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Mechanistic studies of processes involving carbon-carbon bond cleavage in gas-phase organometallic reactions using product kinetic energy release distributions: Co+ reacting with cyclopentane

Petra A. M. Van Koppen, Michael T. Bowers, and J. L. Beauchamp

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Rh colloid solution. Analysis of the reaction product by GCMS showed the expected single product, (octyl)$_3$SiCH$_2$CH$_2$SiMe$_3$, *m/e* 468 (25%, M^+), 367 (85%, $M^+ - CH_2CH_2SiMe_3$), 355 (25%, M^+ - octyl), 255 (80%), 243 (100%).

Relative Activity of Et_3SiH and Et_2SiH_2. For the triethylsilane reaction the stock solution contained (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), Et_3SiH (0.44 mL, 2.77 mmol), and decane (0.4 mL, 2 mmol). For the diethylsilane reaction the stock solution contained (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), Et_2SiH_2 (0.35 mL, 2.7 mmol), and decane (0.4 mL). The reactions were initiated by addition of the Pt Karstedt catalyst (7 μL of a 5% Pt solution, 1.8 μmol of Pt). The Rh-catalyzed reactions were carried out in exactly the same way except Rh colloid solution was used (58 μL of a 0.3% Rh colloid solution, 1.7 μmol). For the Rh-catalyzed reaction, the diaddition product was obtained in >98% conversion. GCMS analysis showed the expected product, $Et_2Si[CH_2CH_2SiMe_3]_2$, *m/e* 288 (25%, M^+), 187 (80%, $M^+ - CH_3CH_2SiMe_3$), 171 (80%), 158 (70%), 157 (80%), 87 (100%), 73 (100%). The authentic monoaddition product, $Et_2Si(H)(CH_2CH_2SiMe_3)$, was prepared to confirm its retention time and response factor on the GC. In an addition funnel was placed (vinyl)SiMe$_3$ (5.63 mL, 38.8 mmol) and Rh colloid catalyst (35 μL of a 0.3% Rh solution, 0.5 μmol of Rh). In a three-neck flask was placed Et_2SiH_2 (5 mL, 38.8 mmol). The diethylsilane was heated to reflux, and then the (vinyl)SiMe$_3$/Rh mixture was slowly added. Analysis by GC showed complete conversion to the single monoaddition product $Et_2Si(H)(CH_2CH_2SiMe_3)$. GCMS analysis showed *m/e* 187 (35%, $M^+ - 1$), 159 (20%, M^+ - Et (100%)). The product of Et_3SiH and (vinyl)SiMe$_3$ was consistent with $Et_3SiCH_2CH_2SiMe_3$:

$$\underset{a}{(CH_3}\underset{b}{CH_2)_3}Si\underset{c}{CH_2}\underset{d}{CH_2}Si\underset{e}{(CH_3)_3}$$

^1H NMR (CDCl$_3$) δ 0.95 (t, 9 Hz, a), 0.55 (m, b), 0.42 (m, c + d), 0.02 (s, e); ^{13}C NMR (CDCl$_3$) δ 9.08 (c), 7.88 (b), 3.34 (a + d), −1.91 (e); HRMS 216.1729 (M^+, calcd for $C_{11}H_{28}{}^{28}Si_2$ 216.1729).

Relative Activity of (hexyl)$_3$SiH and (hexyl)SiH$_3$. For the reaction of eq 7, (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), decane (0.4 mL, 2.06 mmol), and (hexyl)$_3$SiH (0.98 mL, 2.75 mmol) were combined. The reaction was initiated by addition of Pt colloid solution (35 μL of a 1.03; Pt solution, 1.8 μmol of Pt) or Rh colloid solution (116 μL of 0.3% Rh solution, 1.8 μmol of Rh). For the reaction of eq 8, (vinyl)SiMe$_3$ (4 mL, 27.5 mmol), decane (0.4 mL), and (hexyl)SiH$_3$ (0.44 mL, 2.72 mmol) were combined. The reaction was initiated with Pt or Rh as described for eq 7.

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Mechanistic Studies of Processes Involving C–C Bond Cleavage in Gas-Phase Organometallic Reactions Using Product Kinetic Energy Release Distributions: Co^+ Reacting with Cyclopentane

Petra A. M. van Koppen and Michael T. Bowers*

Department of Chemistry, University of California, Santa Barbara, California 93106

J. L. Beauchamp*

Arthur Ames Noyes Laboratory of Chemical Physics,[†] *California Institute of Technology,*
Pasadena, California 91125

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A reverse-geometry mass spectrometer is used to obtain product ion kinetic energy release distributions to probe the energetics and mechanisms of several gas-phase organometallic reactions. In particular, we examine the mechanism for C_2H_4 and C_3H_6 elimination from Co(cyclopentane)$^+$. The kinetic energy release distribution associated with these processes can be modeled by using phase space calculations assuming, for the C_3H_6 elimination process, propene rather than cyclopropane is being eliminated as the product neutral, and for the C_2H_4 elimination process, Co(propene)$^+$ rather than (cobaltacyclobutane)$^+$ is being formed as the product ion. In addition, we obtain a heat of formation for the cobalt ethylene ion of 255 kcal/mol at 0 K, corresponding to a bond dissociation energy of 42 kcal/mol at 0 K, by fitting the theoretical results to the experimental distribution. The proposed mechanism for cobalt ions reacting with cyclopentane involves a ring-opening process that eventually leads to a Co(1-pentene) ion complex, which then decomposes. The internal energy content of this Co(1-pentene)$^+$ complex is too low to allow elimination of C_3H_6 as cyclopropane, in contrast to the same complex formed directly from Co^+ and 1-pentene, where both cyclopropane and propene are eliminated.

Introduction

A variety of techniques are now available to probe mechanisms of gas-phase organometallic reactions.[1-16] Kinetic energy release distributions associated with the decomposition of nascent organometallic complexes generally provide additional insight into both the energetics and mechanisms of these reactions. For example, decarbonylation of cyclobutanone by either Fe^+ or Co^+ was shown to proceed via a metallacyclobutane intermediate,

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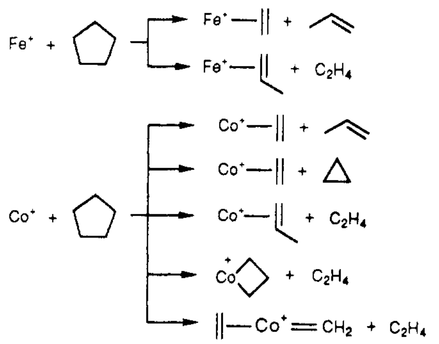
[†] Contribution No. 7957.

(1) For a recent review see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628, and references therein.

(2) See, for example: (a) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1985**, *89*, 5626. (b) Sunderlin, L.; Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 78. (c) Georgiadis, R.; Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 4251. (d) Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 411.

Table I. Reaction Enthalpies and Experimental and Theoretical Average Kinetic Energy Releases for C–C Bond Cleavage Reactions of Co^+ and Fe^+ with Cyclopentane



ΔH,[a] eV	$\bar{E}_t$, eV expt	$\bar{E}_t$, eV theory[b]
−0.06	*c*	
−0.15	*c*	
−0.37	0.069	0.068
0.0	*c*	
−0.45	0.084	0.084
+0.75	*c*	
+1.1[d]	*c*	

[a] Heat of reaction at 0 K. [b] Statistical phase space theory using the methods outlined in ref 20c. [c] Not observed. [d] See ref 24.

yielding cyclopropane as the neutral product.[17] Mechanistic details for the formation and fragmentation of metallacycles are important since metallacycles, especially metallacyclobutanes, play an important role in catalysis.[18]

The interaction of an atomic metal ion M^+ with an organic molecule A leads to the formation of a chemically activated association complex MA^+. The excited complex either can be collisionally stabilized or can rearrange and subsequently fragment to yield one or more products (e.g. reaction 1).[19]

$$M^+ + A \rightarrow (MA^+)^* \rightarrow MB^+ + C \qquad (1)$$

The kinetic energy release distribution for this process will reveal details about the potential energy surface, mainly in the region of the exit channel.[20] If there is no barrier in the exit channel, the kinetic energy release distribution is expected to be statistical, in which case complete energy randomization occurs prior to dissociation.[17] If, however, there is a barrier in the exit channel, the rate of product formation generally exceeds that of energy randomization after the barrier has been passed. In this case, the kinetic energy release distribution is not statistical and a large discrepancy is observed between the theoretical and experimental distributions.[17]

Statistical theories,[21-23] such as phase space theory,[23c] have been successful in modeling translational energy release distributions for reactions on a surface where there is no barrier, excluding a centrifugal barrier,[24] for the reverse association reaction. Fitting the statistical phase space theory to the measured distribution has been shown to yield heats of formation for both organometallic product ions[16,17] and neutrals.[25] In addition, insight into the reaction mechanism is often obtained by modeling these distributions.

The kinetic energy release distribution for the elimination of ethene from Co(cyclopentane)$^+$ has previously been published primarily for the thermochemical information that was obtained.[16b] In this paper the emphasis is on determining the mechanism of atomic cobalt ions reacting with cyclopentane to yield C–C bond cleavage products (reactions 2 and 3). Two quite different mechanisms have

$$Co(c\text{-}C_5H_{10})^+ \rightarrow Co^+\text{–}C_2H_4 + C_3H_6 \qquad (2)$$

$$Co(c\text{-}C_5H_{10})^+ \; Co^+\text{–}C_3H_6 + C_2H_4 \qquad (3)$$

been proposed in the literature to account for these processes.[11b,12] By using kinetic energy release distributions as a probe, we will attempt to distinguish between these mechanisms and decide which best describes the reactions of interest.

Experimental Section

Measurements of the metastable kinetic energy release distributions were obtained using a reverse-geometry double-focusing mass spectrometer (VG Instruments ZAB-2F[26]) with a temper-

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

(16) (a) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1985**, *107*, 1788. (b) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1.

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(18) The importance of metallacycles in catalysis has prompted many recent studies. See, for example, refs 6 and 7 and references therein.

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

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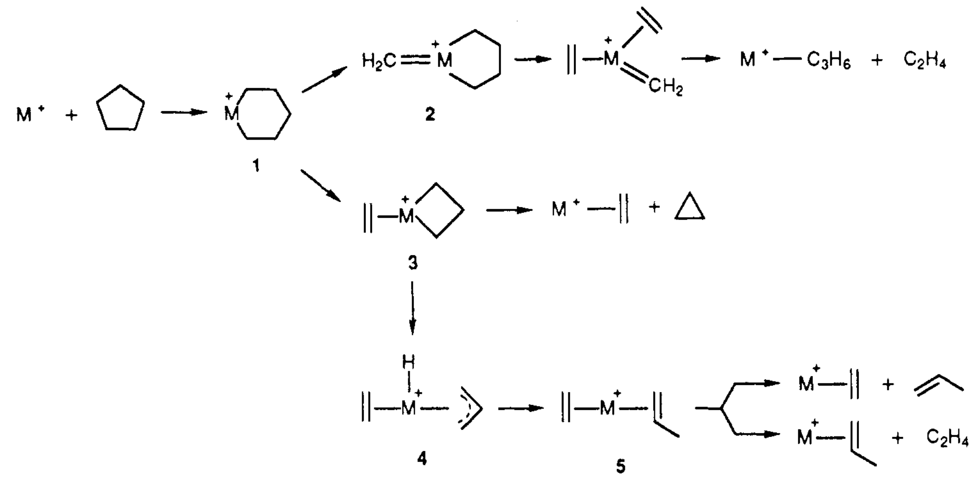
(24) For discussion see: Su, T.; Bowers, M. T. In *Gas-Phase Ion Molecule Chemistry*; Bowers, M. T. Ed.; Academic Press: New York, 1979.

(25) Brodbelt, J.; van Koppen, P. A. M.; Bowers, M. T.; Beauchamp, J. L., to be submitted for publication.

Scheme I



ature-variable ion source constructed at UCSB.[27] The iron and cobalt ions were formed by electron impact (150 eV) on $Fe(CO)_5$ and $Co(CO)_3NO$, respectively. Typical source pressures were 10^{-3} Torr, and source temperatures were generally kept below 270 K to minimize decomposition of the $Fe(CO)_5$ or $Co(CO)_3NO$ on insulating surfaces.

The organometallic ions were formed in the ion source by reaction of the bare metal ions with the neutral substrate molecules. The source was kept field free to avoid translational excitation of the reactant metal ions. Upon exiting the source, the ions were accelerated to 8 kV and mass analyzed. Metastable ions which decompose in the second field-free region between the magnetic and electric sectors were detected by scanning the voltage of the electric sector. The metastable peaks were accumulated in a multichannel analyzer and numerically differentiated to obtain the kinetic energy release distributions.[27] The energy resolution was such that the main beam did not contribute significantly to the metastable peak widths.

All chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases.

Results and Discussion

Metastable decomposition reactions of nascent Fe^+ and Co^+ complexes with cyclopentane were studied. The product branching ratios have been previously reported for Co^+[23] but not for Fe^+. Dehydrogenation occurs essentially exclusively for Fe^+ reacting with cyclopentane, whereas both dehydrogenation and C–C bond cleavage processes are observed for Co^+. The observed product distributions are in good agreement with previous studies,[11b,13] which utilized quite different experimental methods.

In this study we are primarily interested in carbon–carbon bond activation; specifically, C_2H_4 and C_3H_6 elimination reactions from Co(cyclopentane)⁺ (reactions 2 and 3). The average kinetic energy releases, $\bar{E}_t$, for the metastable decompositions are given in Table I (both the experimental and theoretical values). The theoretical values are calculated by using statistical phase space theory.[23c] A comparison is made between the experimental and theoretical distributions to determine whether a statistical model, assuming equipartitioning of the excess energy, is adequate to describe the experimental distribution. Details of the calculations have been presented previously.[16b] The parameters used in the calculations are summarized in the Appendix. The experimental and theoretical average kinetic energy releases correspond almost exactly (see Table I).

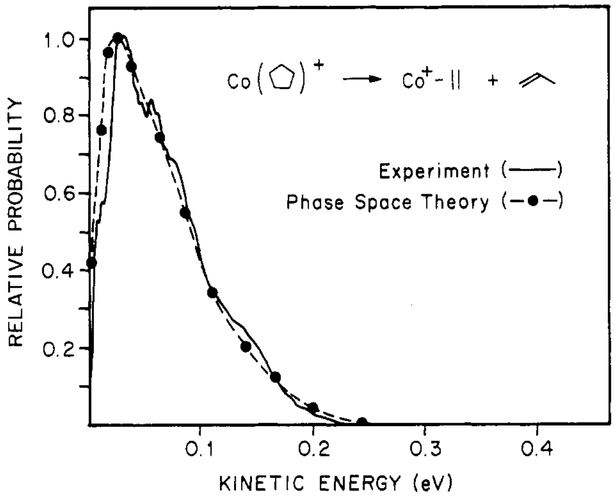


Figure 1. Experimental and theoretical kinetic energy release distributions for the loss of C_3H_6 from Co(cyclopentane)⁺. A theoretical distribution assuming 100% propene elimination gives an excellent fit with experiment.

The kinetic energy release distributions obtained for the loss of C_3H_6 and C_2H_4 from Co(cyclopentane)⁺ are shown in Figures 1 and 2, respectively. Narrow, apparently statistical, distributions are obtained in both cases. These results suggest smooth transitions to products in the exit channels without barriers. This suggestion is confirmed by the essentially exact fit between experiment and statistical phase space theory (see Figures 1 and 2). The results in Figures 1 and 2 also imply a single reaction mechanism is operative, where the C_2H_4 elimination process forms Co(propene)⁺ as the product ion and the C_3H_6 elimination process forms propene as the product neutral.

A possible mechanism similar to those proposed by Grubbs and Miyashita for decomposition of titanacyclohexanes and nickelacyclohexanes in solution[30] is outlined in Scheme I. Armentrout and Beauchamp[11b] have pres-

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(26) Morgan, R. P.; Beynon, J. H.; Bateman, R. H.; Green, B. N. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 171.

(27) (a) Jarrold, M. F.; Illies, A. J.; Bowers, M. T. *Chem. Phys.* **1982**, *65*, 19. (b) Kirchner, N. J.; Bowers, M. T. *J. Phys. Chem.* **1987**, *91*, 2573.

(28) Hanratty, M. A.; Paulsen, C. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5074.

(29) The heat of formation of the cobalt carbene ethene ion is estimated to be 284 kcal/mol relative to the cobaltacyclobutane ion, which was determined to be 274 kcal/mole.[12]

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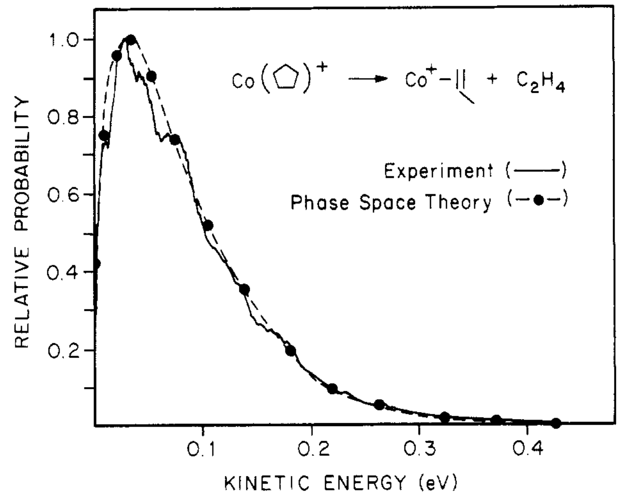
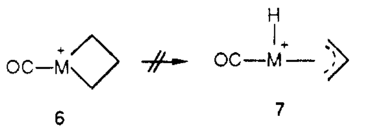


Figure 2. Experimental and theoretical kinetic energy release distributions for the loss of C_2H_4 from Co(cyclopentane)$^+$. A theoretical distribution assuming 100% Co(propene)$^+$ structure gives an excellent fit with experiment.

ented this mechanism to account for the C–C bond cleavage products for reaction of Co^+ with cyclopentane. The key point in this mechanism is the formation of the four- and five-member metallacycles **3** and **2** from the six-member metallacycle **1**.

The mechanism in Scheme I suggests **3** could either directly eliminate cyclopropane or rearrange to the hydridoallyl complex **4** and then eliminate propene. However, we have previously shown[17] that rearrangement of the metallacyclobutane carbonyl intermediate **6** to the hydridoallyl complex **7** is not observed. This suggests



6 **7** (4)

intermediate **3**, if formed, is not likely to rearrange to the hydridoallyl complex **4** since intermediates **6** and **3** are very similar. Hence, loss of propene would not be observed. If this is the case, elimination of C_3H_6 would correspond to the loss of cyclopropane exclusively. However, cyclopropane loss is not likely since it is endothermic for both cobalt and iron reacting with cyclopentane. In addition, the kinetic energy release distribution for C_3H_6 elimination is quite narrow, suggesting elimination of C_3H_6 as propene. Elimination of C_2H_4 via intermediate **2**, producing the metal carbene ethene ion, is not expected to occur since it is endothermic by approximately 26 kcal/mol (Table I). The mechanism outlined in Scheme I is therefore not consistent with the experimental results observed.

An alternative mechanism for the elimination of C_2H_4 and C_3H_6 from Co(cyclopentane)$^+$, shown in Scheme II, is similar in part to the proposal of Jacobson and Freiser.[12] Initial C–C or C–H bond insertion followed respectively by a β-H or β-alkyl shift leads as indicated to a coordinated 1-pentene complex, which subsequently eliminates either ethane or propene in agreement with experiment. Further support is given to Scheme II by the fact that platinacycloheptanes decompose in solution yielding 1- and 2-hexenes exclusively,[31,32] presumably by a 2,5-hydrogen atom shift analogous to that in Scheme II. However, recent studies of processes in which C–C bond cleavage occurs in reactions of Co^+ with acyclic alkanes have provided strong evidence that initial C–C insertion does not take place and that alkane elimination involves an initial C–H insertion followed by a β-alkyl shift.[33]

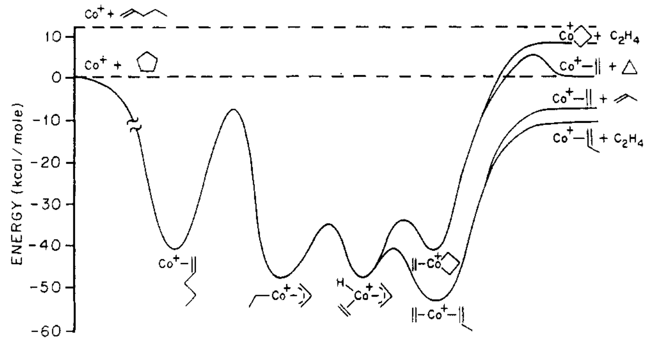
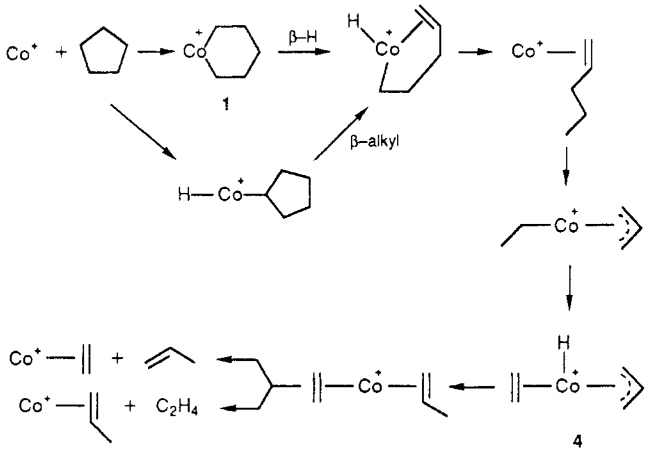


Figure 3. Qualitative potential energy diagram for reactions of Co^+ with 1-pentene and cyclopentane.

Scheme II



If the Co(cyclopentane)$^+$ complex does in fact rearrange to the coordinated pentene, as shown in Scheme II, the kinetic energy release distributions for the loss of C_3H_6 or C_2H_4 from Co(cyclopentane)$^+$ and Co(1-pentene)$^+$ should be similar. The mechanism for Co^+ reacting with 1-pentene is shown in Scheme III, with the process involving intermediate **8** being the same as the mechanism proposed in Scheme II. Once the hydridoallyl complex **4**, is formed, C_2H_4 and C_3H_6 are eliminated via **8** and **9**.

The observed kinetic energy release distributions[17] are consistent with this model since both C_3H_6 and C_2H_4 elimination from Co(1-pentene)$^+$ are composites, indicating two available reaction channels. The kinetic energy released for propene elimination from **8** is less than for cyclopropane elimination from *9*, corresponding to a low- and high-energy component in the kinetic energy release distribution. The kinetic energy release distribution for ethene elimination was also shown to be a composite of two reaction channels, in this case yielding the metallacyclobutane and the metal–propene product ions as the high- and low-energy components, respectively.[17]

The kinetic energy release distribution for C_3H_6 elimination for Co(cyclopentane)$^+$ (Figure 1) does not have the high-energy component found for Co(1-pentene)$^+$, indicating no cyclopropane is eliminated. This result is con-

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[31] (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *Ibid.* **1976**, *98*, 6529.

[32] McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.

[33] van Koppen, P. A. M.; Brodbelt-Lustig, J.; Bowers, M. T.; Dearden, D. V.; Beauchamp, J. L.; Fisher, E.; Armentrout, P. B., manuscript in preparation.

Scheme III

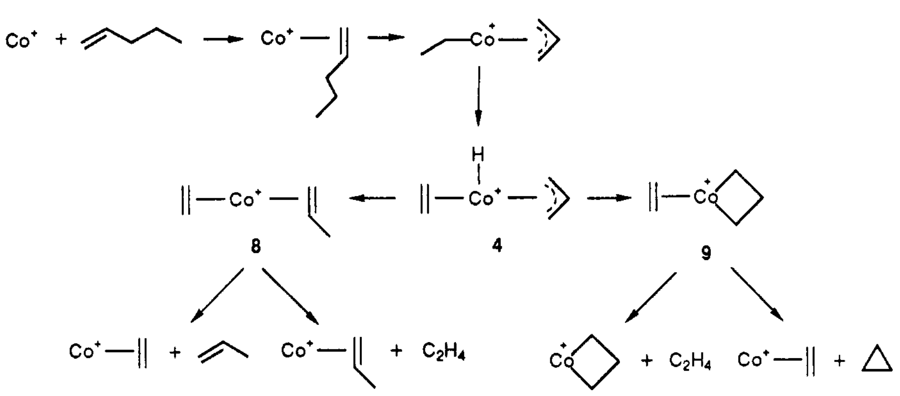
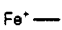
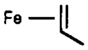
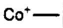
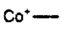
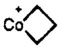
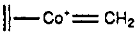
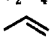


Table II. Heats of Formation and Bond Energies Used in Calculations

molecule	ΔH_f,[a] kcal/mol	bond energy D_0^0, kcal/mol
	260[b]	35
	252[b]	37
	255[c]	42
	247[d]	44
	274[e]	25[f]
	283[e]	
Co^+	282.3	
Fe^+	280.4	
C_2H_4	14.52	
	8.26	
	16.84	
	-10.75	

[a] Heat of formation at 0 K. [b] Rough estimate (see Appendix in ref 17). [c] Determined in this study. [d] Reference 16b. [e] Reference 17. [f] Bond energy for cobaltacyclobutane decomposing to Co^+ and cyclopropane.

Table III. Input Parameters for Cyclopentane Used in Calculations

ΔH_f[a]	-10.75				
B[b]	0.175				
σ[c]	1				
α[d]	8.95				
ν_i[e]	2966 (3)	2949 (2)	2906	2904 (2)	2878 (2)
	1462 (2)	1453 (3)	1350 (2)	1312 (2)	1311
	1295	1283 (2)	1207 (2)	1030 (2)	1004 (2)
	897 (2)	886	717 (2)	628 (2)	545
	283 (2)				

[a] Heat of formation at 0 K in kcal mol^{-1}. [b] Rotational constant in cm^{-1}. [c] Symmetry number. [d] Polarizability in $Å^3$. [e] Vibrational frequencies in cm^{-1}.

sistent with the fact that the $Co(C_5H_{10})^+$ complex from cyclopentane contains 13.5 kcal mol^{-1} less energy than the $Co(C_5H_{10})^+$ complex from 1-pentene[34] (see Figure 3), and hence cyclopropane elimination is endoergic.

The kinetic energy release distribution for C_2H_4 elimination from $Co(cyclopentane)^+$ is statistical. The theoretical distribution, assuming 100% $Co(propene)^+$ product, fits the experimental distribution exactly, as shown in Figure 2. Consequently, cobaltacyclobutane ions are not formed. The results are therefore consistent with the mechanism presented in Scheme II.

The absence of C_2H_4 and C_3H_6 elimination reactions for Fe^+ reacting with cyclopentane may be due to the fact that the reactions may be slightly endoergic. Available estimates of metal-ligand bond energies suggest that the reactions are slightly exoergic (Table I). However, the uncertainty of these numbers is such that the reactions may in fact be endoergic. Alternatively, there may be a slight barrier to C–C bond insertion into the cyclopentane ring.

Conclusion

Reactions of Co^+ and Fe^+ with cyclopentane differ both from each other and from their common reaction with 1-pentene. Dehydrogenation is nearly exclusively observed for Fe^+, whereas both dehydrogenation and C–C bond cleavage processes are observed for Co^+. The data presented for C–C bond cleavage processes for the $Co(cyclopentane)^+$ system support the mechanism outlined in Scheme II where the 1-pentene metal ion complex is generated prior to further decomposition. The 1-pentene metal ion complex formed will have 13.5 kcal mol^{-1} less internal energy than that formed from reaction of Co^+ directly with 1-pentene. As a result the higher energy pathway, loss of cyclopropane, is not accessible, leaving the loss of propene as the only reaction channel observed. The kinetic energy release distribution for the loss of C_2H_4 from $Co(cyclopentane)^+$ was shown to be statistical in support of a single product channel with $Co(propene)^+$ product ion being exclusively formed. Again, the higher energy pathway, yielding the cobaltacyclobutane ion, is not energetically available.

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Appendix

The model for statistical phase space calculations has been previously outlined.[16b] Here the parameters used in the calculations are summarized and the thermochemistry involved is discussed.

To calculate the kinetic energy distributions, structures and vibrational frequencies for the various species are required. These were taken from the literature where possible or estimated from literature values of similar

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(34) Thermochemical information taken from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys, Chem. Ref. Data, Suppl.* 6 1977, *No. 1.*

species.[35] The details of the kinetic energy distributions were found to vary only weakly with structure or vibrational frequencies over the entire physically reasonable range for these quantities. The distributions were strongly dependent on the total energy available to the dissociating complex and hence in our model to the $\Delta H°$ of reaction.

Often all heats of formation of products and reactants were well-known except one, the organometallic product ion. The heats of formation for Co(propene)$^+$ and Co(ethylene)$^+$ have been previously determined.[16b] The bond energies for the corresponding iron species as well as cobalta- and ferracyclobutane have also been determined.[17] These heats of formation were consistently used throughout the calculations and are summarized in Table II. All the parameters, except those for cyclopentane, have been previously published.[17] The parameters for cyclopentane are summarized in Table III.

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[35] (a) Shimanouchi, T. *Table of Molecular Vibrational Frequencies*; National Bureau of Standards: Washington, DC, 1972; Consolidated, Vol. I. (b) Sverdlov, L. M.; Kovner, M. A.; Krainov, E. P. *Vibrational Spectra of Polyatomic Molecules*; Wiley: New York, 1970.

Electron-Transfer-Catalyzed Chelation of $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5R_5})(\eta^1\text{-}\mathrm{SC(S)NMe_2})(\mathrm{CO})_2]$ (R = H, Me) Induced by Oxidation

Jean-Noël Verpeaux,[†] Marie-Hélène Desbois,[‡] Alex Madonik,[§] Christian Amatore,[*,†] and Didier Astruc[*,‡]

Laboratoire de Chimie, UA CNRS No. 1110, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cêdex 05, France, Laboratoire de Chimie Organique et Organométallique, UA CNRS No. 35, Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence Cêdex, France, and Laboratoire de Chimie des Organométalliques, UA CNRS No. 415, Université de Rennes I, 35042 Rennes Cêdex, France

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The chelation of the monodentate dithiocarbamate complexes $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5R_5})(\eta^1\text{-dtc})(\mathrm{CO})_2]$ (dtc = SC(S)NMe$_2$; R = H (**1a**), Me (**1b**)) to $[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5R_5})(\eta^2\text{-dtc})(\mathrm{CO})]$ (R = H (**2a**), Me (**2b**)) is catalyzed by $[\mathrm{FeCp_2}]^+\mathrm{X}^-$ ($\mathrm{X}^- = \mathrm{PF_6}^-$ (**3a**), $\mathrm{BF_4}^-$ (**3b**), $\mathrm{SbCl_6}^-$ (**3c**)) in THF. The yields depend on the amount of **3** and on the size of its counteranion. The mechanism involves the oxidation $\mathbf{1} + \mathbf{3} \rightarrow \mathbf{2}^+\mathrm{X}^- + \mathrm{FeCp_2}$ and the cross electron transfer (ET) $\mathbf{2}^+\mathrm{X}^- + \mathbf{1} \rightarrow \mathbf{2} + \mathbf{1}^+\mathrm{X}^-$. However, the large endergonicity of the latter (>10 kcal mol^{-1}) makes it slow and side-reaction process(es) of $\mathbf{2}^+\mathrm{X}^-$ (decomposition or precipitation) compete(s) efficiently with the cross-ET step. Accordingly the ETC mechanism proceeds eith low Coulombic efficiency (<5). Cyclic voltammetry (CV) does not allow the observation of $\mathbf{1}^+\mathrm{X}^-$ even at scan rates $\simeq$5000 V s^{-1}, indicating that the chemical propagation step $\mathbf{1b}^+\mathrm{X}^- \rightarrow \mathbf{2b}^+\mathrm{X}^-$ proceeds at rate constants of ca. 10^7 s^{-1}. It shows that the deactivating step of $\mathbf{2b}^+\mathrm{X}^-$ proceeds with a rate constant of ca. 10^{-1} s^{-1}. CV's, in the presence of PPh$_3$, show the existence of $[\mathrm{FeCp^*}(\eta^2\text{-dtc})(\mathrm{PPh_3})]^{+/0}$ ($\mathbf{4b}^+\mathrm{X}^-/\mathbf{4b}$), and electrolysis of **1b** in the presence of electrolyte gives a THF-soluble one-electron-oxidation complex, presumably $[\mathrm{FeCp^*}(\eta^2\text{-dtc})(\mathrm{THF})]^+\mathrm{X}^-$ ($\mathbf{5b}^+\mathrm{X}^-$).

Introduction

There has been considerable interest, during this decade, in electron-transfer-chain (ETC) catalyzed organometallic reactions, i.e. reactions of organometallic complexes catalyzed by electrons or electron holes.[1-3] The principle of reactions catalyzed by electrons was pioneered by Kornblum[4] and Russell[5] in organic chemistry a quarter of a century ago, the most well-known series being Bunnett's $S_{RN}1$ reactions.[6] Using electrochemical techniques, Feldberg[7] established the theoretical and experimental basis for this electrocatalytic $\overline{\mathrm{E}}\mathrm{C}\overline{\mathrm{E}}$ mechanism in 1971 at the same time as he disclosed the first example of a ligand-exchange reaction in organometallic chemistry. The dimensionless analysis of electrochemical kinetics by Savéant's group[8] was furthermore of considerable importance for the studies of, inter alia, the $\overline{\mathrm{E}}\mathrm{C}\overline{\mathrm{E}}$ mechanism, particularly in the field of $S_{RN}1$ and related mechanisms.

Almost all the examples reported so far with the ETC mechanism have an exergonic cross-ET propagation step and, thus, are fast and complete.[8c] However, as already shown in $S_{RN}1$ reactions by Savéant's group, side reactions, a key problem in ETC catalysis, become especially im-

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[†] Ecole Normale Supérieure.
[‡] Université de Bordeaux I.
[§] Université de Rennes I.

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