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of the pulse, the remaining molecules decay in the usual fashion according to their internal energy. In the MPI field a similar process by which excitation switches from one molecular species to another was termed "ladder switching"[31] and used to account for extensive fragmentation.

Overtone excitation, particularly to the $v = 5$ state, results by statistical arguments with considerable vibrational excitation of the product. We expect that some of them will be formed at energies exceeding 700 cm^{-1} above the S_1 origin and thus have a fast decay component. The fact that this component is not observed can be understood in terms of the kinetic analysis presented above and in ref 16.

Assume that X, formed in process 4, is actually two species, X_f, which decays in 10^{-8} s (the fast component) and X_s, that decays at a slower rate ($k_6 = 10^4$–1^6 s^{-1}). Equation 12 can be written for each component as follows:

$$X_f(t) = \frac{k_4^f[D^+]_o}{k_u - k_x^f}\{\exp(-k_x^f t) - \exp(-k_u t)\} \qquad (12a)$$

for the fast component, and for the slow one

$$X_s(t) = \frac{k_4^s[D^+]_o}{k_u - k_x^s}\{\exp(-k_x^s t) - \exp(-k_u t)\} \qquad (12b)$$

k_4^f and k_4^s denote the unimolecular dissociation rate constants of TMD to form X_f and X_s, respectively. They are not necessarily different. Inspection of eq 12a and 12b shows that since per assumption $k_x^f \gg k_u$, the contribution of $X_f(t)$ to the observed signal intensity is much smaller than that of $X_s(t)$. This is evident from the fact that the denominator of eq 12a is much larger (by 2 or 3 orders of magnitude) than that of eq 12b as $|k_u - k_x^f| \gg |k_u - k_x^s|$.

In order that the fast component be observed, the energy states giving rise to it should be formed preferentially by the reaction.

(31) For possible examples of ladder switching, see: Catanzerite, J. H.; Haas, Y.; Reisler, H.; Wittig, C. *J. Chem. Phys.* **1983**, *78*, 5606. Boesl, U.; Neusser, H. G.; Schlay, E. W. *J. Chem. Phys.* **1980**, *72*, 4327; Bernstein, R. B. *J. Phys. Chem.* **1982**, *86*, 1178.

As the optical studies show, this is not the case for energies at least up to 2000 cm^{-1} above the origin. We thus conclude that in the overtone experiments (up to $v = 5$) the dominant contribution to the chemiluminescence signal is due to the slowly decaying product molecules.

In the high-intensity IRMPE experiments, excitation may well exceed 2000 cm^{-1} above the acetone S_1 origin, leading to preferential population of short-lived X states. Thus, a third possibility for the observation of the spike in the high-power IRMPE experiments is provided.

Summary

Comparison of the decay kinetics of acetone excited by pulsed ultraviolet radiation with those obtained upon fast ground-state dissociation of TMD using IRMPE or OTE shows that the primary products of TMD dissociation may be assigned as vibrationally excited acetone in the nπ^* state. In the absence of collisions, distinction between singlet and triplet components is not as clear-cut as in condensed phases. Still, it appears that the triplet contribution is dominant and in agreement with statistical expectations. Vibrational relaxation leads to preparation of T_1^{VR}, the thermal triplet, which is the major product in condensed phases.

The rapid decay component observed upon IRMPE at high fluence levels is assigned to one (or all) of the following possibilities: decomposition of electronically excited acetone molecules formed in the reaction, made possible by the fact that TMD is pumped by the IR laser to energies far beyond the dissociation threshold of acetone; dissociation of electronically excited acetone molecules that absorb CO$_2$ laser photons during the laser pulse (ladder switching) or preparation of a large fraction of high energy, short-lived S_1 acetone molecules. These short-lived states are observed upon optical excitation of acetone, both in the bulk and in supersonic nozzle beam expanded molecular beams.

Multiphoton Infrared Laser Activation of Organometallic Species: A Novel Probe of the Potential Energy Surfaces for Reactions of Cobalt Ions with C5H10 Isomers

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Abstract: Multiphoton infrared activation has been used to probe the potential energy surfaces for the reactions of cobalt ions with C5H10 isomers. Infrared activation of stable Co(C5H10)$^+$ adducts, formed by ligand-exchange processes, is highly selective, with dissociation occurring only by the lowest energy pathway. For example, infrared multiphoton activation of Co(1-pentene)$^+$ and Co(2-pentene)$^+$ adducts leads to the exclusive loss of C2H4 and CH4, respectively, in processes which can be interpreted as resulting from the facile insertion of the metal ion into an allylic carbon–carbon bond. This can be compared to the bimolecular association reactions of cobalt ions with these molecules, which result in the formation of a highly energetic species having sufficient energy to decompose by competitive elimination of H2, CH4, C2H4, and C3H6. On the basis of the observed photoproducts, 1-pentene and cyclopentane are readily distinguished from each other and from 2-pentene and the methylbutenes. Photodissociation rates are determined for all the cobalt pentene isomers. Dissociation yields are independent of IR excitation wavelength in the region accessible to the CO2 laser. This contrasts with the single photon absorption spectra of the neutral pentenes which are highly structured in this wavelength region.

Preparation of an active transition-metal catalyst often involves the creation of a coordinately unsaturated species. The ability of the metal to shuttle between a stable, saturated electron configuration and one capable of undergoing oxidative addition is
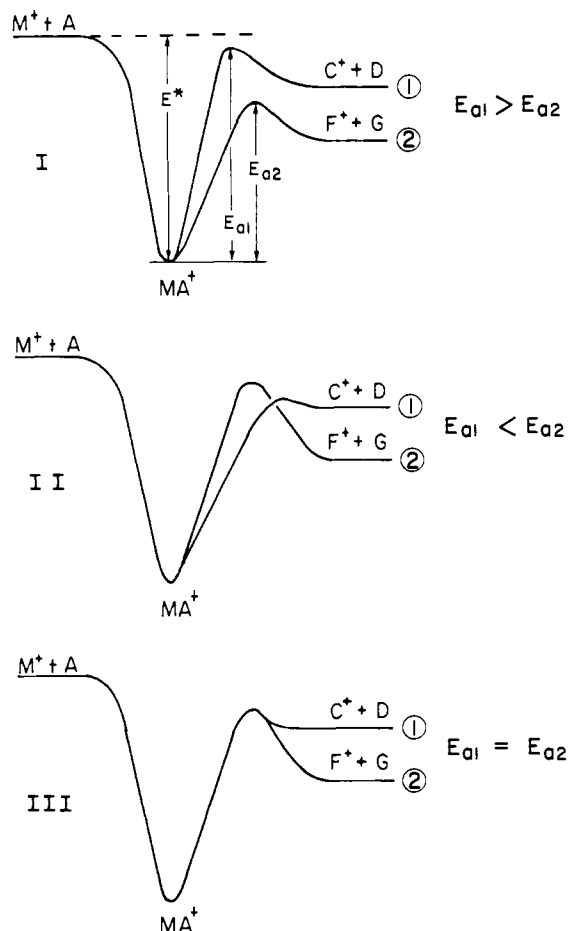
Multiphoton IR Activation of Organometallic Species

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Figure 1. Three possible potential energy surfaces for the exothermic reactions of M^+ with A resulting in formation of products $C^+ + D$ and $F^+ + G$.

an integral part of many proposed catalytic cycles.[1] Representing the extreme case of an unsaturated species, a bare transition-metal atom or ion exhibits reactivity that surpasses that of the more saturated metal complexes.[2-5] The extent to which the behavior of metal ions differs from the ligated metal species is apparent when their reactivity toward unactivated hydrocarbons is compared. While there are examples of ligated metals inserting into carbon–hydrogen bonds of saturated hydrocarbons, it is not generally a facile process.[6-9] Bare transition-metal ions, on the other hand, react with unsaturated hydrocarbons via C–H and C–C bond cleavage.[2-5] The accessibility of multiple and sequential competitive pathways leads to numerous reaction products even

Figure 2. Variation in experimental cross-sections for the reactions of Co^+ with pentene isomers as a function of kinetic energy in the center of mass scale (lower scale) and laboratory frame (upper scale). Symbols represent products corresponding to elimination of H_2 (O), CH_4 (■), C_2H_4 (△), and C_3H_6 (●). Data taken from ref 3.

for relatively simple systems such as cobalt ions reacting with isomeric pentenes.[3]

Examination of the energetics of a general gas-phase ion-molecule reaction suggests reasons for the observed multiplicity of products.[10] Consider, for example, the reaction of an ion M^+ with a neutral molecule A which has two exothermic reaction channels 1 and 2. In a bimolecular collision between an ion and a neutral which involves a strong interaction such as bond formation, the resulting collision adduct MA^+ will contain a significant amount of internal excitation. The internal energy, E^*, available to the "chemically activated" complex may allow access to competitive reaction pathways such as 1 and 2. Three possible potential energy surfaces for this system, simplified for purposes of discussion, are presented in Figure 1. If C^+ and F^+ are both observed from the reaction of M^+ and A, all that can be inferred is that no point along the potential energy surface connecting MA^+ to products is higher in energy than the initial energy E^*. No

$$M^+ + A \rightarrow (MA^+)^* \rightarrow C^+ + D \qquad \Delta H < 0 \qquad (1)$$

$$M^+ + A \rightarrow (MA^+)^* \rightarrow F^+ + G \qquad \Delta H < 0 \qquad (2)$$

(1) For general reviews, see, for example: (a) Masters, C. "Homogeneous Transition-Metal Catalysis"; Chapman and Hall: New York, 1981. (b) Khan, M. M. T.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974.

(2) (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (b) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.

(3) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6624.

(4) (a) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Ibid.* **1981**, *103*, 4360. (c) Byrd, G. D.; Freiser, B. S. *Ibid.* **1982**, *104*, 5944.

(5) (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (b) Allison, J.; Freas, R. B.; Ridge, D. P. *Ibid.* **1979**, *101*, 1332.

(6) See also: Parshall, G. W. "Catalysis"; Chemical Society: London, 1977; Vol. 1, p 335.

(7) (a) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (b) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738.

(8) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276.

(9) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Janowicz, A. H; Bergman, R. G. *Ibid.* **1983**, *105*, 3929. (c) Hoyano, J. K.; Graham, W. A. G. *Ibid.* **1982**, *104*, 3723.
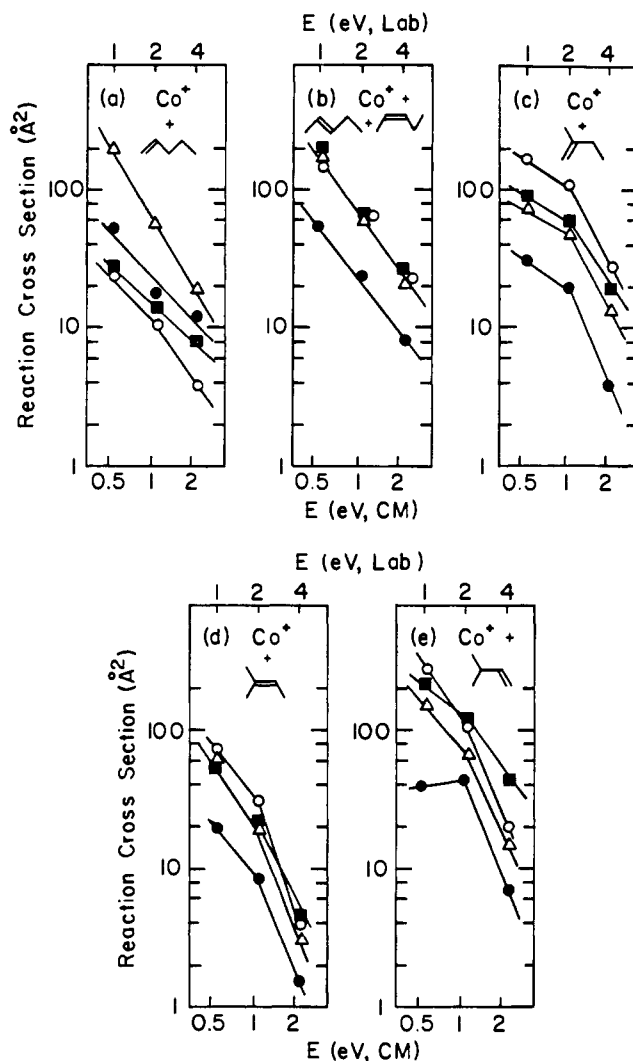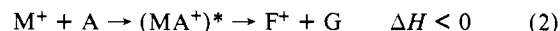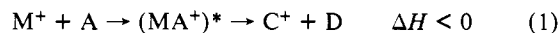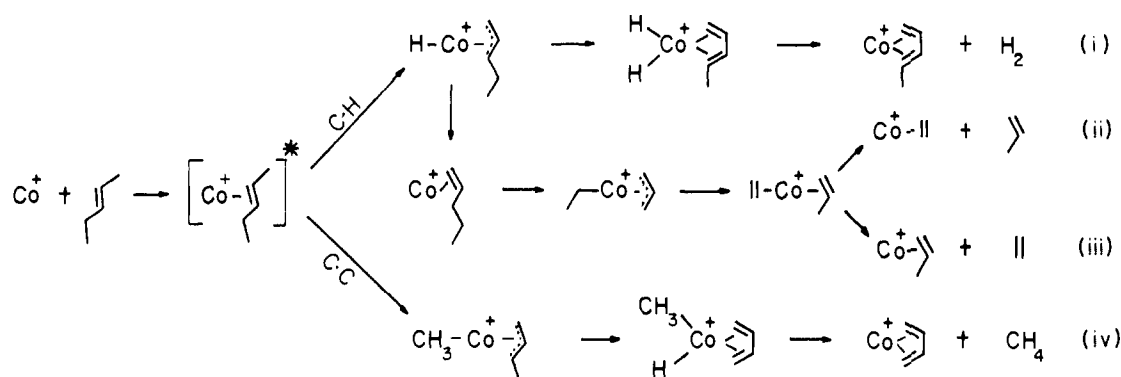
(10) For a general discussion see: Beauchamp, J. L. In "Interactions Between Ions and Molecules"; Ausloos, P., Ed.; Plenum: New York, 1975; p 413. A more extensive treatment of the subject may be found in: Bowers, M. T., Ed. "Gas Phase Ion Chemistry"; Academic Press: New York, 1979; Vol. 1 and 2.

Scheme I

information is obtained regarding the relative heights of the barriers to reactions, E_{a1} and E_{a2}, and hence it is not possible to distinguish between the three distinct cases depicted in Figure 1.

A more complete description of the potential energy surfaces can often be deduced from the observed changes in product ratios as the internal energy, E^*, of the collision complex is continuously varied. One method for achieving this is to use an ion beam apparatus[11,12] in which the reactant ion, M^+, is translationally excited prior to collision with the neutral molecule, A. In this manner, the internal excitation of MA^+ is increased beyond the initial interaction energy. The cross sections for the exothermic reactions of Co^+ with isomeric pentenes are plotted as a function of relative collision energy in Figure 2.[3] Here the cobalt–pentene adduct resulting from bimolecular association is analogous to MA^+. As is typical for exothermic reactions, the total cross sections decrease with increasing energy.[12] Note, however, that product ratios do not vary greatly with energy.[13] Scheme I is proposed to account for all observed products via intermediates which are energetically accessible to the chemically activated Co(2-pentene)$^+$ adduct. The proposed reaction pathways can be grouped into two classes: those involving initital C–H bond insertion (i, ii, and iii) and those initiated by C–C insertion (iv). A similar scheme can be envisaged for the other isomers.

Product ratios for the reactions of Co^+ with isomeric pentenes determined from ion beam experiments (Figure 2) are similar to those obtained for these reactions at thermal energies.[15,16] The energy-independent product yields suggest that the $Co(C_5H_{10})^+$ complexes contain internal excitation which is considerably in excess of the activation energies for the processes considered (i.e., $E^* \gg E_{a1}, E_{a2}$). Product yields reflect predominantly differences in the frequency factors.[14] Thus, the internal energy available to the chemically activated Co(pentene)$^+$ complex is sufficiently high to obscure quantitative details of the potential energy surfaces such as relative activation energies for competitive processes.

If the complex MA^+ could be prepared with very little internal excitation, it could then be trapped in the potential well illustrated in Figure 1. A convenient method for creating a stable adduct is through a nearly thermoneutral ligand exchange reaction such as 3. In contrast to the direct association adduct, the MA^+

$$ML^+ + A \rightarrow MA^+ + L \qquad (3)$$
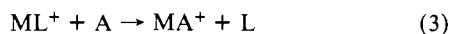
complex formed from the ligand exchange will contain only the difference between the two metal–ligand bond energies as the maximum internal excitation. By increasing the energy available to MA^+ in small increments, it would be possible to determine
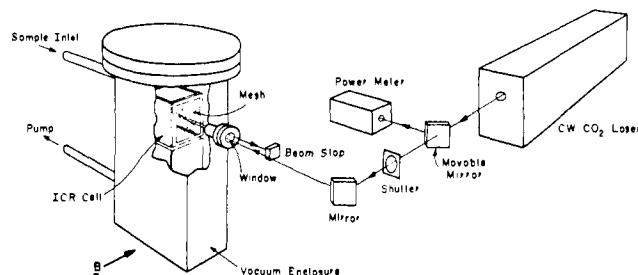

Figure 3. Schematic of experimental apparatus for infrared multiphoton activation studies.

which of the surfaces represented in Figure 1 is a more appropriate description of the system. If case I best represents the reaction coordinate, only the thermodynamically most stable products would be observed. In case II the higher energy products which have the lower activation energy would be observed. Finally, if a common transition state were involved as in case III, both sets of products would be formed.[17]

Absorption of infrared photons provides a relatively easy method for depositing small increments (~ 2.5 kcal/photon) of energy into a molecule. Using low-power continuous wave infrared laser radiation, gas-phase ions have been shown to undergo decomposition at energies near threshold.[17,18] This facet of IR multiphoton decomposition has attracted attention due to the fact that it allows identification of the lowest energy pathway, which may be different for different isomers.[19,20] In addition, isomeric ions may exhibit dissociation yields which vary with wavelength in a manner which allows them to be distinguished.[18-20] Thus, infrared multiphoton decomposition can yield details relating to activation parameters as well as structural information.

In this study, ion cyclotron resonance (ICR) in conjunction with infrared multiphoton dissociation is used to probe the potential energy surfaces for the reaction of cobalt ions with isomeric pentenes and cyclopentane. Augmented by results from previous investigations, a more complete picture of the potential energy surfaces can be formulated.

Experimental Section

The theory and techniques of ion cyclotron resonance spectroscopy (ICR) have been previously described.[21,22] All experiments were performed on a conventional ion cyclotron resonance spectrometer with a marginal oscillator detector. Modifications to allow photochemical in-

(11) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (b) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.

(12) Henchman, M. In "Ion-Molecule Reactions"; Franklin, J. L., Ed.; Plenum Press: New York, 1972; p 101.

(13) Above ~1 eV contributions from endothermic reaction pathways which are not shown become significant.

(14) (a) Forst, W. "Theory of Unimolecular Reactions"; Academic Press: New York, 1973. (b) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley Interscience: New York, 1972.

(15) Hanratty, M. A.; Illies, A. J.; Bowers, M. T.; Beauchamp, J. L. *J. Am. Chem. Soc.*, to be submitted.

(16) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(17) Examples of all three cases have been demonstrated. (a) Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3292. Multiple products resulting from a photochemically prepared intermediate have also been reported. (b) Moylan, C. R.; Janiski, J. M.; Brauman, J. I. *Chem. Phys. Lett.* **1983**, *98*, 1.

(18) Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

(19) (a) For a review, see: Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. In "Chemical and Biochemical Applications of Lasers"; Moore, C. B., Ed.; Academic Press: New York, 1979; Vol. IV.

(20) Bomse, D. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1981**, *77*, 25.

(21) Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley-Interscience: New York, 1976.

(22) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.
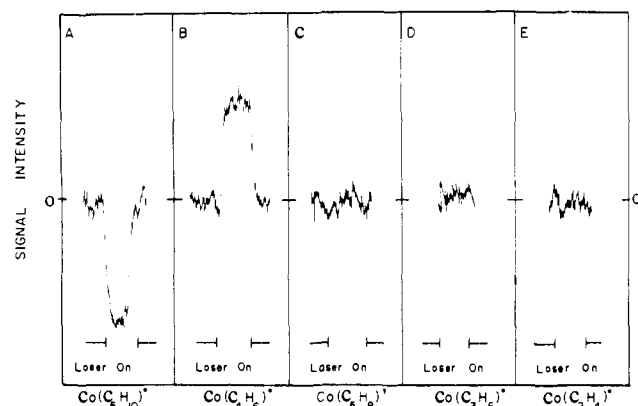
Figure 4. Variation in ICR signal intensities for five ions present in the cobalt-2-pentene system 436 ms after the initial ion-formation pulse. Ions were exposed to infrared radiation (15 J cm^{-2} at 944 cm^{-1}) on alternate cycles. The signal intensity without laser radiation was subtracted from the signal with laser radiation to produce the difference spectrum. For comparison the signal intensities of A, B, C, D, and E should be multipled by 1.00, 1.14, 1.01, 1.28, and 1.48, respectively.[22]

Figure 5. Normalized Co(2-pentene)$^+$ ion intensity following irradiation (40 W/cm^{-2} at 944 cm^{-1}) during a 110-ms window with a variable time delay. Ions were irradiated on alternate cycles as indicated.

vestigations include replacement of one drift plate with a 92% transmissive mesh and installation of a NaCl window as previously described.[18] Light is directed into the center of the ion storage region and reflected by the back plate. Correcting for the absorption of the NaCl window and assuming the back plate is 100% reflective, the irradiance inside the cell is 1.77 times the incident irradiance.[23]

Figure 3 displays a schematic of the experimental apparatus. An Apollo 550A line-tunable continuous wave CO$_2$ laser provides the infrared radiation. An unfocused beam with a nearly Gaussian intensity profile (fwhm 6 mm) is used to ensure complete and uniform overlap with the ion cloud.[18] Irradiances from 12 to 60 W cm^{-2} are used. All laser power measurements are made with a Laser Precision RK 3440 radiometer. The reported irradiances are calculated by dividing the total beam power in the cell by the area of the beam.

Neutral pressures typically are in the 3 × 10^{-7} to 2 × 10^{-6} torr range. Pressure measurements are obtained by using a Schulz-Phelps gauge calibrated against an MKS Instrument Baratron (Model 90H1-E) capacitance manometer. It was necessary to keep pressures below 2 × 10^{-6} torr to avoid further reaction of the cobalt–pentene ions.

CoCO$^+$ is formed from electron impact ionization of Co(CO)$_3$NO. Unless otherwise specified, the electron energy is 20 eV. Typically, a 10-ms pulse of electrons forms ions which are then allowed to react for times up to 1 s. Irradiation of the ions during any portion of the trapping cycle is achieved with a mechanical shutter. A dual channel boxcar is used to record spectra for alternate cycles of laser irradiation. Reaction pathways with and without the laser irradiation are confirmed by using double-resonance techniques.[21,22]

Co(CO)$_3$NO (Strem Chemicals) and isomeric pentenes and cyclopentane (>99% purity from Wiley Organics) were used as received. All samples were subjected to repeated freeze–pump–thaw cycles to remove noncondensable gases.

Infrared spectra of C$_5$H$_{10}$ isomers were recorded on a Matteson Sirius 100 FT–IR spectrometer. A 10 cm path length gas cell pressurized to 10 torr was used for all spectra.
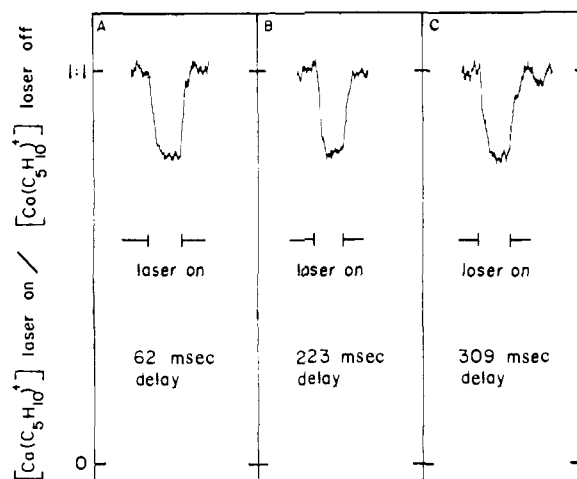
Results

2-Pentene. CoCO$^+$ formed from 20 eV electron impact on Co(CO)$_3$NO readily exchanges carbon monoxide for pentene. Estimated bond energies indicate that Co(C$_5$H$_{10}$)$^+$ formed via reaction 3 should contain very little excess energy.[24,25] Irradiation

of the ions on alternate cycles allows the comparison of signal intensities with and without laser radiation. The data in Figure 4 were obtained 436 ms after the initial ion formation pulse. The laser was turned on as indicated for alternate cycles. Subtracting the intensity for a given ion with laser irradiation from that without the laser radiation produced the difference spectrum shown in Figure 4. As can be seen, irradiation of the ions with a continuous wave infrared laser at low fluences (15 J cm^{-2} at 944 cm^{-1}) leads to a decrease in the Co(C$_5$H$_{10}$)$^+$ signal (Figure 4A) concomitant with an increase in the Co(C$_4$H$_6$)$^+$ signal (Figure 4B). For the three other reaction channels shown in Scheme I, no detectable increase in signal intensity occurred with laser irradiation (Figure 4C–E). When corrected for mass discrimination,[26] the increase in Co(C$_4$H$_6$)$^+$ accounts for 98% of the decrease in Co(C$_5$H$_{10}$)$^+$. Although Co(C$_4$H$_6$)$^+$ ions are formed from other ion–molecule reactions in the system, double-resonance experiments confirm that the increase upon irradiation is due to reaction 4. Any channel present in an amount greater than 2% could be detected. Formation of Co(C$_4$H$_6$)$^+$ (reaction 4) is the only photodissociation channel observed.

$$\text{Co(C}_5\text{H}_{10})^+ + nh\nu \rightarrow \text{Co(C}_4\text{H}_6)^+ + \text{CH}_4 \qquad (4)$$
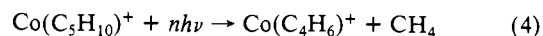
Photodissociation yield is defined as the fraction of ions dissociated during a specified exposure time with a specified laser irradiance (eq 5). Here I is the ion signal intensity after irra-

$$P_d = 1 - I/I_0 \qquad (5)$$

diation, and I_0 is the signal intensity without irradiation at the end of the same period. If the photodissociation process can be described by first-order decay kinetics, then from a plot of ln I/I_0 vs. time a rate constant for dissociation k_d can be extracted (eq 6). This apparent rate constant determined at a given laser energy

$$I/I_0 = \exp(-k_d t) \qquad (6)$$

indicates the ease with which molecules can be photodissociated. A phenomenological cross section σ_d can also be defined for rate constants which are first order in photon flux Φ (eq 7). The photodissociation of cobalt(2-pentene)$^+$ complexes could be

$$k_d = \sigma_d \Phi \qquad (7)$$

characterized in this manner by a photodissociation rate of 0.034 s^{-1} W^{-1} cm^2. Only the single product is observed at all laser powers in the wavelength region from 9.2 to 10.8 μm. At constant fluence, the photodissociation yield shows no variation with wavelength.

A small fraction (<5%) of the Co(C$_5$H$_{10}$)$^+$ population is not observed to decompose with infrared radiation. Photodissociation due exclusively to a vibrationally excited population can be ruled out by the data shown in Figure 5. The ions are irradiated with

(23) This is calculated for 10.6 μm radiation where the absorption of the NaCl window is 4%.

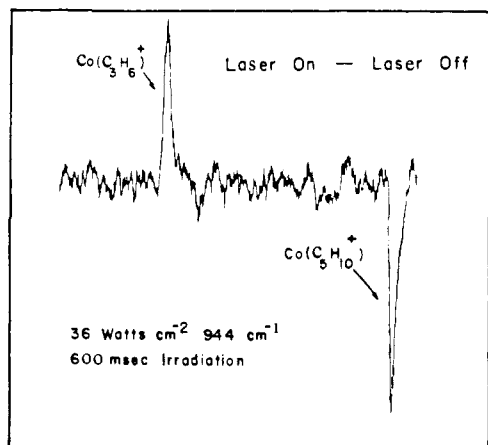(24) D[Ni$^+$–CO] and D[Fe$^+$–CO] were determined from photoionization mass spectrometry to be 48 ± 2 and 60.5 ± 2 kcal/mol, respectively. Distefano, G. *J. Res. Natl. Bur. Stand., Sect. A.* **1970**, *74A*, 233. The latter value appears too large and may be due to an incorrect threshold for formation of Fe(CO)$^+$.[2a] An upper limit of 43 ± 3 kcal/mol for D[Fe–CO]$^+$ has been determined from photodissociation. Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176. With this in mind, D[Co$^+$–CO] is estimated to be 46 kcal/mol. Pentene is observed to displace C$_3$H$_6$ from CoC$_3$H$_6$$^+$, indicating D[Co$^+$–C$_5H_{10}$] > D[Co$^+$–C$_3H_6$] > 36 kcal/mol.[3] D[Co$^+$–C$_5H_{10}$] is estimated to be 55 kcal/mol.

(25) Supplementary thermochemical information is from Cox and Pilcher: Cox, J. D.; Pilcher, G., "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

(26) The decrease in Co(C$_4$H$_6$)$^+$ signal should be multiplied by 1.14 to correct for mass discrimination (ref 22).

Figure 6. Difference mass spectrum at 40 eV for the 1-pentene system obtained by subtracting the observed ion intensity without laser radiation from that with laser radiation. Ions are trapped for 600 ms and exposed on alternate cycles to IR laser radiation (22 J cm^{-2} at 944 cm^{-1}).

40 W cm^{-2} at 944 cm^{-1} during a "window" of 110 ms with a variable time delay. A vibrationally hot population would be expected to relax collisionally at the longer trapping times which would result in a decrease in the percent of ions decomposing.[19,27,28] The constant fraction of ions which photodissociate indicates that vibrationally excited ions do not account for the majority of the decomposition. The photodissociation rates observed with 20 and 70 eV electron impact ionization differ by less than 5%.

1-Pentene. $Co(C_5H_{10})^+$ adducts formed from the ligand exchange reaction 3 with 1-pentene are observed to photodissociate via reaction 8. Figure 6 shows a difference mass spectrum

$$Co(C_5H_{10})^+ + nh\nu \rightarrow Co(C_3H_6)^+ + C_2H_4 \qquad (8)$$
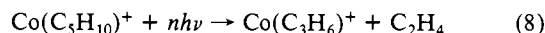
recorded by subtracting the observed intensity without laser irradiation from the signal intensity with laser irradiation at a trapping time of 600 ms. Signals increasing upon exposure to 944-cm^{-1} radiation (36 J/cm^2) appear as positive peaks. Intensities are not directly comparable due to the mass discrimination of the ICR spectrometer.[22] The corrected $Co(C_3H_6)^+$ intensity accounts for only 95% of the decrease in the $Co(C_5H_{10})$ signal. Subsequent reactions of $Co(C_3H_6)^+$ ions with neutral pentenes are responsible for the decrease in the observed photoproduct signal intensity. As with the 2-pentene adducts, only one decomposition channel is observed, and it is independent of wavelength and laser power. The photodissociation rate is found to be 0.047 s^{-1} W^{-1} cm^2.

Methylbutenes. 2-Methyl-2-butene, 2-methyl-1-butene, and 3-methyl-1-butene adducts with cobalt are observed to eliminate CH_4 upon irradiation as in reaction 4. The apparent rates for photodissociation of 2-methyl-2-butene, 2-methyl-1-butene, and 3-methyl-1-butene are 0.029, 0.031, and 0.035 s^{-1} W^{-1} cm^2, respectively.

Cyclopentane. Although adduct formation with cyclopentane is observed, the complex is photoinactive over the accessible range of laser wavelengths and power. Under the experimental conditions, a photodissociation rate faster than 0.006 s^{-1} W^{-1} cm^2 could have been observed. No change in the photodissociation signal was observed with 70 eV electron impact ionization. $Co(C_5H_8)^+$, the dehydrogenation product from bare cobalt ions reacting with cyclopentane, is observed to lose H_2 upon irradiation.

Discussion

Multiphoton dissociation represents one of the few methods for obtaining spectral information for gas-phase ions. In some instances, the photodissociation spectra of the ions are found to resemble the absorption profile for the neutral molecule.[18,29] The
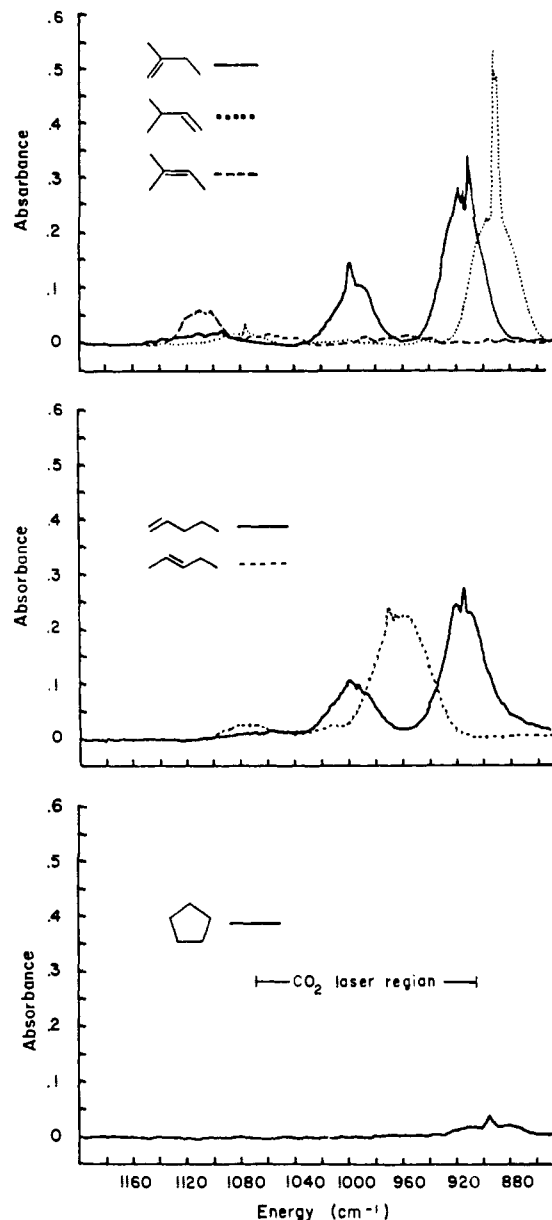
Figure 7. Infrared absorbance spectra for neutral C_5H_{10} isomers recorded at a pressure of 10 torr with a 10 cm path length cell. The wavelength region accessible to the CO_2 laser is indicated.

photodissociation spectrum of perfluoropropene, for instance, exhibits a strong wavelength dependence.[29] The maximum at 1047 cm^{-1} is only slightly shifted from the neutral absorption at 1037 cm^{-1}. In contrast to this, the proton bound dimers of aliphatic alcohols exhibit no strong wavelength dependence in their photodissociation spectra.[17a] Although there are known exceptions,[30] it has been suggested that relatively unstructured absorption is characteristic of many molecules in the vibrational quasi-continuum.[31]

With the exception of cyclopentane and 2-methyl-2-butene, the gas-phase spectra of the neutral C_5H_{10} isomers exhibit intense absorption features in the wavelength range accessible to the CO_2 laser (Figure 7). 2-Methyl-2-butene has an intense absorption at 800 cm^{-1} which is outside the range of the CO_2 laser, while cyclopentane has no strong absorptions near this region. Interestingly, the $Co(C_5H_{10})^+$ adduct formed with cyclopentane is

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(28) At a pressure of 2 × 10⁻⁶ torr a $Co(C_5H_{10})^+$ ion will typically undergo 20 collisions after 0.5 s. See ref 10.

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Table I. Product Distributions for Exothermic Reactions of Co^+ with C_5H_{10} Isomers

C_5H_{10} isomer	neutral lost	ΔH^a (kcal/mol)	product distributions			
			ion beam[b]	metastable[c,d]	CID[c,d]	IR activation
1-pentene	H_2	−46	0.11	0.02	0.02	0
	CH_4	−55	0.13	0.01	0.03	0
	C_2H_4	−29	0.58	0.95	0.72	1.00
	C_3H_6	−25	0.18	0.01	0.10	0
2-pentene	H_2	−43	0.28	0.47	0.35	0
	CH_4	−52	0.33	0.43	0.38	1.00
	C_2H_4	−27	0.29	0.09	0.16	0
	C_3H_6	−23	0.10	0.01	0.02	0
2-methyl-1-butene	H_2	−42	0.46	0.49	0.43	0
	CH_4	−51	0.26	0.43	0.34	1.00
	C_2H_4	−26	0.20	0.08	0.14	0
	C_3H_6	−22	0.08	0.004	0.02	0
3-methyl-1-butene	H_2	−44	0.35	0.47	0.39	0
	CH_4	−53	0.35	0.45	0.38	1.00
	C_2H_4	−28	0.22	0.08	0.14	0
	C_3H_6	−24	0.08	0.004	0.02	0
2-methyl-2-butene	H_2	−41	0.34	0.47	0.42	0
	CH_4	−50	0.35	0.44	0.35	1.00
	C_2H_4	−24	0.26	0.08	0.14	0
	C_3H_6	−20	0.10	0.005	0.02	0
cyclopentane	H_2	−32	0.36	0.35	0.35	0
	CH_4	−41	0.03	0.02	0.02	0
	C_2H_4	−16	0.51	0.58	0.44	0
	C_3H_6	−12	0.07	0.03	0.05	0

[a] Reaction enthalpies estimated from data given in ref 15, 17, 25, and 36. [b] All reported product distribution for ion beam studies for 0.5 eV c.m.. from ref 3. [c] All metastable and collision-induced dissociation data are from ref 15. [d] All values normalized to ΣI_i. Loss of C_5H_{10} not reported.

photoinactive, while the adduct formed with 2-methyl-2-butene does photodissociate. All dissociation yields were independent of wavelength. In this respect, acyclic $Co(C_5H_{10})^+$ ions resemble the proton-bound dimers of alcohols.[17a] Due to the strong interaction with the cobalt ion, the vibrational frequencies in the pentenes are likely to be perturbed as a result of complex formation. In addition, several conformations of the cobalt–pentene complex are possible. This may account for the lack of close correspondence between the photodissociation spectra and the single photon spectra shown in Figure 7 and in part may be responsible for the structureless photodissociation spectra.

The selectivity of infrared-assisted decomposition of $Co(C_5H_{10})^+$ adducts is apparent when compared with the results of chemical activation experiments (Table I). While all four exothermic reaction channels listed in Table I are observed for the chemically activated (bimolecular association) adduct, infrared activation of the stable cobalt–pentene ion leads to only one decomposition product for each acyclic isomer. The implications of these results are most easily demonstrated with the aid of a simplified reaction coordinate diagram such as the one shown in Figure 8 for Co-(2-pentene)$^+$.

Although the potential energy surface depicted in Figure 8 is quite simple, showing only two possible dissociation channels and ignoring the possibility of interconversion of isomers, it is consistent with known features of the system. Infrared multiphoton dissociation clearly identifies loss of CH_4 as the lowest energy pathway. This is analogous to case I discussed above where the thermodynamically more stable products are observed. The IR activation results combined with the results from previous investigations of cobalt ion–pentene reactions can be used to infer more details regarding the surfaces. For instance, the observed intensity of H_2 and CH_4 elimination channels for Co(2-pentene)$^+$ are nearly equal in both the metastable ion decomposition and high-energy collision-induced decomposition (Table I). From the dominance of these two reactions channels, it might be expected that the activation barriers for these two pathways (E_{a1} and E_{a2}) do not differ greatly.[32] The results from infrared activation experiments,
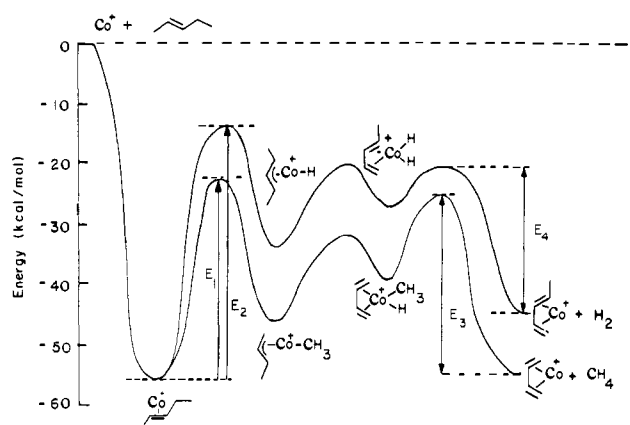

Figure 8. Qualitative potential energy diagram for the reaction of Co^+ with 2-pentene, resulting in the formation of $Co(C_5H_8)^+$ and $Co(C_4H_6)^+$.

however, suggest that methane elimination has the lower barrier. The kinetic energy released to products upon elimination of H_2 or CH_4 from metastable Co(2-pentene) ions[15] suggests the presence of barriers (E_{a3} and E_{a4} in Figure 8) for the reverse association reactions. This is supported by the results from related experiments[33,34] in which ion cyclotron resonance techniques have been used to study the reverse reactions. Failure to observe D_2 or CD_4 addition respectively to cobalt pentadiene and cobalt butadiene complexes is consistent with the features of the potential surfaces as shown in Figure 8. The results of ligand displacement reactions and low-energy collision-induced dissociation (CID) have been used to assign the structure of the products.[16]

The reaction pathways shown in Figure 8 may be viewed as representing competitive carbon–hydrogen and carbon–carbon bond insertion. The transition state for the initial C–C or C–H bond insertion is postulated to be the highest point on the potential energy surface connecting the $Co(C_5H_{10})^+$ collision complex to the respective products. Decomposition is assumed to occur from

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Scheme II
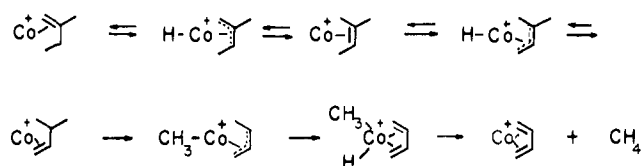
a Co(2-pentene)⁺ adduct formed by ligand displacement rather than from a rearranged species such as a metal hydridopentenyl ion. The photodissociation of Co(2-pentene)⁺ can be described by a single exponential, consistent with the presence of only a single structure. In addition, if C–H bond insertion does occur during complex formation and is reversible, interconversion between 1- and 2-pentene complexes would be expected. The exclusive loss of methane from IR multiphoton activation of cobalt complexes with 2-pentene suggests that isomerization is not occurring. The photodissociation results are consistent with initial insertion into the allylic carbon–carbon bond of 2-pentene being energetically less demanding than carbon–hydrogen bond insertion.

The dissociation pathways for the Co(1-pentene)⁺ adduct can likewise be viewed as involving competitive C–C and C–H bond insertion. In this system, loss of ethene is identified by multiphoton dissociation as the lowest energy pathway. The unrearranged Co(1-pentene)⁺ adduct is assumed to be the dissociating species. A possible mechanism for the formation of Co(C₃H₆)⁺ is shown in Scheme I (reaction iii). Initially coordinated to the π bond of the olefin, the metal can insert into an allylic carbon–carbon bond and transfer a β-hydrogen to form a bis-olefin complex. This, in turn, loses ethene to yield the cobalt–propene ion. In contrast to the 2-pentene system, photoinduced decomposition of Co(1-pentene)⁺ yields the thermodynamically less stable product (case II). Although other structures such as HCo(pentenyl)⁺ and H₂Co(pentadiene)⁺ are postulated intermediates for the higher energy pathways, there is no evidence for their involvement in the photoactivation pathways. It is, in fact, difficult to envision facile loss of ethene from such structures.

It is of interest to note that for both the 1-pentene and 2-pentene complexes, IR multiphoton activation suggests that insertion of the metal ion into the allylic carbon–carbon bond is the lowest energy decomposition pathway. This reaction pathway is favored by the weak allylic C–C bond[35] and the strong metal–allyl[36] and metal–alkyl[2a] bonds which are formed. This preference for C–C bond insertion must, in some respects, be regarded as unique to metal–ion reactions. In contrast to situations with neutral metal complexes, the Co–CH₃⁺ bond is *stronger* than the Co–H⁺ bond, presumably due to stabilization of the positive charge on the metal by the polarizable methyl group. However, analogous reactions have been observed in solution for reactions which have been specifically designed to favor C–C bond insertion over C–H insertion. Evidence for C–C bond cleavage has been obtained for systems which have no β-hydrogens[37] and very weak carbon–carbon bonds[38,39] and for cases where there is a large thermodynamic driving force for carbon–carbon bond cleavage.[40] The reactions observed in this investigation can similarly be viewed

as involving the directed cleavage of an allylic carbon–carbon bond.

Infrared-assisted decomposition of the cobalt-methylbutene complexes yields the same photoproducts as the Co(2-pentene)⁺ adducts. The isomerization reactions shown in Scheme II followed by decomposition of the resulting Co⁺–allyl intermediate are proposed to account for the observed products. The results of metastable ion decomposition[15] studies support the conclusion that isomerization to a common intermediate precedes fragmentation. There is also evidence of this in the analogous iron system where the high-energy collision-induced decomposition spectra of Fe-(methylbutene)⁺ adducts are observed to be similar to the Fe-(2-pentene)⁺ spectrum.[41]

The lack of photodissociation for the Co(cyclopentane)⁺ complex is consistent with the weak absorption for cyclopentane in the region of the CO₂ laser and suggests that the cyclopentane ring maintains its integrity. If, upon association with the metal, a linear pentene were formed, loss of CH₄ or C₂H₄ from infrared photodecomposition would be expected. High-energy CID and kinetic-energy release distributions from metastable Co(cyclopentane)⁺ ions are consistent with the ring remaining intact.[15,42]

Related Studies with Saturated Hydrocarbons

Complexes of cobalt ions with various saturated hydrocarbons (propane, butane-*1,1,1,4,4,4-d₆*, pentane, cyclohexane, and methylcyclohexane) were also formed by ligand exchange (reaction 3). The neutral hydrocarbons have fairly weak absorptions in the wavelength region of the CO₂ laser, and as was the case for cyclopentane the respective ionic cobalt complexes are not observed to photodissociate. Apparently, complexation to the metal does not give rise to a species with a strong absorption in the 9.2–10.8 μm region. Interestingly, for all the systems examined in the present study, the adducts are observed to photodissociate whenever the hydrocarbon has a strong absorption in the CO₂ laser tuning region. This is the case even though the photodissociation spectra of the complexes do not resemble the single photon absorption spectra of the neutrals.

Conclusions

In comparison to chemical activation techniques which allow access to multiple decomposition pathways of isomeric cobalt ion–pentene adducts, infrared multiphoton dissociation is shown to be much more selective. On the basis of the observed decomposition products, 1-pentene and cyclopentane are readily distinguished from 2-pentene and methylbutenes. In addition, IR-assisted decomposition identifies the lowest energy dissociation channel. For adducts of cobalt ions with 1- and 2-pentene, this process is postulated to involve initial insertion into the allylic carbon–carbon bond. Complexes of cobalt ions with the methylbutanes apparently isomerize prior to dissociation.

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