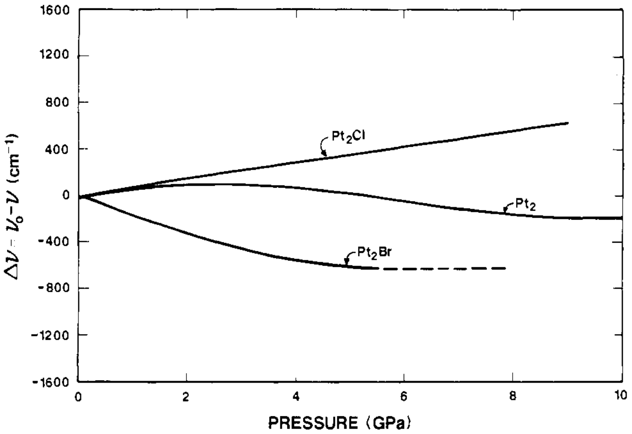

Figure 14. Relative energy shifts of the $d\sigma^* \rightarrow p\sigma$ transition in Pt_2Cl, Pt_2, and Pt_2Br.

varies, thereby indicating that there is a delicate balance among several competing effects. Increased coupling between the d_{z^2} and p_z orbitals, which may be somewhat larger in the monohalides because of the presence of the bridging halide, blue shifts $d\sigma^* \rightarrow p\sigma$. This appears to be the dominant effect in Pt_2Cl. The observed red shift in Pt_2Br can be explained in terms of band broadening of the $d\sigma^*$ and $p\sigma$ orbitals due to enhanced intermolecular interactions along the z axis. The band broadening should be larger in Pt_2Br than in Pt_2Cl, since Pt_2Br becomes delocalized more rapidly with increasing pressure.[17] A red shift of the $d\sigma^* \rightarrow p\sigma$ transition also results from an increase in the coupling of $d\sigma^*$ with the phosphorus σ orbitals, an effect that becomes important in Pt_2 at high pressure.

Acknowledgment. We acknowledge helpful discussions with Drs. Stephen F. Agnew, P. Jeffrey Hay, and Vincent M. Miskowski. M.A.S. thanks Dr. Agnew, Dr. Phillip D. Stroud, and Douglas G. Eckhart for technical assistance. This work was supported in part by the Center for Materials Science at Los Alamos National Laboratory. This work was performed under the auspices of the U.S. Department of Energy and was partially supported by the Materials Science Division under contract DE-AC02-76ER01198. Research at the California Institute of Technology was supported by the National Science Foundation (CHE8419828).

Registry No. Pt_2Cl, 99632-89-0; Pt_2Br, 85553-24-8; Pt_2, 89462-52-2; Pt_2Cl_2, 82135-56-6.

$[HNCO]^{\bullet+}$, $[HCNO]^{\bullet+}$, and $[CNOH]^{\bullet+}$ and Their Neutral Counterparts Studied by Mass Spectrometry[1]

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Abstract: The isomeric ions $[HNCO]^{\bullet+}$, $[HCNO]^{\bullet+}$, and $[CNOH]^{\bullet+}$ have been generated and characterized in the gas phase by mass spectrometry. The neutralization–reionization technique was used to identify their neutral counterparts as stable species in the gas phase. The ions and their neutral counterparts were not observed to isomerize or tautomerize.

In 1826 the first experimental evidence was presented for isomerism, a concept earlier put forward by Berzelius; Liebig and Wöhler, after long debate, reached agreement that fulminic acid, HCNO, and isocyanic acid, HNCO, have the same elementary composition but are structurally distinct.[2]

It was long believed that isocyanic acid, HNCO, and cyanic acid, NCOH, were in tautomeric equilibrium with the hydroxy form prevailing. During the period of 1935–1950 it was established, mainly from spectroscopic evidence, that the free acid exists exclusively as HNCO.[3] Spectroscopy[4] also showed that gaseous fulminic acid has exclusively the HCNO structure and not, as proposed by Nef in 1894,[5] the tautomeric CNOH structure. Although cyanic acid, NCOH, could be produced by photolysis of isocyanic acid in an argon matrix at 4 K,[6a] similar experiments with fulminic acid failed to produce isofulminic acid, CNOH.[6b]

Because of their historic importance and their possible participation in interstellar chemistry, these four [H, C, N, O] isomers have received considerable attention from theoreticians.[7] From recent ab intio molecular orbital theory calculations[7b] it was concluded that all four isomers are stable and that high energy barriers prevent their interconversion. HNCO was the most stable isomer; its experimental heat of formation, ΔH_f°, is ca. −105 kJ•mol^{-1}.[8] By using the calculated relative energies, ΔH_f°(NCOH) = −17 kJ•mol^{-1}, ΔH_f°(HCNO) = 228 kJ•mol^{-1}, and ΔH_f°(CNOH) = 235 kJ•mol^{-1}. In spite of their predicted stability, NCOH and CNOH have eluded observation in the gas phase.

No calculations are available for the four radical cations, and experimental results[9] have been limited. For HNCO its photo-

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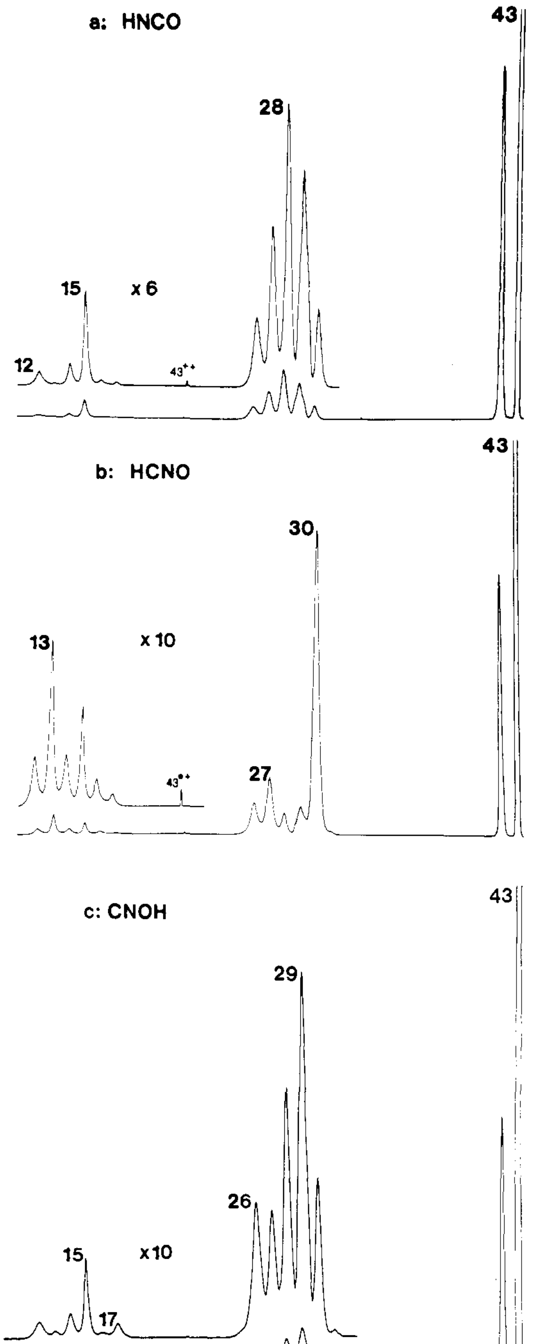

Figure 1. Collisional activation mass spectra, He (90% T), of [HNCO]$^{\bullet+}$ (a), [HCNO]$^{\bullet+}$ (b), and [CNOH]$^{\bullet+}$ (c).

electron spectrum,[9d] normal electron impact mass spectrum,[9a–c] and major metastable dissociation characteristics[9b,c,e] have been described. For HCNO only the photoelectron spectrum has been reported.[9f]

The structure and stability of gaseous ions can often uniquely be probed by the current mass spectrometric methodology.[10] Once the structure of the mass-selected ion is established, the neutralization–reionization (NR) technique[11] can be used to assess the stability of the neutral counterpart. We report here such an investigation for ionized and neutral HNCO, HCNO, and CNOH.

Table I. Kinetic Energy Releases of the Metastable Processes of the Three [H, C, N, O]$^{\bullet+}$ Isomers

	m/z 42	*m/z* 29	
	$T_{0.5}{}^{a}$	$T_{0.5}{}^{a}$	$T_{h}{}^{b}$
[HNCO]$^{\bullet+}$	204	863	606
[HCNO]$^{\bullet+}$	149	873	443
[CNOH]$^{\bullet+}$	118	908	624

[a] Measured from the peak width at half height of the metastable peak. [b] Measured from the width between the summits of the dished metastable peak.

Experimental Section

All experiments were performed with VG Analytical ZAB-2F mass spectrometers, modified for NR experiments as described elsewhere.[12] Briefly, the second field-free region of the mass spectrometer contains two gas cells with a beam deflector electrode between them. Xenon was admitted to the first cell for charge exchange neutralization of the mass-selected ions. Remaining ions were deflected away, and the neutrals were thereafter reionized by collision with helium in the second cell. Collisional activation (CA) mass spectra were recorded also with helium as target gas. Gas pressures were adjusted to give a main beam transmission of 90%, 90% T. In the above experiments all beam-defining slits were fully open to obtain maximum signal strength and to minimize energy resolving effects. Metastable peak shapes were recorded under higher energy resolution conditions: the main ion beam width at half height was 2 V at an accelerating voltage of 8 kV.

Contributions from natural isotopic abundances from adjacent ions of lower mass to the mass-selected ions were negligible.

Results and Discussion

Isocyanic acid, HNCO, can be made by depolymerization of cyanuric acid or by heating KNCO with $KHSO_4$ or a fatty acid (e.g., stearic acid).[13] Figure 1a shows the CA mass spectrum of ionized isocyanic acid. The intense peaks at *m/z* 28, [CO]$^{\bullet+}$, and 15, [NH]$^{\bullet+}$, are in keeping with the HNCO structure, and there was little sign of tautomerization to [NCOH]$^{\bullet+}$ (compare *m/z* 15, [NH]$^{\bullet+}$, and *m/z* 17, [OH]$^{\bullet+}$, note that the peak at *m/z* 29[14] was mainly of metastable origin). Additional support was obtained from the CA mass spectra of the *m/z* 42 and 27 ions generated by collision of *m/z* 43 with He in the first field-free region. The *m/z* 42 ions were clearly [NCO]$^{+}$ (intense peaks at *m/z* 28, [CO]$^{\bullet+}$, and 14, [N]$^{+}$), and the *m/z* 12–15 region showed that the *m/z* 27 ions were [HNC]$^{\bullet+}$.[15]

Unlike earlier methods, which required elaborate precautions,[3] gaseous fulminic acid, HCNO, was simply generated by thermolysis of chlorooximinoacetic acid, HON=C(Cl)COOH,[16] in the ion source of the mass spectrometer. The CA mass spectrum of the *m/z* 43 ions, Figure 1b, was in keeping with the HCNO structure, having major peaks at *m/z* 13, [CH]$^{+}$, *m/z* 27, [HCN]$^{\bullet+}$, and *m/z* 30, [NO]$^{+}$ (base peak). This spectrum differed sufficiently from that of [HNCO]$^{\bullet+}$ to preclude significant interconversion between those two isomers. Tautomerization to [CNOH]$^{\bullet+}$ must be very small because the daughter ion [CH]$^{+}$ was more prominent than [OH]$^{+}$ even though the product energies are similar: $\Delta H_f°([CH]^+) + \Delta H_f°(NO^\bullet) = 1713$ kJ·mol^{-1} and $\Delta H_f°([OH]^+) + \Delta H_f°(CN^\bullet) = 1731$ kJ·mol^{-1}.[8]

A signal due to [H, C, N, O]$^{\bullet+}$ ions was also present in the normal electron impact mass spectrum of methyl chloro-

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oximinoacetate, HON═C(Cl)C(O)OCH$_3$;[17] *m/z* 43 was 12% of *m/z* 59, [C(O)OCH$_3$]$^+$ (base peak). The CA mass spectrum of these ions, Figure 1c, was distinctly different from those of [HNCO]$^{•+}$ and [HCNO]$^{•+}$ and could not be constructed by any combination of Figure 1, parts a and b. Therefore a third [H, C, N, O]$^{•+}$ isomer had to be generated upon dissociative ionization of HON═C(Cl)C(O)OCH$_3$. On the basis of the relatively intense peaks at *m/z* 30, [NO]$^+$, 26, [CN]$^+$, and 17, [OH]$^+$, and the presence of *m/z* 31, [NOH]$^{•+}$ (all four thermochemically unfavorable dissociations[8]), we propose that these ions had the [CNOH]$^{•+}$ structure, a unit present in the precursor molecule. From the weak *m/z* 13, [CH]$^+$, peak it can be concluded that, as for [HCNO]$^{•+}$, tautomerization was unimportant (see above).

That we are dealing with three different isomers can also be concluded from their metastable ion (MI) mass spectra; generation of *m/z* 42 and 29, [HCO]$^+$,[14] were the sole metastable processes, but the kinetic energy releases (KER) were different, see Table I. Although the $T_{0.5}$ values of *m/z* 29 were closely similar, the peak shapes were not, the T_h value of *m/z* 29 from [HCNO]$^{•+}$ being considerably smaller. Thus we conclude that [HCNO]$^{•+}$ yields [HCO]$^+$ via a dissociation channel unavailable to [HNCO]$^{•+}$ and [CNOH]$^{•+}$. Consequently the barrier for rearrangement of [HNCO]$^{•+}$ into [HCNO]$^{•+}$ must be at least 375 kJ•mol^{-1}; $\Delta H_f°$([HNCO]$^{•+}$) ≈ 1016 kJ•mol^{-1},[18] and the appearance energy of *m/z* 29 from HNCO was 15.52 eV,[9e] yielding an energy for the transition state for generation of [HCO]$^+$ of 1392 kJ•mol^{-1}. The barrier for rearrangement of [HCNO]$^{•+}$ into [HNCO]$^{•+}$ and [CNOH]$^{•+}$ must be at least 120 kJ•mol^{-1} above [HCNO]$^{•+}$; with $\Delta H_f°$([HCNO]$^{•+}$) ≈ 1273 kJ•mol^{-1}.[19]

[H, C, N, O]$^{•+}$ ions were also obtained upon metastable fragmentation of the *m/z* 78 ions (expected structure [HON═CCl]$^+$) from methyl chlorooximinoacetate, and the kinetic energy release for this process, $T_{0.5}$, was 61 meV. The CA mass spectrum of the [H, N, C, O]$^{•+}$ ions generated upon *metastable* fragmentation of *m/z* 78 in the first field-free region of the mass spectrometer showed that these *m/z* 43 ions were predominantly [HNCO]$^{•+}$. Thus, the heat of formation of [CNOH]$^{•+}$ must be significantly larger than that of [HNCO]$^{•+}$, i.e., >1016 kJ•mol^{-1}. However, the CA mass spectrum of the *m/z* 43 ions generated *collisionally* from *m/z* 78 in the first field-free region (the most prominent CA process) closely matched that of the ion source generated *m/z* 43 ions (Figure 1c). Therefore C–Cl bond cleavage took place upon collision of [HON═CCl]$^+$ in the first-free region, yielding [CNOH]$^{•+}$ ions. On the basis of these results it is likely, although not evident from the CA mass spectrum (Figure 1c), that the *source generated* [H, C, N, O]$^{•+}$ flux from the methyl ester contains a small amount of [HNCO]$^{•+}$ in addition to [CNOH]$^{•+}$.[20]

To examine the stability of the neutral counterparts of these three [H, C, N, O]$^{•+}$ isomers NR mass spectra were recorded; those for [HNCO]$^{•+}$ and [HCNO]$^{•+}$ (Figure 2 (parts a and b, respectively)) showed a large recovery peak at *m/z* 43 and generally agreed well with their respective CA mass spectra. Thus HNCO and HCNO, generated by vertical neutralization, had sufficient lifetimes (about 0.5 μs in these experiments) to be reionized with helium, and neither isomerized nor tautomerized, showing that there is indeed a large barrier for their interconversion, in keeping with theory.[7b] Interpretation of the intense recovery signal[21] in the NR mass spectrum of the [H, C, N, O]$^{•+}$ ions from methyl chlorooximinoacetate (Figure 2c) is difficult. Does this signal represent stable CNOH and/or the small amount of cogenerated (stable) HNCO? From the smaller *m/z* 27:43 and *m/z* 15:43 ratios in this spectrum compared with that of [HNCO]$^{•+}$ (0.075 and 0.026 versus 0.101 and 0.039) it was concluded that at least part of the *m/z* 43 signal in the former spectrum must be due to neutralized and reionized [CNOH]$^{•+}$. Additional evidence came from the more intense *m/z* 29 peak in the NR mass spectrum of the [H, C, N, O]$^{•+}$ ions from the methyl ester (compare Figure 2 (parts c and a)). The *m/z* 29 ions were most likely generated upon dissociative ionization of stable CNOH, an important dissociation channel for the ion, see Figure 1c; fragmentation of CNOH into HCO$^•$/COH$^•$ + N$^•$ being much more energy demanding than direct N–O bond cleavage.[8] Thus, CNOH has to be stable on the time and energy scale of NR experiments, as predicted by theory.[7b] Like [HNCO]$^{•+}$ and [HCNO]$^{•+}$, the NR mass spectrum of [CNOH]$^{•+}$ resembled the CA mass spectrum; again *m/z* 29, [H, C, O]$^+$, 26, [CN]$^+$, and 17, [OH]$^+$, are prominent. The only significant difference between the CA and NR mass spectra was the decreased intensity of *m/z* 29 in the latter, a phenomenon also observed for [HNCO]$^{•+}$; for both ions the *m/z* 29:28 ratio was 2.6 times smaller in the NR mass spectrum than in the CA mass spectrum.

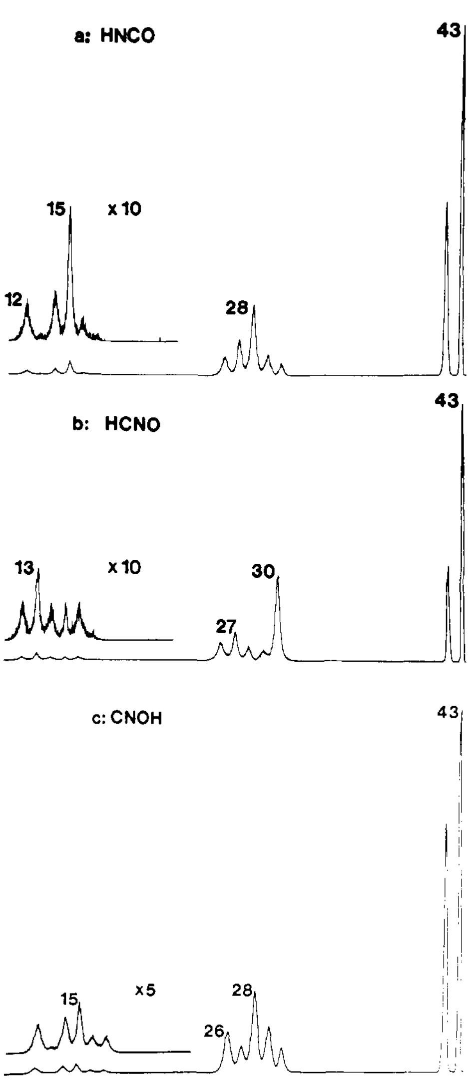

Figure 2. Neutralization–reionization mass spectra, Xe (90% T)–He (90% T), of [HNCO]$^{•+}$ (a), [HCNO]$^{•+}$ (b), and [CNOH]$^{•+}$ (c).

Conclusions

Winnewisser[22] recently pointed out that "We must conclude from the many unsuccessful attempts to detect the gas phase spectrum of the two isomers NCOH and CNOH, that they are kinetically unstable under laboratory conditions. The dominant

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[17] Methyl chlorooximinoacetate was made out of the ethyl ester[16] via transesterification.

[18] From $\Delta H_f°$(HNCO) = −105 kJ•mol^{-1} [8] and IE(HNCO) = 11.62 eV.[9d]

[19] From $\Delta H_f°$(HCNO) ≈ 228 kJ•mol^{-1} (see text) and IE(HCNO) = 10.83 eV.[9f]

[20] The source generated *m/z* 42 ions clearly were a mixture of [CNO]$^+$ and [NCO]$^+$.

[21] Note that the relative recovery ratios [*m/z* 43 yield in the NR mass spectrum: *m/z* 43 flux entering the neutralization cell] for [HNCO]$^{•+}$ and the [H, C, N, O]$^{•+}$ ions from the methyl ester were 1.0 and 0.7, respectively.

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mechanism for their interconversion seems to be reprotonation upon wall collisions of NCOH to HNCO and CNOH to HCNO". The NR technique provides walless conditions and so should be well suited for investigating these sensitive molecules. Indeed, the first experimental evidence for the stability of CNOH has been presented. It was also shown that $[\mathrm{HNCO}]^{\bullet+}$, $[\mathrm{HCNO}]^{\bullet+}$, and $[\mathrm{CNOH}]^{\bullet+}$ as well as their neutral counteparts do not isomerize or tautomerize in the microsecond timeframe. All these observations are in keeping with theoretical predictions.[7b]

Finally, experiments on the gas phase protonated analogues are in progress and will be reported in the near future.

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Osmium Tetroxide and Its Fragment Ions in the Gas Phase: Reactivity with Hydrocarbons and Small Molecules

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Abstract: Gas-phase ion-molecule reactions of OsO_n^+ (n = 0–4) with a number of hydrocarbons and small molecules, including CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, H_2, CO, NH_3, and SiH_4, have been investigated by Fourier transform ion cyclotron resonance spectrometry. Anion chemistry was briefly investigated. Thermochemical quantities derived include $D(\mathrm{Os}^+{-}\mathrm{O}) = 100 \pm 12$, $D(\mathrm{OsO}^+{-}\mathrm{O}) = 105 \pm 12$, $D(\mathrm{OsO}_2^+{-}\mathrm{O}) = 105 \pm 12$, $D(\mathrm{OsO}_3^+{-}\mathrm{O}) = 71 \pm 12$, $D(\mathrm{OsO}_3{-}\mathrm{O}) = 78 \pm 14$, $D(\mathrm{OsO}_4^+{-}\mathrm{H}) = 132 \pm 3$ kcal/mol, $D(\mathrm{OsO}_3^+{-}\mathrm{OH}) = 101 \pm 16$ kcal/mol, and $\mathrm{PA}(\mathrm{OsO}_4) = 161 \pm 2$ kcal/mol. Many diverse and novel reactions are observed. Among them are $[2_s + 2_s]$ cycloaddition with H_2, bond metathesis, oxo transfer, and hydrogen atom abstraction. These ions are also extraordinarily active dehydrogenation reagents; the most dramatic example is the sequential, complete dehydrogenation of SiH_4 to mono-, di-, and trisilicides. Another intriguing process is the double bond metathesis with NH_3, in which one or two oxo ligands are exchanged for imido groups. The number of oxo ligands is found to have a striking effect on the chemistry; mechanisms are discussed for the reactions observed. For example, the relative inertness of OsO_3^+ is attributed to a failure of the Os(+7) center to undergo oxidative addition. OsO_2^+ emerges as a potential model catalyst for the conversion of methane and dioxygen to aldehydes.

Gas-phase transition-metal ions have been the focus of much attention in recent years, with the library of reactions and the thermochemical base growing rapidly. The bulk of the early work emphasized the chemistry of naked, unligated metal ions. Although progress is being made in the investigation of ligand effects on reactivity, including some systematic studies by Freiser and co-workers,[1] much remains to be done in order to provide enough specific information for useful generalizations to be drawn.

Previous work on gas-phase transition-metal oxide ions includes studies of FeO^+ and CrO^+, among others. In early work, Kappes and Staley[2] determined that the relatively weak bond in FeO^+ permitted this species to catalyze the oxidation of small organic molecules by N_2O. Jackson et al.[3] subsequently found the oxo ligand to increase the reactivity of Fe^+ as well as appearing to favor C–H over C–C insertion in alkanes. The enhanced reactivity is ascribed to the exothermicity of H_2O elimination. In addition to chemistry typical of unligated metal ions, FeO^+ was found to react with hydrocarbons by radical loss processes. Neither FeO^+ nor Fe^+, however, is reactive with methane. In ion beam studies,[4] CrO^+ was found to react readily with hydrocarbons, while Cr^+ is unreactive. For example, CrO^+ oxidizes ethylene to acetaldehyde[4a] and ethane to ethanol.[4b] In another investigation,[5] MnO^+ has been observed to react with ethylene to yield both C_2H_4O and MnCH_2^+, the double bond metathesis products. This metathesis has also been identified as the minor channel in the reaction of ethylene with ClCrO_2^+.[6] The major products in this case correspond to oxygen transfer.

Despite the number of cases in which an oxo ligand increases reactivity, it is hazardous to generalize too freely. In the case of VO^+, reactivity is reduced relative to unligated V^+.[7] Since the $\mathrm{V}^+{-}\mathrm{O}$ bond is very strong, it is not cleaved during reactions, and the oxygen is thought to have little effect other than to occupy a coordination site on the metal.

Aside from the basic interest in ligand effects, motivation for studying the oxo ligand comes partly from condensed phase studies of metal oxides. In particular, hydrocarbon oxidation is a field of great scope and economic volume. A corresponding amount of effort and ingenuity has been directed to this area of research, and transformations mediated by metals and their oxides are increasingly prominent.[8] From an economic viewpoint, methane is a uniquely attractive target for controlled oxidation; its high abundance and low cost make it an ideal feedstock. For example, direct conversion to methanol would permit natural gas to be transported in a convenient and inexpensive liquid form.[9] Unfortunately, this particular process has not yet materialized on a commercial scale. There is also heavy demand for other potential products of direct methane oxidation, such as formaldehyde.[10]

For the present study, we have chosen to compare reactivity among the series of oxo ions derived from OsO_4. This compound

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