Table II. Thermochemistry. Comparison of Experiment with Theory

E_{-1}[a]	$\log (A_{-1}/s^{-1})$	$-\Delta H°$[a]	$\Delta S°$[b]	ref
9.09	10.36	3.15	8.3 (9.7)[c]	this work
		5.2	6.6	6
17.3		8.6		8
12.4	11.46	0.25	7.2	9
12.9		0.5		10

[a] In kilocalories/mole. [b] In calories/mole K. [c] Statistically corrected. It is not clear whether the other $\Delta S°$ values have or have not been corrected.

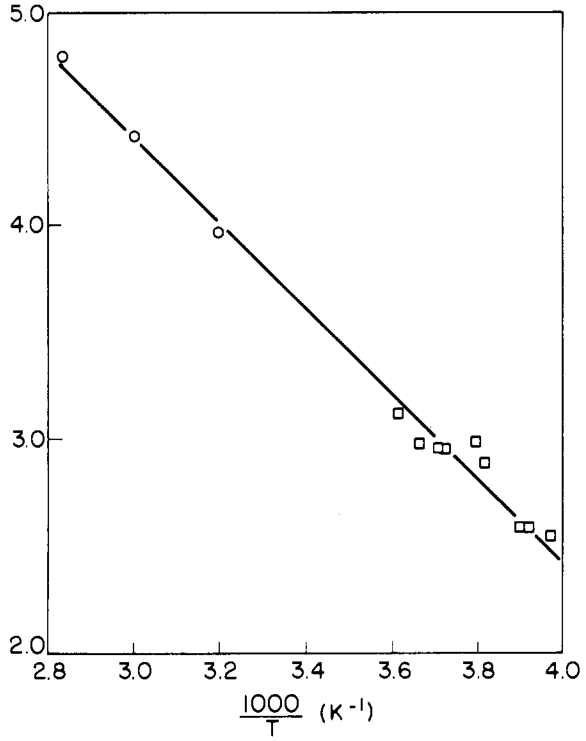

Figure 1. Plot of $\log (k_{-1}/s^{-1})$ against $1/T$: ○, technique 1; □, technique 2.

The relative concentrations of **1** and **2** under equilibrium conditions must be calculated from the relation

$$\log K' = \log (2k_1/k_{-1}) = 2.12 + 3.15/\theta$$
$$K' = 2.6 \times 10^4 \text{ at } 25\ °\text{C} \qquad (5)$$

Our present experimental results are compared in Table II with thermochemical quantities that have been previously estimated or calculated.

Finally, we estimate that line broadening in the EPR spectrum of the unlabeled 3-butenyl radical resulting from rapid exchange of the α and β hydrogens should occur at a temperature of ~400 °C. Unfortunately, EPR experiments at such elevated temperatures, though possible,[26] are not easy to carry out.

Acknowledgment. We thank Professor J. Warkentin and an unnamed referee for some extremely valuable comments on this work.

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(16) Calculated from the integrated rate expression

$$[\mathbf{7}]_f = \frac{k_1}{2k_H}\left\{\frac{[\mathrm{Bu_3SnH}]_i + (k_{-1}/k_H)}{[\mathrm{Bu_3SnH}]_f + (k_{-1}/k_H)}\right\}$$

where the subscripts i and f refer to initial and final concentrations. Values of k_{-1} are averages of 6, 10, and 16 determinations at 40, 60, and 80 °C, respectively. The tin hydride was normally consumed completely. Three typical experiments at 80 °C follow: $[\mathrm{Bu_2SnH}]_i = 0.202, 0.125$, and 0.077 M which gave $[\mathbf{7}]_f = 0.0270, 0.0232$, and 0.0175 M, respectively. Taking $k_H = 2.4 \times 10^6\ M^{-1}\ s^{-1}$, these experiments yield $k_{-1} = 5.8, 6.5$, and $6.0 \times 10^4\ s^{-1}$.

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(19) With hexa-*n*-butylditin the desired radical, **4**, was produced, but It was "contaminated" by a significant concentration of *n*-butyl which arises by direct photocleavage of the tin–carbon bond. This problem was much less severe with hexamethylditin, no trace of $CH_3\cdot$ radicals being detectable in this system.

(20) After allowing for the difference in the spin and gyromagnetic ratio of deuterium, the EPR parameters for **4** and **5** were in agreement with those reported previously for 3-butenyl.[21]

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(24) Which has the same molecular weight as dideuterio-3-butenyl.

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Ion Beam Studies of Organometallic Chemistry. High Energy "Sampling" of Reaction Intermediates Involved in Carbon–Carbon Bond Cleavage by Transition Metals

Sir:

Chemical transformation often involves reactive intermediates which correspond to local minima on a complex potential energy surface. Ordinarily, these species are not revealed in conventional kinetic and mechanistic studies. One approach to the characterization of such intermediates is to deprive them of sufficient energy to continue to react by deposition or formation in a low temperature matrix. An alternative method, described here, relies conversely on providing the intermediate with substantially more energy than needed for reaction. In

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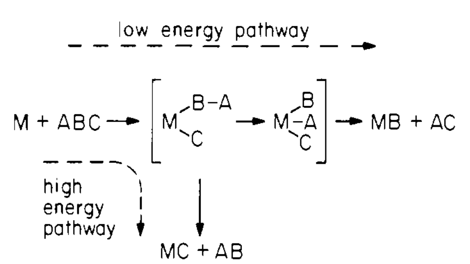
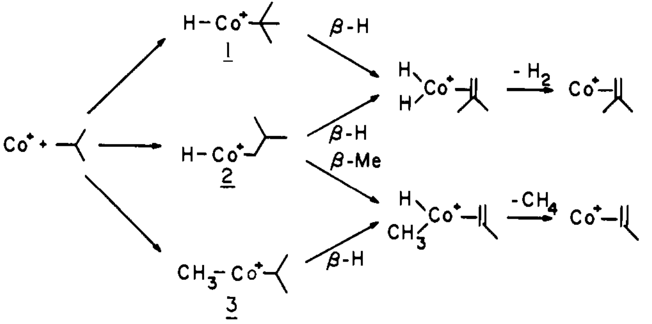
Scheme I



Scheme II



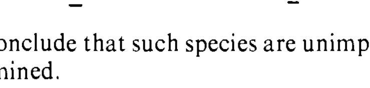
this paper, we demonstrate the method using as examples the reactions of cobalt ions with alkanes.

A generalized organometallic reaction is shown in Scheme I. The low energy pathway consists of association of a metal center with molecule ABC followed by oxidative insertion into the B-C bond, migration of A to the metal, and reductive elimination of AC. As the energy of the system is increased, the lifetimes of the intermediates decrease. At sufficiently high energies, reaction pathways such as simple bond cleavage not accessible at thermal energies may become the dominant decomposition route, since these processes often have favorable frequency factors[1] (Scheme I). Observation of the high energy products, MC and AB, provide evidence for formation of the first intermediate. Hence, species present on the complex energy surface are "sampled".

An ion beam tandem mass spectrometer[2,3] shown schematically in Figure 1 has been utilized in the present studies. In our experiments, singly charged cobalt ions are produced by thermal decomposition of $CoCl_2$ and surface ionization of the resulting Co on a hot (~2500 K) rhenium surface.[4] These ions are collimated, mass and energy selected, and allowed to interact with the target gas in a collision chamber. Product ions are monitored using an in-line quadrupole mass filter and electron multiplier. Neutral products are not detected but inferred. These experiments yield reaction cross sections and product distributions as a function of relative kinetic energy.

Results for the reaction of Co^+ with 2-methylpropane are shown in Figure 2. The behavior of the cross sections for the products $CoC_3H_6^+$ and $CoC_4H_8^+$ as a function of translational energy is typical of species formed in exothermic reactions.[3] In light of the discussion above, the observation of species such as CoH^+ and $CoCH_3^+$ at higher energies suggests that oxidative addition of both C-H and C-C bonds are important reaction steps. Scheme II outlines the low energy mechanism proposed:[6] oxidative addition of the three types of bonds available in isobutane, followed by β-hydrogen or β-methyl transfer to the metal and reductive elimination of an alkane or hydrogen molecule. At high energies, intermediates **1** and **2** decompose to yield CoH^+ and $C_4H_9^+$, while **3** gives $CoCH_3^+$ and $C_3H_7^+$.

Additional insights relevant to the proposed mechanisms may be garnered from the reaction of Co^+ and 2,2-dimethylpropane. Dehydrogenation processes analogous to those proposed in Scheme II are not possible in this system. However, alternative reaction pathways which include formation of alkylidene, **4**, or metallocyclobutane, **5**, intermediates are still accessible. We observe only $CoC_4H_8^+$ at low energies. At high energies, the predominant product is $C_4H_9^+$. These observations are consistent with a reaction mechanism analogous to Scheme II. Since **4** and **5** would be expected to eliminate hydrogen, we conclude that such species are unimportant in the systems examined.



4 5

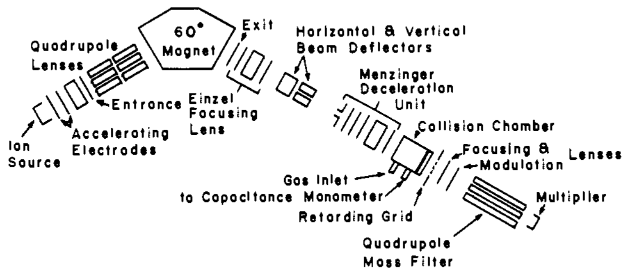


Figure 1. Schematic drawing of the ion beam apparatus.

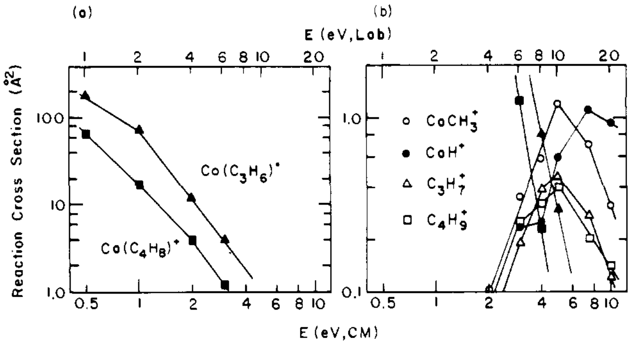


Figure 2. Variation in experimental cross section with relative kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for the interaction of cobalt ions with 2-methylpropane, showing (a) exothermic channels and (b) endothermic channels. Note change of scale.

In the studies detailed above, a quantitative assessment of the fragmentation of reaction intermediates can provide thermodynamic data. In the dissociation of a charged collision complex, such as **3**, the preferred ionic product is the fragment having the lower ionization potential (IP).[7] The observation that the cross section for production of $CoCH_3^+$ is always greater than that of $C_3H_7^+$ (Figure 2) implies that IP($CoCH_3$) < IP(*iso*-C_3H_7) = 7.36 eV.[9] A similar analysis of the 2,2-dimethylpropane system establishes IP($CoCH_3$) > IP(*tert*-C_4H_9) = 6.70 eV.[9] The behavior of the other products in Figure 2, CoH^+ and $C_4H_9^+$, may also be understood using analogous considerations.

In addition, measurement of the thresholds for the endothermic processes observed at high energies provides bond energies of the products. Preliminary data for the endothermic reactions of Co^+ with hydrogen and ethane indicate that $D°(Co^+-H) = 52 \pm 4$ and $D°(Co^+-CH_3) = 61 \pm 4$ kcal/mol.[10] Combined with the ionization potentials, IP(CoH) = 7.3 ± 0.1 and IP($CoCH_3$) = 7.0 ± 0.3 eV, derived as discussed above, we find the neutral bond dissociation energies, $D°(CoH) = 39 \pm 6$ and $D°(CoCH_3) = 41 \pm 10$ kcal/mol.

To our knowledge these are the first investigations of organo transition metal reactions using ion beam techniques. Such studies provide a wealth of thermochemical data and mechanistic insights. The above results provide substantial evidence for the viability of a mechanism for carbon-carbon bond cleavage of alkanes which involves direct insertion of a metal into the carbon-carbon bond as a first step. Thermochemical data indicating strong metal-carbon bonds corroborate this hypothesis. Further studies are underway in our laboratories to extend this technique to other systems.

Acknowledgment. This research was supported by the U.S. Department of Energy. We are indebted to Professor Robert Grubbs and his co-workers for their input relating to these studies.

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Preference for the Syn Ene Additions of $^1O_2$ to 1-Methylcycloalkenes. Correlation with Ground-State Geometry

Sir:

We[1,2] and others[3] have recently demonstrated a strong, unexpected preference for the ene-type additions of $^1O_2$ at the disubstituted side of simple, acyclic, trisubstituted [$(-CH_2R)_3$] olefins: preference for the syn ene additions (PSEA). We now point out that the 4-, 5-, 7-, 8- (with *Z* geometry), and 12-membered (*Z* and *E* geometry) 1-methylcycloalkenes also show a PSEA (Scheme I) and that only 1-methylcyclohexene and its derivatives do not. Preoccupation with the latter, mainly terpenes, has obscured the fact that *PSEA is the rule in acyclic and cyclic systems, cyclohexenes excepted.* (*E*)-1-Methylcyclooctene, the 9 to 11 rings, and ≥12 rings have not yet been investigated.[4,5] We rely largely on published photooxygenation studies;[6] that these were carried out in different solvents and at different temperatures does not matter because product distributions are known to be insensitive to changes of either, and even of phase.[6,7] The available data are collected in Chart I. In the *Z* series, the 4, 5, and 7 rings (**1, 2, 4**) show a very strong PSEA, the 8 and 12 rings [(*Z*)-**5**, (*Z*)-**6**] a less pronounced PSEA, and the 6 ring (**3**) none. (*E*)-1-Methylcyclododecene [(*E*)-**6**] also shows a very strong PSEA. 1-Ethyl- or 1-propylcycloalkenes would be more suitable substrates for demonstrating the PSEA[5] and Chart I includes data on (*Z*)- and (*E*)-1-ethylcyclododecene [(*Z*)-, (*E*)-**7**], which parallel those for the 1-methylcyclododecenes [(*Z*)-, (*E*)-**6**].

Scheme I

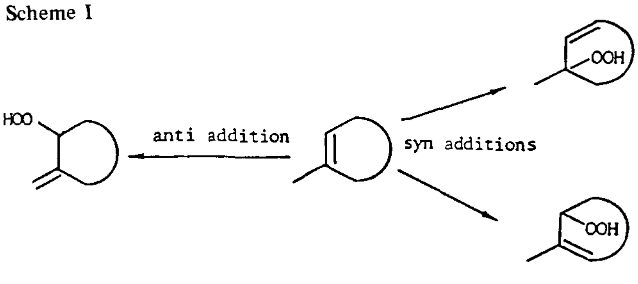
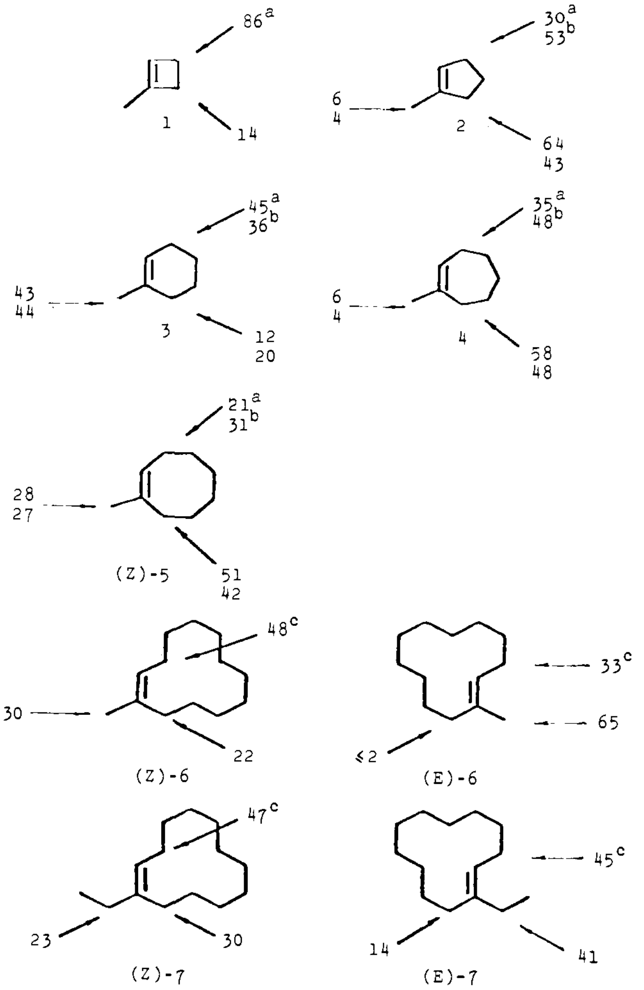


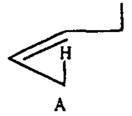
Chart I. Ene Additions of $^1O_2$ to 1-Methyl- and 1-Ethylcycloalkenes. Product Distributions[a]

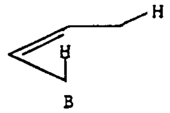


[a] In percent; the arrows indicate the sites of the H-atom abstractions throughout; (a) ref 8; (b) ref 9; (c) note 10.

Chart II summarizes the available data on terpenes and data on a related substrate, **11**. The simple 4- and 5-substituted 1-methylcyclohexenes (**9–12**) all show no PSEA,[11] like the parent, **3**. The derived bicyclo[4.1.0]heptenes, 3-carene (**13**) and 2-carene (**14**),[18] do show a PSEA, as does the cyclopentene-derived bicyclo[3.1.0]hexene, 3-thujene (**8**).

It appears that ground-state geometry and reactivity, PSEA, can be correlated: we note that the ground-state geometries of the H—C_n—C_1=C_2—C_3—H sites of the (*Z*)-cycloalkenes in Charts I and II are essentially of only two types (A, B), and that all rings with one type of geometry (A) show a PSEA and all rings with the other (B) do not. In the former, the 4-, 5-, 7-,


A


B

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