rightarrow \mathrm{Ru(bpz)_3^{2+}} + \mathrm{MV^+} \tag{3}$$

Formal reduction potentials vs. SCE were obtained from cyclic voltammagrams on a Pt electrode in acetonitrile containing 0.1 M [Et$_4$N]ClO$_4$. Scan rates were 100 mV/s, and the separation between cathodic and anodic waves was approximately 60 mV. Ru(bpz)$_3^{2+}$ undergoes three reversible one-electron reductions, giving successively Ru(bpz)$_3^+$ ($E_{1/2}$ = −0.86 V), Ru(bpz)$_3^0$ ($E_{1/2}$ = −1.02 V), and Ru(bpz)$_3^-$ ($E_{1/2}$ = −1.26 V). Ru(bpy)$_3^{2+}$ shows the same behavior[20] but at reduction potentials approximately 0.5 V more negative. The 0.5-V positive shift in the reduction potential of Ru(bpz)$_3^{2+}$ probably explains why MV^{2+} does not oxidatively quench Ru(bpz)$_3^{2+*}$ and TEOA does reductively quench Ru(bpz)$_3^{2+*}$. The formal reduction potential of Ru(bpy)$_3^{2+*/+}$ is 0.78 V.[6] When a positive shift of 0.5 V is assumed, an estimated formal reduction potential of Ru(bpz)$_3^{2+*/+}$ is approximately 1.3 V. On the basis of the reduction potential of TEOA, E_0 (TEOA$^+$/TEOA) = 0.82 V,[1] reaction 2 is energetically favorable by approximately 0.5 V. A reduction potential of 1.3 V is thermodynamically capable of oxidizing water, E_0 (O$_2$/H$_2$O) = 0.82 V, pH 7.[4] The thermal oxidation of water, at lower reduction potentials, in the presence of RuO$_2$ catalyst, has been observed for Fe(bpy)$_3^{3+}$ [E_0(Fe(bpy)$_3^{3+/2+}$) = 0.980 V][21] and Ru(bpy)$_3^{3+}$[9,22] [E_0(Ru(bpy)$_3^{3+/2+}$) = 1.29 V].[8]

Further work on the Ru(bpz)$_3^{2+}$ photocatalyst is in progress.

Acknowledgment. We are indebted to Imperial Esso and the Natural Sciences and Engineering Research Council for financial support. We also thank Paul C. Minor for the electrochemical studies.

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R. J. Crutchley, A. B. P. Lever*
Department of Chemistry, York University
Downsview, Ontario, M3J 1P3 Canada

Received June 19, 1980

Characterization of Complexes of Butanes with Transition-Metal Atomic Ions in the Gas Phase

Sir:

We report observation and characterization of complexes of transition-metal atomic ions with alkanes in the gas phase. The complexes are formed in processes exemplified by reaction 1 where

$$\mathrm{Fe(CO)^+} + i\text{-}\mathrm{C_4H_{10}} \rightarrow \mathrm{FeC_4H_{10}^+} + \mathrm{CO} \tag{1}$$

Fe(CO)$^+$ is formed by electron impact on Fe(CO)$_5$ or Fe$_2$(CO)$_9$. Collision-induced decomposition (CID) spectra of the metal–alkane complexes indicate structural differences between complexes formed from isomeric alkanes as well as differences between complexes of different metal ions with the same alkane. The differences in the CID spectra are related to differences in the reactions of the atomic metal ions with the alkanes.

The reactions of several alkanes with the M$^+$ and MCO$^+$ fragments formed by electron impact on transition-metal carbonyls are summarized in Table I. The reactions were identified by using ion cyclotron resonance techniques.[1] We recently reported the reactions of Fe$^+$ with isobutane, forming Fe(C$_3$H$_6$)$^+$ and Fe(C$_4$H$_8$)$^+$.[2] As indicated in Table I, Co$^+$ and Ni$^+$ reactions with isobutane are very similar to those of Fe$^+$. We postulated a mechanism involving metal insertion followed by β hydrogen-atom shift and reductive elimination to account for the Fe$^+$ reaction (Scheme I).[3] All the reactions of Fe$^+$, Co$^+$, and Ni$^+$ with the butanes are consistent with this basic scheme. Note particularly the dominance of the M(C$_2$H$_4$)$^+$ product in the reactions of *n*-butane. This suggests initial metal insertion into the middle carbon–carbon bond, the weakest bond in *n*-butane. An MC$_2$H$_4^+$ product could not be formed from *i*-C$_4$H$_{10}$ by the metal insertion β H-shift mechanism and is not observed as a product of the *i*-C$_4$H$_{10}$ reaction.

Mechanisms analogous to Scheme I have been proposed by Remick, Asunta, and Skell to account for the reaction of Ta atoms with butanes[4] and by Armentrout and Beauchamp to account for

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[1] For reviews of ion cyclotron resonance techniques, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971; T. A. Lehman and M. M. Bursey, "Ion Cyclotron Resonance Spectrometry", Wiley, New York, 1971.

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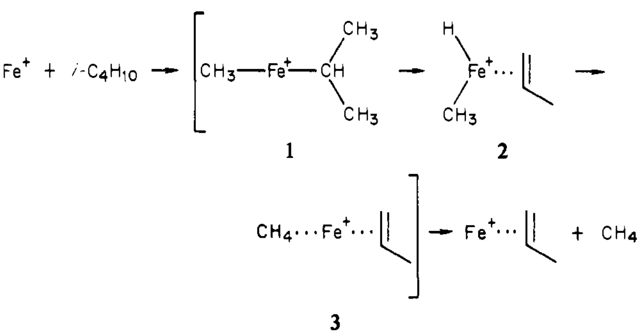
Table I. Relative Rate Constants of Reactions of M^+ and MCO^+ with Butanes[a]

	n-C_4D_{10} product ions					i-C_4D_{10} product ions		
reactant ion (M^+)	$MC_2D_4^+$	$MC_3D_6^+$	$MC_4D_6^+$	$MC_4D_8^+$	$MC_4D_{10}^+$	$MC_3D_6^+$	$MC_4D_8^+$	$MC_4D_{10}^+$
Cr^+ [b]	0.22	0	0.16	0.16	0	0	0.09	0
Fe^+ [c]	0.53	0.07	0.04	0.04	0	0.46	0.09	0
Co^+ [d]	0.53	0.09	0	0.13	0	0.82	0.15	0
Ni^+ [e]	0.14	0.02	0	0.07	0	0.29	0.04	0
$CrCO^+$ [b]	0	0	0	0	[1.00]	0	0	0.47
$FeCO^+$ [c]	0	0	0	0	0.07	0	0	0.07
$CoCO^+$ [d]	0	0	0	0	0.13	0	0	0.15
$NiCO^+$ [e]	0.33	0.04	0	0.18	0.26	0.29	0.09	0.46

[a] Estimated from relative abundances of product ions in the ion cyclotron resonance spectrum of the reaction mixture under conditions of low extent of conversion to products. The fastest reaction is assigned an arbitrary magnitude of 1.00. On this scale, the upper limit on the relative rate constants of unobserved processes is about 0.005. The absolute reaction rates are of the order $\sim 10^{-9}$ cm^3 molecule^{-1} s^{-1}. [b] Formed by electron impact on $Cr(CO)_6$. [c] Formed by electron impact on $Fe(CO)_5$ or $Fe_2(CO)_9$. [d] Formed by electron impact on $Co_2(CO)_8$. [e] Formed by electron impact on $Ni(CO)_4$.

Scheme I



the results of beam studies of the reaction of Co^+ with alkanes.[5] The reactions of Ni clusters with pentane reported by Davis and Klabunde[6] may also involve oxidative addition of the type suggested in Scheme I. Davis and Klabunde, however, conclude that Ni atoms are unreactive with alkanes. This contrasts with our observation that while the atomic ions are reactive Mn_2^+ and Co_2^+ formed by electron impact on $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ are unreactive.

Cr^+ reacts with both butanes, but primarily to eliminate hydrogen and form metal-butene and metal-butadiene complexes. Only with n-C_4H_{10} does Cr^+ react to eliminate an alkane. In that case, $CrC_2H_4^+$ is 40% of the overall product. This is in contrast to the reactions of Fe^+, Co^+, and Ni^+ with n-butane where $MC_2H_4^+$ is 78%, 71%, and 67% of the overall product. Furthermore, $Cr(C_3H_6)^+$ is not a product of reaction of Cr^+ with either i-C_4H_{10} or n-C_4H_{10}. Evidently, the only C–C bond in either butane susceptible to attack by Cr^+ is the C_2H_5–C_2H_5 bond in n-C_4H_{10}. That bond is the weakest bond in either butane [$D(CH_3$-i-$C_3H_7)$ = 83.8 kcal/mol, $D(CH_3$-n-$C_3H_7)$ = 84.8 kcal/mol, and $D(C_2H_5$–$C_2H_5)$ = 81.6 kcal/mol[7]]. Another difference between Cr^+ and the group 8 atomic ions is that the latter react with CH_3I to form MCH_3^+ while the former does not.[3b] Thus, Cr^+ contrasts quite markedly with the group 8 atomic ions. It prefers to attack C–H bonds rather than C–C bonds, and it is more selective than the group 8 atomic ions in attacking the weakest C–C bond. Mn^+ is less reactive still. It produces no observable product of reaction with small hydrocarbons.

The reactions of MCO^+ provide us with an opportunity to explore the potential surface on which the atomic metal ion reactions occur. The metal–alkane complexes formed in these reactions are lower in energy than metal–alkane complexes formed by direct association of the metal and the alkane. They are lower in energy by an amount equal to the dissociation energy of the M^+–CO bond. Thus, while direct bimolecular association is dissociative, leading to decomposition products such as $M(C_2H_4)^+$ and $M(C_3H_6)^+$, the reaction of MCO^+ leads to stable complexes such as $MC_4H_{10}^+$. If there is little or no energy barrier to metal insertion and if the β H-atom shift is a low-energy process, then these metal–alkane complexes should have structures such as **1**, **2**, or **3**.

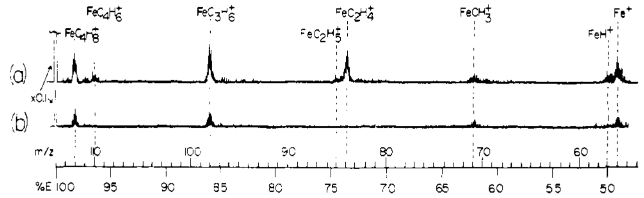


Figure 1. The collision-induced decomposition spectrum of $FeC_4H_{10}^+$ (m/z 114) formed in the ion source by reaction of $FeCO^+$ with n-butane (a) and isobutane (b). The accelerating energy was 6 kV, and the collision gas was He.

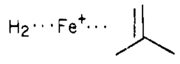
The collision-induced decomposition (CID) spectra[8] of the Fe^+-n-butane and Fe^+–isobutane complexes are shown in Figure 1a,b, respectively. The FeC_4H_{10} ions were formed by reaction 1 in the source of a reversed-geometry double-focusing mass spectrometer. The $FeC_4H_{10}^+$ ions (m/z 114) were accelerated to 6 kV and focused by the magnetic sector onto the entrance of a collision chamber containing He gas. The products of collision-induced decompositions emerge from the collision chamber with approximately the same velocity as the m/z 114 ions transmitted without collision. Hence, the collision products can be mass analyzed by the electrostatic energy selector. The collision-induced decomposition spectra are essentially the mass spectra of ions from which the ionic structures may be deduced by the usual rules of mass spectrometry.[8] Although rearrangements are possible, fragments are typically formed by cleavage of the weaker bonds in the parent ion.

The major fragments in both the Fe^+-n-butane complex (Figure 1a) and the Fe^+–isobutane complex (Figure 1b) are Fe^+–olefin complexes. This suggests that structure **3** dominates structures **1** and **2** in the isobutane case, and that **3** and the analogous structure **6** dominate **4** and **5** in the n-butane case. The absence

$$CH_3\!-\!Fe^+\!-\!CH_2CH_2CH_3 \qquad C_2H_5\!-\!Fe^+\!-\!C_2H_5 \qquad C_2H_6\cdots Fe^+\cdots \|$$

4 5 6

of $FeC_2H_4^+$ in the CID spectrum of the Fe^+–isobutane complex supports the notion that only structures accessible by metal insertion followed by β H-atom shift are formed. The Fe^+–butene complexes which are important fragments in the CID spectra of both Fe^+–butane complexes suggest structures **7** and **8**, analogous



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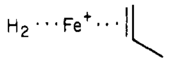

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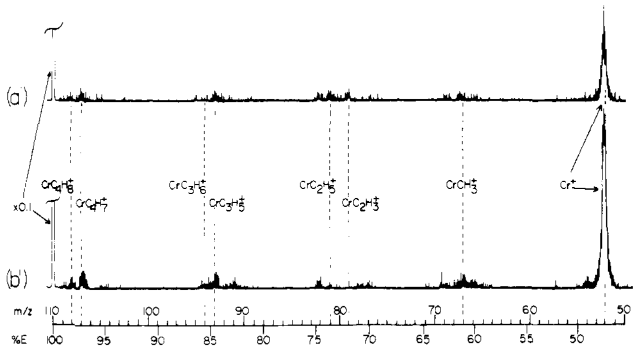

Figure 2. The collision-induced decomposition spectrum of $CrC_4H_{10}^+$ (m/z 114) formed in the ion source by reaction of $CrCO^+$ with *n*-butane (a′) and isobutane (b′). The accelerating voltage was 6 kV, and the collision gas was He. The small m/z 82 peak is $^{54}CrCO^+$ originating from $^{54}Cr(CO)_2^+$, which is a small fraction of the m/z 110 primary beam.

to **3** and **6**, which might be formed by insertion into a C–H bond followed by a β H-atom shift. Note that small amounts of $FeCH_3^+$ and $FeC_2H_5^+$ are observed, suggesting the occurrence of **1** in the isobutane case and **4** and **5** in the *n*-butane case. If we assume that $FeCH_3^+$ in the isobutane spectrum is formed from structure **1**, the absence of isopropyl cation from the spectrum suggests that $IP(FeCH_3) < IP(i\text{-}C_3H_7) = 7.36$ eV.[9] This in turn implies that $D(Fe^+\text{–}CH_3) - D(Fe\text{–}CH_3) > 11.8$ kcal/mol.

The striking feature of the CID spectra of the Cr^+–butane complexes shown in Figure 2 is the dominance of the Cr^+ fragment. This suggests that the Cr^+ is only loosely bound to the butane and that the butane tends to retain its integrity in the complex. This is consistent with the lesser extent of reactivity of Cr^+ with the butanes. Other fragments do appear in the CID spectrum, but they are mostly Cr^+–alkyl radical clusters rather than Cr^+–olefin clusters. These fragments suggest that there is some degree of incipient metal–carbon bond formation in the Cr^+–butane complexes but that β H-atom shift and reductive elimination do not proceed readily in the complexes. The lowest energy forms of the Cr^+–butane complexes are therefore very different from the lowest energy forms of the Fe^+–butane complexes.

Note Added in Proof: The reaction of Cr^+ with *n*-butane may result from the presence of ions in a long-lived excited state among the Cr^+ ions formed by electron impact on $Cr(CO)_6$. We observe Cr^+ from $Cr(CO)_6$ to react with CH_4 with a rate constant of ca. 10^{-10} cm^3 molecule s^{-1} to form $CrCH_2^+$. This reaction is almost certainly endothermic for ground state species. (See A. E. Stevens and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 6449 (1979), for data on $D(M^+\text{–}CH_2)$.) We also observe, using ion trapping techniques, that the kinetics of the reaction of Cr^+ with $Cr(CO)_6$ suggest two states of Cr^+ which react with different rates. The abundance of the slowly reacting state is roughly twice that of the rapidly reacting state. We have obtained no evidence that the reactions of Co^+, Fe^+, and Ni^+ with the butanes are affected by excited states.

Acknowledgement is made to Professor M. S. B. Munson for advice and helpful discussion; to the DuPont Co., Dr. C. E. McEwen, and Dr. M. Rudat for use of a VG Micromass ZAB mass spectrometer and assistance in obtaining the collision-induced decomposition spectra; to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work; and to the NSF for partial support of this work under Grant CHE-09952.

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R. B. Freas, D. P. Ridge*
Department of Chemistry, University of Delaware
Newark, Delaware 19711

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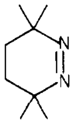
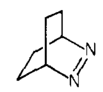
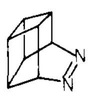
Facile Liquid-Phase Denitrogenation of "Reluctant" Azoalkanes on Photolysis with 185-nm Radiation

Sir:

While it is a well-established fact that cyclic azoalkanes, which contain the –N=N– linkage within a six-membered ring, resist denitrogenation (ϕ_r <0.05) on irradiation at 350 nm ($n_- \rightarrow \pi^*$ excitation),[1] we now report that at 185 nm ($n_+ \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ excitations) such "reluctant" azoalkanes can be smoothly and effectively denitrogenated into their corresponding hydrocarbons. Although it was suggested[2] that shorter wavelength radiation should promote denitrogenation, to the best of our knowledge the liquid phase 185-nm photochemistry of azoalkanes had not been previously investigated. The rich and abundant $\pi \rightarrow \pi^*$ photochemistry of cycloalkenes on 185-nm excitation[3] stimulated our interest in exploring the fate of the "reluctant" azoalkanes **1–3** on exposure to such "high-energy" radiation. As


	1	2	3	4
ϕ_{350}	0.008	0.011	0.00006	1.0
ϕ_{185}	0.22	0.50	0.20	1.0
ϕ_{185}/ϕ_{350}	~30	~50	~3000	1

the quantum yields show, 185-nm radiation causes a dramatic increase [especially for the diazabasketene (**3**)] in the photodenitrogenation efficiency of such "reluctant" azoalkanes, thus confirming our expectation that $n_+ \rightarrow \pi^*$ and/or $\pi \rightarrow \pi^*$ excitation should be effective for such purposes.

The 185-nm photolysis of the azoalkanes, prepared according to literature procedures,[4] was performed in Baker-Photrex pentane (0.01 M solution). A 50-W hot cathode mercury resonance lamp was used as the irradiation source; this was accommodated in a Suprasil immersion well and suspended into an outer vessel which contained the azoalkane solution.[5] The 254- and 350-nm (broad excitation band covering the range 310–420 nm) photolyses were performed in a Rayonet photoreactor under the same conditions as the 185-nm photolysis. Product analyses were made by vapor phase chromatography on a Perkin-Elmer Model 900 instrument equipped with a Perkin-Elmer Model II electronic integrator. The product composition, percent product formation, and quantum yields are reported in Table I.

Photodenitrogenation of azoalkane **4** and the cis–trans isomerization of cyclooctene were used as actinometers. The latter was previously used for 185-nm actinometry.[6] Consequently, the azoalkane **4**, which photodenitrogenates with essentially unit efficiency,[7] was first calibrated against the cyclooctene standard. An independent check confirmed gratifyingly that azoalkane **4**

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