Caldwell et al.[14] showed a minimum around 530 K although those authors interpreted their data with a linear Arrhenius fit. It would be interesting to carry out experiments at higher T to confirm the minimum.

The KIEs are also compared in Table I. The experiments show that the KIE increases by 1.10 ± 0.08[15] over the range studied. Theory also predicts an increasing KIE by approximately the same amount, 10%. Both theory and experiment agree with the previously measured result[3] that the KIE is inverse at 300 K. The theoretical model indicates that the inverse KIE is due to both low-frequency (<300 cm^{-1}) transitional modes (i.e., modes that correlate with zero frequency at reactants) and C–H stretches, whose frequencies are higher at the transition state than at the reactants. Furthermore it indicates that the C–H stretches dominate the T dependence of the KIEs. Extended basis set ab initio SCF calculations[16] of reactant and transition-state frequencies confirm the qualitative correctness of these low- and high-frequency effects. Use of the ab initio C–H stretch frequencies both lowers the predicted KIEs and increases their T dependence (this may be the dominant error in the semiempirical modeling effort). The present results provide experimental support for previous theoretical work[13,17] on the $Cl^- + CD_3Cl$ and $H + HCD_3$ reactions which implicated both C–H stretches and low-frequency transitional modes as strong contributors to inverse α-deuterium secondary KIEs.

These studies suggest that the measurement and modeling of the temperature dependence of kinetic isotope effects are a sensitive probe of organic transition states for gas-phase reactions.

Acknowledgment. This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences. A.G.-L. acknowledges a Fulbright Scholarship at the University of Minnesota, 1989–1990.

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Emission of Radiation by Collisionally Activated Ions: A New Approach to Ion Structure Determination

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Received July 1, 1991

Experimental techniques for assigning structures to polyatomic organic ions in the gas phase have been vigorously developed over the past 20 years and were reviewed in 1985.[1] The chief methods have involved ion energetics and mass spectral fragmentation behavior. The collision-induced dissociation (CID) of mass-selected, fast (keV) ion beams has provided vital information for ion structure assignment. Many ingenious collision-based methods have been described, e.g. charge stripping,[2] charge reversal,[3] neutralization–reionization,[4] angle resolved mass spectrometry,[5] and surface-induced dissociation,[6] but their limitation lies in that they all produce another mass spectrum which must then be empirically analyzed. With this in mind the present work was begun to investigate the relationship between ion structure, fragmentation characteristics, and the collision-induced emission of radiation.

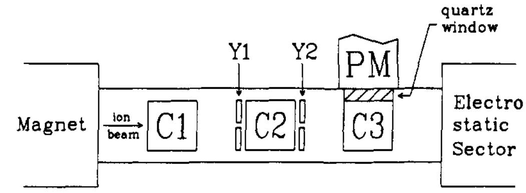

Figure 1. Schematic diagram of the experimental region of the mass spectrometer (details in text).

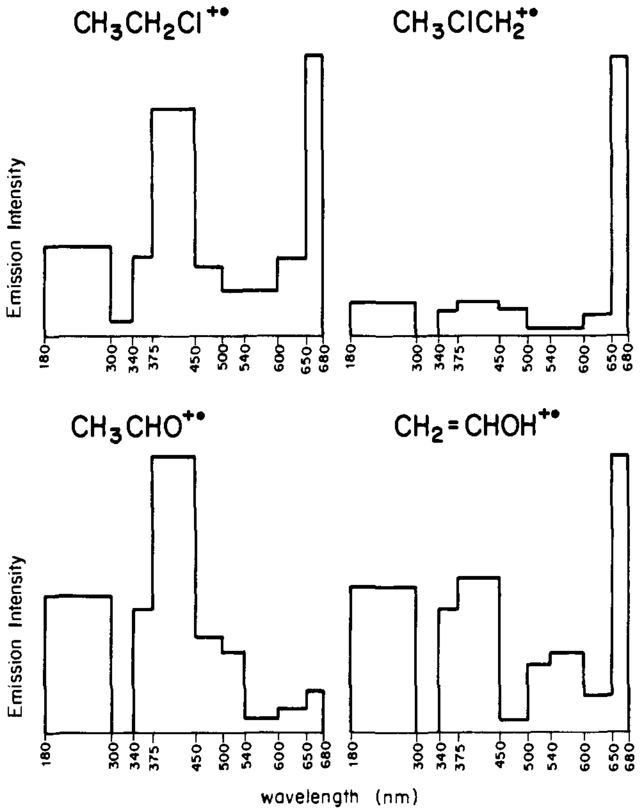
$CH_3CH_2Cl^{+\bullet}$ $CH_3ClCH_2^{+\bullet}$ $CH_3CHO^{+\bullet}$ $CH_2{=}CHOH^{+\bullet}$

Figure 2. Collision-induced emission spectra for $CH_3CH_2Cl^{\bullet+}$, $CH_3ClCH_2^{\bullet+}$, $CH_3CHO^{\bullet+}$, and $CH_2{=}CHOH^{\bullet+}$. He target gas in collision cell C2; 80% beam transmission; emission intensity in arbitrary units.

To study light emitted by collisionally excited ions, a new collision cell was constructed for the second field-free region of our VG ZAB-2F mass spectrometer[7] (Figure 1). C1 and C2 are conventional collision cells. Y1 and Y2 are variable y-axis ion beam collimating slits. The new cell, C3, has a quartz window and highly polished interior. Radiation from ions excited by collision in C1, C2, or C3 is detected by a photomultiplier (THORN EMI 9924QB) placed beyond the quartz window. For the preliminary experiments described here, spectra were obtained by sequentially placing eight wavelength cutoff filters[8] between the window and the photomultiplier, dividing its response range (180–680 nm) into nine regions (see Figure 2). The spectra were corrected for the average photomultiplier response over each region. Without data accumulation, signal-to-noise was between 10 and 2, depending on the wavelength (PM response). Signal averaging (5–10 min) sufficed reliably to measure weak signals,

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especially in the "red" region of each spectrum, where the photomultiplier response is low.

The spectra reported here were from ions collisionally excited in C2; therefore only relatively long lived excited states (0.1 μs) are involved. At present we cannot *quantitatively* correct for other identified sources of radiation resulting from a collision experiment performed in C3, e.g. target gas emissions and emissions from metal surfaces caused by collisions with scattered ions.

The ions, H_3^+ and $H_2^{\bullet+}$, were studied as model systems, using He target gas, to limit the number of emitting species. Before presenting our results, previous studies will be reviewed. Ford et al.[9] have also studied H_3^+ and $H_2^{\bullet+}$ using ion beams of 75–400 keV and He target gas. For H_3^+, the lifetime of $H^\bullet(n=3)$ produced was assessed by detecting Balmer-α photons. Emissions between 550 and 580 nm, recorded ca. 3×10^{-8} s after neutralization of keV beams of H_3^+ using alkali metal vapors as the electron transfer target, have been reported by Figger et al.[10,11] They proposed that the emission arose from $H_3^\bullet$ transitions originating in the $n = 3$ and 2 electronic levels. Measurements of the kinetic energy released in the formation of product ions and neutrals by keV collisions of H_3^+ with He target gas showed[12] $H^\bullet$ (2p) and H_2 (B $^1\Sigma_u^+$) as the only excited state products. Yenen and Jaecks[13] detected Lα photons in the reaction $H_3^+ + He \rightarrow H_2^{\bullet+} + H^\bullet(n=2) + He$. Emissions from H_3^+, $H_3^\bullet$, $H_2^{\bullet+}$,[14-16] and H_2[16] may lie outside either our wavelength range or time scale. Indeed, our only observed emission, 650–680 nm, coincided with the Balmer-α transition for $H^\bullet$ ($n = 3$ to 2, 656 nm), indicating that some $H^\bullet$ resulting from the dissociation of H_3^+ is in the $n = 3$ electronic state, consistent with the work by Ford et al.[9]

The $H_2^{\bullet+}$ spectrum in the present work was more complex. A strong signal in the 650–680-nm region implies that excited-state $H^\bullet$ was formed, consistent with earlier observations.[9,17] Spectral structure observed between 375 and 500 nm may be due to neutralization of $H_2^{\bullet+}$ to form excited H_2.[17] Huber and Herzberg[18] list numerous singlet–singlet transitions within this region, terminating in the B $^1\Sigma_u^+$ electronic state of neutral H_2. A gap between 500 and 600 nm is consistent with the above singlet–singlet transitions. UV emission between 180 and 340 nm was also observed by Gellene et al.[19] in the emission spectrum of $H_2^{\bullet+}$ using K as the target gas. It was assigned to the triplet–triplet transition, $a^3\Sigma_g^+ \rightarrow b^3\Sigma_u^+$. Once wavelength resolution is improved by the use of a monochromator, transitions will be more accurately identified.

In contrast, the emission spectra for polyatomic organic ions were more complex. The isomeric ions $CH_3CH_2Cl^{\bullet+}$ and $CH_3ClCH_2^{\bullet+}$ are distinguishable by their O_2 CID mass spectra,[20] with the former displaying a much more intense m/z 28 peak than the latter, for which loss of $CH_3^\bullet$ is more significant. Figure 2 shows their collision-induced emission spectra which have significant differences in the 300–500-nm spectral range. Spectral differences are probably due to both parent ion emissions and different product ions and neutrals (and hence different emitting species) being formed.

The He CID mass spectra of the isomers $CH_3CHO^{\bullet+}$ and $CH_2{=}CHOH^{\bullet+}$ are distinguishable only in that the latter ion produces a significant peak at m/z 30.[21,22] Their He CID emission spectra (Figure 2), however, are markedly different, with $CH_2{=}CHOH^{\bullet+}$ exhibiting more signal between 500 and 680 nm. Since predominantly the same product ions and neutrals are formed, this result suggests that either different electronic states are involved or only the parent ions emit radiation. These preliminary results show that collision-induced emission spectroscopy may evolve into a sensitive probe of ion structure.

Acknowledgment. J.L.H. thanks the Natural Sciences and Engineering Research Council of Canada for continuing financial support and P.M.M. thanks the same agency for a Post Graduate Scholarship during the tenure of which this work was completed.

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Coordination and Interconversion of a Ketonic Grouping between One and Two Transition-Metal Atoms

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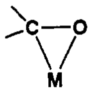
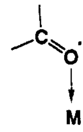
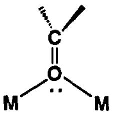
Electrophilic activation of carbonyl groups with Lewis acids is a well-established method for enhancing their reactivity toward nucleophiles.[1] Coordination of ketones to chiral metal centers has been found to promote nucleophilic additions with significant asymmetric induction.[2] The two principal modes of coordination of ketones to metals are the η^2-π-bonded and the η^1-σ-bonded modes **A** and **B**.[3] Double electrophilic activation of ketones, types **C**,[4] **D**,[5] and **E**,[6] should produce a much greater reactivity toward nucleophilic addition. Examples of these bridging types of coordination are rare, and the μ-di-σ mode **E** has been especially elusive.[6] We have now obtained the first structural characterization of a ketonic grouping exhibiting type **E** coordination to two transition-metal atoms and have also demonstrated its reversible conversion to the η^1-σ mode **B**.



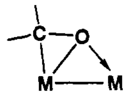
A



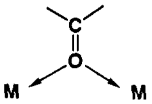
B



C



D



E

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