Gas-Phase Studies of Alkene Oxidation by Transition-Metal Oxides. Ion-Beam Studies of CrO+
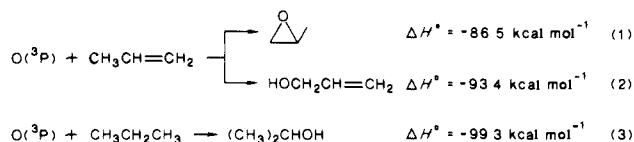
H. Kang and J. L. Beauchamp*

Contribution No. 7321 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received February 11, 1986

Abstract: An examination of reaction thermochemistry and metal oxide bond dissociation energies focuses attention on the chromium oxide ion as an interesting candidate for investigations of hydrocarbon oxidation processes. Reactions of this species, formed by surface ionization, have been examined with ion-beam reactive scattering techniques. In reactions with alkenes, CrO^+ abstracts allylic hydrogen to form $CrOH^+$ and adds to double bonds to yield aldehydes and other products which are rationalized by postulating metallacyclic intermediates. In comparison with other first-row transition-metal oxides, which are either too stable (Sc, Ti, and V) or too reactive (Mn, Fe, Co, and Ni), CrO^+ exhibits a balance in being reactive but selective. Bond dissociation energies derived in this study include $D°(Cr^+-O) = 85.3 \pm 1.3$ kcal mol^{-1} and $D°(Cr-O) = 110 \pm 2$ kcal mol^{-1}.

Oxidation reactions involving metal oxide reagents[1] and catalysts[2] play an important role in organic synthesis owing to their capacity for selective oxygen transfer to a wide variety of substrates. A key mechanistic feature common in these reactions is the participation by one or more oxometal groups (M–O) in the transformation. Although the mechanisms of these reactions have received a considerable amount of attention, it is often difficult to completely characterize important reactive intermediates in condensed-phase studies. In the present work, we report ion-beam studies of the reactions of the simplest metal oxide reagent, which is a diatomic metal oxide ion, with alkenes in the gas phase, where the identities of reactants and nascent products are readily ascertained. Topics relating to selective oxidation of alkanes by CrO^+ in the gas phase will be presented in a subsequent paper.[3] A discussion of the energetics and mechanisms of the observed reactions derives benefit from the growing thermochemical data base being obtained in recent gas-phase studies of the reactions of atomic transition-metal ions with various organic molecules.[4]

Several factors are important in selecting a metal oxide system for detailed studies. Consider the energetics[5] of several oxidation processes involving alkenes and alkanes, including expoxidation (reaction 1), allylic oxidation (reaction 2), and formation of alcohols from saturated alkanes (reaction 3). Reactions such as

$$O(^3P) + CH_3CH=CH_2 \quad \begin{cases} \to \triangle\!/ & \Delta H° = -86.5 \text{ kcal mol}^{-1} \quad (1) \\ \to HOCH_2CH=CH_2 & \Delta H° = -93.4 \text{ kcal mol}^{-1} \quad (2) \end{cases}$$

$$O(^3P) + CH_3CH_2CH_3 \to (CH_3)_2CHOH \qquad \Delta H° = -99.3 \text{ kcal mol}^{-1} \quad (3)$$

these in which oxygen is transferred from a transition-metal center will be roughly thermoneutral when the metal–oxygen bond

dissociation energy is in the range 85–100 kcal mol^{-1}. Consider next the available bond dissociation energies for transition-metal oxide ions in Table I. The early transition metals, Sc, Ti, and V, form stable metal oxide ions which would be unreactive with alkanes and alkenes. These atomic metal ions might be expected to react with oxygen-containing organic molecules to regenerate hydrocarbons and metal oxide ions. This behavior is exemplified by reaction 4 in which Sc^+ reacts with acetone to yield ScO^+ and propene.[6]

$$Sc^+ + (CH_3)_2CO \to CH_3CH=CH_2 + ScO^+ \qquad (4)$$

The late transition metals Mn, Fe, Co, and Ni have metal oxide ion bond dissociation energies [$D°(M^+-O)$] which are low, leading

(1) For a review of oxidation reactions by oxometal reagents, see: Sheldon, R. A.; Kochi, J. A. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981; Chapter 6. Wiberg, K. B. *Oxidations in Organic Chemistry*; Academic Press: New York, 1965; Part A, pp 69–184.

(2) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1984; Chapter 4.

(3) Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc.*, submitted for publication.

(4) (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1984**, *1*, 963. (b) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403. (c) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (d) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (e) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (f) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565. (g) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4373 and references therein. (h) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065. (i) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 1286. (j) Kappes, M. M.; Staley, R. H. *J. Phys. Chem.* **1981**, *85*, 942.

(5) Cox, J. C.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. $\Delta H_f°(Cr^+) = 250.3$ kcal mol^{-1} from the following: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl. 6* **1977**.

(6) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.

*Author to whom correspondence should be addressed.

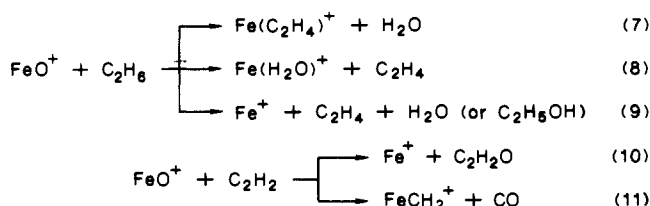**Table I.** Thermochemical Data of the First-Row Transition-Metal Oxides

metal	$D°(M^+-O)$, kcal mol^{-1}	$D°(M-O)$, kcal mol^{-1}	IP(MO), eV	$D°(M^+-OH)$, kcal mol^{-1}	$D°(MO^+-H)$, kcal mol^{-1}
Sc	159 ± 7[a]	161.5 ± 3[a]	6.6 ± 0.3[a]		
Ti	161 ± 5[a]	158.4 ± 2[a]	6.7 ± 0.1[a]		
V	131 ± 5[b,p]	146 ± 4[c]	7.4 ± 0.3[o]		
Cr	85.3 ± 1.3[d]	110 ± 2[d]	7.85 ± 0.02[e]	73 ± 5[q]	89 ± 5[q]
Mn	57 ± 3[f]	85 ± 4[g]	8.65 ± 0.2[f]		
Fe	69 ± 3[f]	93 ± 4[h,i]	8.9 ± 0.16[f,h,i]	73 ± 3[h,j]	106 ± 4[h,n]
Co	64 ± 3[f]	87 ± 4[k,l]	8.9 ± 0.2[f,k]	71 ± 3[j]	107 ± 4[n]
Ni	45 ± 3[f]	89 ± 5[l,m]	9.5 ± 0.2[f,m]		

[a] Murad, E. *J. Geophys. Res.* **1978**, *83*, 5525.   [b] Reference 4h.   [c] Farber, M.; Manuel Uy, O.; Srivastava, R. D. *J. Chem. Phys.* **1972**, *56*, 5312. [d] This study.   [e] Reference 12.   [f] Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.   [g] Cheetam, C. J.; Barrow, R. F. *Adv. High. Temp. Chem.* **1967**, *1*, 7.   [h] Murad, E. *J. Chem. Phys.* **1980**, *73*, 1381.   [i] Hildenbrand, D. L. *Chem. Phys. Lett.* **1975**, *34*, 352.   [j] Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176.   [k] Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1966**, *45*, 4158.   [l] Smoes, S.; Mandy, F.; Auwera-Mahieu, A.; Drowart, J. *Bull. Soc. Chim. Belg.* **1972**, *81*, 45.   [m] Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1961**, *35*, 551.   [n] Derived from $D°(MO^+-H) = D°(M^+-OH) - D°(M^+-O) + D°(O-H)$.   [o] Derived from IP(MO) = $D°(M-O) - D°(M^+-O) +$ IP(M).   [p] Reference 4j.   [q] Reference 3.

to the possibility of exothermic processes for the reactions of these metal oxide ions with alkanes and alkenes. While favorable overall thermochemistry does not ensure a facile reaction, a growing number of examples support the contention that barriers in exothermic reactions of transition-metal oxide ions are rare. For example, MnO$^+$ undergoes reactions 5 and 6 with ethene.[7] FeO$^+$

$$MnO^+ + C_2H_4 \longrightarrow \begin{cases} C_2H_4O + Mn^+ & (5) \\ CH_2O + MnCH_2^+ & (6) \end{cases}$$
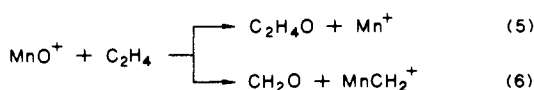
reacts with various hydrocarbons, reactions 7–11 being examples.[4i,8] Freiser and co-workers have reported an extensive study of the reactions of FeO$^+$ with alkanes, demonstrating the exceptional and relatively nonselective reactivity of this weakly bonded metal oxide. Processes such as reactions 1–3 are energetically more favorable when the metal ion remains bound to one of the products as in reactions 7 and 8. Bridging these extremes in behavior is the chromium oxide molecular ion, with

$$FeO^+ + C_2H_6 \longrightarrow \begin{cases} Fe(C_2H_4)^+ + H_2O & (7) \\ Fe(H_2O)^+ + C_2H_4 & (8) \\ Fe^+ + C_2H_4 + H_2O \ (or\ C_2H_5OH) & (9) \end{cases}$$

$$FeO^+ + C_2H_2 \longrightarrow \begin{cases} Fe^+ + C_2H_2O & (10) \\ FeCH_2^+ + CO & (11) \end{cases}$$

a metal oxide ion bond dissociation energy (85.3 kcal mol^{-1}) which renders processes such as reactions 1–3 only *slightly* exothermic when Cr$^+$ is the ionic product and possibly very selective. For this reason we considered this species an interesting subject for study, particularly in view of the many investigations of the oxidation reactions involving various chromium oxide reagents in solution.

Experimental Section

A detailed description of the ion-beam apparatus used for these experiments is available elsewhere.[9-11] Briefly, ions generated from a source are accelerated and focused into a 60° sector magnet for mass separation. The mass selected beam is decelerated to a selected energy and focused into a collision chamber containing the reactant gas. Product ions scattered in the forward direction are focused into a quadrupole mass filter and detected by using a channeltron electron multiplier operated in a pulse counting mode. Ion signal intensities are corrected for the mass discrimination of the quadrupole mass filter.

(7) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449.
(8) Jackson, T. C.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1252.
(9) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 2819.
(10) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.
(11) Armentrout, P. B.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 375.

Table II. Low-Lying States of Cr$^+$ and CrO$^+$

ion	low-lying electronic states	energy, eV	vib freq cm^{-1}
Cr^{+a}	X^{6}S	0.0	
	^{6}D	1.52	
CrO^{+b}	X$^4\Sigma^-$	0.0	640 ± 30
	$^4\Pi$	0.65	

[a] Moore, C. E. *Atomic Energy Levels* National Bureau of Standards: Washington, D.C., 1971. State energies are averaged over *J* states.   [b] References 12-14. See discussion in text.

The reactant ion CrO$^+$ is formed by surface ionization of CrO$_2$Cl$_2$. CrO$_2$Cl$_2$ vapor is introduced through a leak valve onto a hot rhemium filament where dissociation and ionization of the resulting fragments occur. In order of decreasing yield, the three most abundant species observed are Cr$^+$, CrO$^+$, and CrCl$^+$. No significant amounts of triatomic species are produced. CrO, having a relatively strong metal oxide bond and low ionization potential (Table I), yields the CrO$^+$ ion in greater abundance than can be obtained with the group 8-10 metal oxides. At the filament temperature used, $\sim$1300 K, it is estimated that over 99% of the Cr$^+$ produced is in the ^{6}S electronic ground state (Table II). The low-lying electronic states of CrO$^+$ are controversial.[12-14] In their photoelectron spectrum of CrO, Dyke and co-workers[12] observe only *one* state of CrO$^+$ below 1.5 eV and assign it as a $^4\Sigma^-$ state with a vibrational frequency of 640 ± 30 cm^{-1}. Theoretical calculations by Bauschlicher, Nelin, and Bagus[13] support this assignment and predict a $^4\Pi$ state at 0.65 eV. More recently, Harrison[14] has performed calculations which reverse the ordering of these two states, giving the $^4\Sigma^-$ above the $^4\Pi$ ground state. Unless the two states have almost exactly the same energy, the photoelectron spectrum is not in accord with the theoretical predictions, since both states are accessible. As a result of these uncertainties, it is difficult to assess the composition of the thermionic CrO$^+$ beam. In the discussion below it is mainly significant that the reacting species is in a quartet state. The vibrational state distribution of CrO$^+$ is estimated to be 51% $v = 0$, 25% $v = 1$, and 12% $v = 2$, with the remainder in higher vibrational levels.

Reaction cross sections for specific products, σ_i, are obtained by using eq 12 and 13 which relate the total reaction cross section, σ, the number

$$I_0 = (I_0 + \Sigma I_i) \exp(-n\sigma l) \tag{12}$$

$$\sigma_i = \sigma I_i / \Sigma I_i \tag{13}$$

density of the target gas, *n*, and the length of the collision chamber, *l*, to the transmitted reactant ion-beam intensity, I_0, and the sum of the product ion intensities, ΣI_i. The pressure of the target gas is kept low ($<2 \times 10^{-3}$ Torr) to ensure that observed reaction products are the result of only a single bimolecular collision. The collision cell is operated at ambient temperature (21 °C).

It is important to point out that neutral products are not detected in these experiments. However, except where noted below, the identity of these products can usually be inferred without ambiguity. In addition, these experiments provide no direct structural information about the ionic

(12) Dyke, J. M.; Gravenor, B. W. J.; Lewis, R. A.; Morris, A. *J. Chem. Soc.* **1983**, *2*, 79, 1083.
(13) Bauschlicher, C. W., Jr.; Nelen, C. J.; Bagus, P. S. *J. Chem. Phys.* **1985**, *82*, 3265.
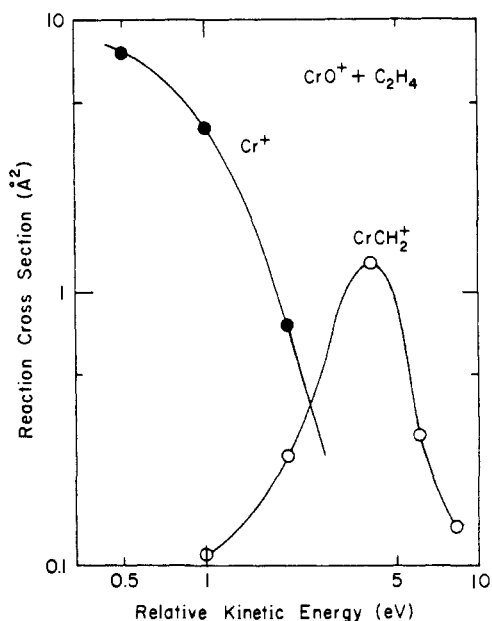(14) Harrison, J. F. *J. Phys. Chem.* **1986**, *90*, 3313.

Ion-Beam Studies of CrO⁺

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Figure 1. Variation with relative kinetic energy of the experimental cross section for the reaction of CrO^+ with ethene. The products Cr^+ and $CrCH_2^+$ exhibit cross sections characteristic of exothermic and endothermic reactions, respectively.
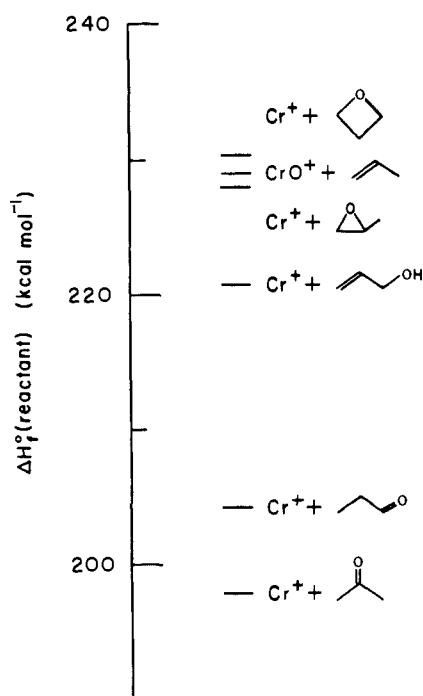

Figure 2. Heats of formation of various combinations of Cr^+ and CrO^+ with C_3 organic molecules. Data taken from ref 5.

products. Thermochemical arguments can often distinguish possibilities for isomeric structures.

Results and Discussion

Reaction of CrO^+ with Ethene. Reaction of CrO^+ with ethene in the kinetic energy range 0.5–10 eV yields Cr^+ and $CrCH_2^+$ as ionic products (reactions 14 and 15). Cr^+ is the major product at low kinetic energy. The experimental cross section for Cr^+

$$CrO^+ + C_2H_4 \longrightarrow \begin{cases} Cr^+ + C_2H_4O & (14) \\ CrCH_2^+ + CH_2O & (15) \end{cases}$$
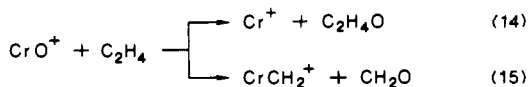
formation, shown in Figure 1, has a large value at low kinetic energy and decreases with increasing kinetic energy; this cross section behavior is characteristic of an exothermic reaction.[9-11]
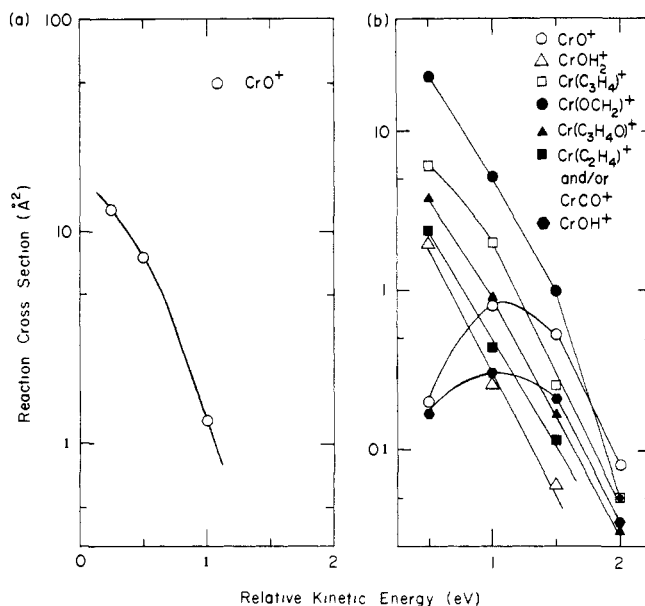

Figure 3. Variation in experimental cross section with relative kinetic energy for (a) the reaction of Cr^+ with ethylene oxide and (b) the reaction of Cr^+ with propylene oxide.

Formation of $CrCH_2^+$ occurs at kinetic energies above ~ 1 eV. The experimental cross section increases with increasing kinetic energy above this threshold and reaches a maximum at ~ 4 eV, after which it decreases, which is characteristic of an endothermic product channel.[9-11] Thus, an examination of the variation of reaction cross sections with kinetic energy permits exothermic and endothermic channels to be distinguished as in the case of Cr^+ and $CrCH_2^+$, respectively.

In order to assign the structure of the neutral product C_2H_4O, the reverse of reaction 14 was examined for two possible structural isomers, acetaldehyde and ethylene oxide. As shown in Figure 3a, Cr^+ reacts with ethylene oxide in an exothermic process to yield CrO^+ and ethene (reaction 16). On the other hand, no

$$Cr^+ + \text{ethylene oxide} \rightarrow CrO^+ + C_2H_4 \qquad (16)$$

$$Cr^+ + \text{acetaldehyde} \rightarrow \text{no reaction} \qquad (17)$$
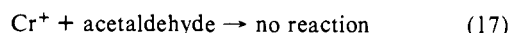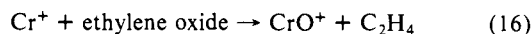
exothermic reaction is observed with acetaldehyde (eq 17). Hence, the neutral product in reaction 14 must be acetaldehyde. It is interesting to note that reactions 14 and 16 comprise a catalytic cycle which converts ethylene oxide into acetaldehyde with zero activation energy.[15]

The metallacycle intermediate **1**, produced by a four-center cycloaddition process, may be postulated to account for the observed products in the reaction of CrO^+ with ethene. Subsequent

$$\begin{array}{c} \text{Cr}^+\text{—O} \\ | \quad | \\ \text{CH}_2\text{—CH}_2 \end{array}$$

1
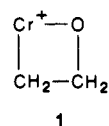
decomposition of the metallacycle intermediate may result in formation of Cr^+ (reaction 14), $CrCH_2^+$ (reaction 15), or CrO^+ (regeneration of reactants). Generation of $CrCH_2^+$ in the reaction of CrO^+ with ethene (reaction 15) is calculated to be 28 kcal mol⁻¹ endothermic.[16]

Reactions of CrO^+ with Larger Alkenes. Reactions of CrO^+ with larger alkenes yield a variety of products at low energy (Table

(15) Small activation barriers along the reaction coordinate can often be overcome by the ion–molecule association energy, rendering the overall process exothermic. For a discussion, see: Henis, J. M. S. *J. Chem. Phys.* **1970**, *52*, 282.
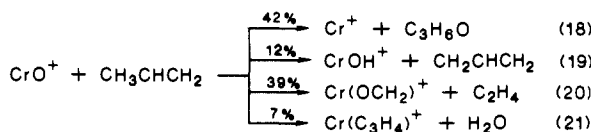
(16) $D^\circ(Cr^+-CH_2) = 54 \pm 5$ kcal mol⁻¹ from the following: Armentrout, P. B., et al., to be published. $D^\circ(Mn^+-CH_2) = 94 \pm 7$ kcal mol⁻¹ from the following: Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

Table III. Product Distributions for the Exothermic Reactions of CrO⁺ with Alkenes[a]

alkene	total cross section, Å²	neutral lost	ion product	% of total
ethene	8	CH_3CHO	Cr^+	100
propene	70	H_2O	$Cr(C_3H_4)^+$	7
		C_2H_4	$Cr(OCH_2)^+$	39
		CH_2CHCH_2	$CrOH^+$	12
		C_3H_6O	Cr^+	42
2-methyl-propene	52	CH_3	$Cr(C_3H_5O)^+$	11
		H_2O	$Cr(C_4H_6)^+$	11
		CH_3CHCH_2	$Cr(OCH_2)^+$	9
		$CH_2C(CH_3)CH_2$	$CrOH^+$	34
		C_4H_8O	Cr^+	35
1-butene	88	CH_4	$Cr(C_3H_4O)^+$	11
		H_2O	$Cr(C_4H_6)^+$	5
		C_2H_4	$Cr(C_2H_4O)^+$	30
		CH_3CHCH_2	$Cr(OCH_2)^+$	6
		C_4H_6	$CrOH_2^+$	5
		C_4H_8O	Cr^+	43
cis-2-butene	140	H_2	$Cr(C_4H_6O)^+$	13
		CH_4	$Cr(C_3H_4O)^+$	5
		H_2O	$Cr(C_4H_6)^+$	4
		C_2H_4	$Cr(C_2H_4O)^+$	40
		C_4H_6	$CrOH_2^+$	7
		C_4H_8O	Cr^+	31

[a] Product distributions are measured at 0.5 eV relative kinetic energy. [b] Parentheses are placed for unidentified ligand structures.

III). The reaction with propene will be discussed in detail to exemplify the observed processes. CrO⁺ reacts with propene to yield Cr⁺, CrOH⁺, Cr(OCH₂)⁺, and Cr(C₃H₄)⁺ (reactions 18–21).

$$CrO^+ + CH_3CHCH_2 \longrightarrow \begin{cases} \xrightarrow{42\%} Cr^+ + C_3H_6O & (18) \\ \xrightarrow{12\%} CrOH^+ + CH_2CHCH_2 & (19) \\ \xrightarrow{39\%} Cr(OCH_2)^+ + C_2H_4 & (20) \\ \xrightarrow{7\%} Cr(C_3H_4)^+ + H_2O & (21) \end{cases}$$

Product distributions are obtained by correcting measured ion signal intensities for the measured mass discrimination of the quadrupole mass spectrometer. These product distributions should nearly represent true branching ratios into the various product channels. However, discrimination may occur in the case of product ions which are formed with little momentum transfer from the reactant ion.
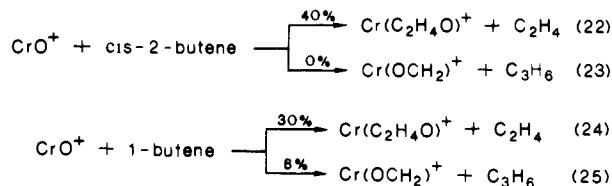
The hydrogen atom abstraction by CrO⁺ (reaction 19) very likely occurs as a result of the weak allylic C–H bond. The exothermicity of this process indicates that the (CrO)⁺–H bond dissociation energy is greater than the allylic C–H bond dissociation energy, $D°(CH_2CHCH_2–H) = 86.3$ kcal mol⁻¹.[18] This bond energy is higher than any known metal ion–hydrogen bond dissociation energy. On the other hand, MO⁺–H bonds are usually strong enough to render abstraction of a hydrogen atom from the allylic C–H bond by a metal oxide ion an exothermic process (Table I).[17] Thus, the CrOH⁺ structure is suggested to be chromium hydroxide and not a metal hydride [Cr(O)(H)⁺].

The mechanism shown in Scheme I is postulated to account for the observed products in reactions 18–21. The initial association of propene and CrO⁺ results in allylic hydrogen atom transfer to the oxygen center (path A). Since the formation of CrOH⁺ is an exothermic process by itself, the allyl radical could either be eliminated to yield CrOH⁺ (6) or remain bonded to CrO⁺ forming an energetic intermediate (2 or 3). Both 2 and 3 can rearrange to an allyl hydroxy complex ion (4) and in turn to 5, 6, or 7. Hence, we consider Cr⁺, CrOH⁺, and Cr(C₃H₄)⁺ as products which may be generated via this mechanism.

Scheme I
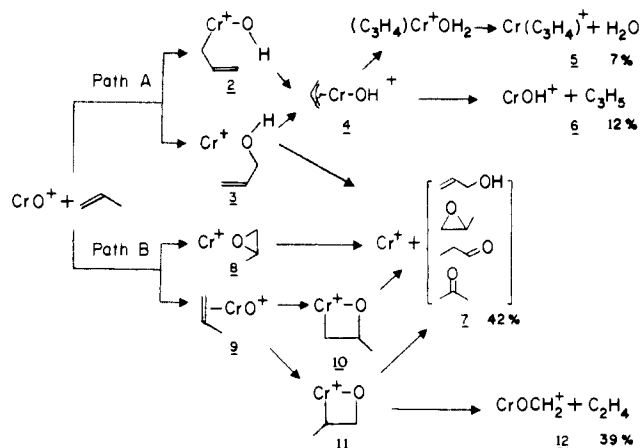
Scheme II
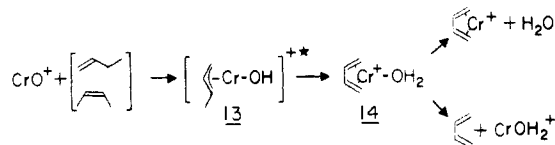
Another product of the reaction with propene, Cr(OCH₂)⁺, which involves cleavage of the carbon–carbon bond of propene, cannot be explained by the mechanism proposed above. The product can be rationalized by postulating a metallacycle intermediate similar to 1 for the reaction with ethene. The initial step probably involves formation of an ion–molecule complex (9), which is followed by a four-center cycloaddition reaction to yield either 10 or 11. Decomposition of 11 can lead either to CrOCH₂⁺ and ethene (12) or to Cr⁺ and C₃H₆O (7). Direct addition of an oxygen atom to the double bond is also possible (8), which probably yields Cr⁺ and propylene oxide (7). Decomposition of metallacycle intermediate 10 into CrCH₂⁺ and acetaldehyde is estimated to be 21 kcal mol⁻¹ endothermic.[15] Formation of the metal carbene product by decomposition of such metallacycle intermediates should become an energetically facile process as the metal oxide bond strength decreases relative to the metal carbene bond strength. This conjecture is substantiated by observation of metal carbene products in the reactions of ethene with MnO⁺[7] and ClCrO₂⁺.[19]

Several interesting points can be noted in the reactions of CrO⁺ with 1-butene and cis-2-butene. Reactions 22–25 involve cleavage of C–C bonds in the alkene, possibly via a mechanism similar to

$$CrO^+ + cis\text{-}2\text{-butene} \longrightarrow \begin{cases} \xrightarrow{40\%} Cr(C_2H_4O)^+ + C_2H_4 & (22) \\ \xrightarrow{0\%} Cr(OCH_2)^+ + C_3H_6 & (23) \end{cases}$$

$$CrO^+ + 1\text{-butene} \longrightarrow \begin{cases} \xrightarrow{30\%} Cr(C_2H_4O)^+ + C_2H_4 & (24) \\ \xrightarrow{8\%} Cr(OCH_2)^+ + C_3H_6 & (25) \end{cases}$$

the one proposed for the reaction with propene (Scheme I). Reaction with cis-2-butene yields Cr(C₂H₄O)⁺ (reaction 22), representing cleavage of an internal double bond. This suggests a *specific* cleavage of the alkene double bond and leads to the conjecture that an analysis of the reaction products might yield the position of a double bond in the precursor molecule. The reaction with 1-butene yields Cr(OCH₂)⁺, which can be simply accounted for by the cleavage of the terminal double bond. This, however, is a *minor* product (reaction 25). The major product in which C–C bond cleavage occurs is Cr(C₂H₄O)⁺, which can

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Table IV. Product Distributions for the Reactions of Cr⁺ with Several Oxygen-Containing C₃ Organic Molecules[a]

| reactants	rel kinetic energy, eV	total cross section, Å²	product, % of total cross section							
			Cr⁺	CrO⁺	CrOH⁺	CrOH₂⁺	Cr(C₂H₄)⁺ or Cr(CO)⁺	Cr-(OCH₂)⁺	Cr-(C₃H₄)⁺	Cr-(C₃H₄O)⁺
CrO⁺ + propene	0.5	70	42		12	0	0	39	7	0
	1.0	12	40		10	0	0	30	0	20
Cr⁺ + trimethylene oxide	0.5	140		0	0	0	30[b]	70	0	0
	1.0	20		0	0	0	40	60	0	0
Cr⁺ + propylene oxide	0.5	50		0	0	6	7	60	11	11
	1.0	10		8	3	2	4	55	19	9
Cr⁺ + allyl alcohol	0.5	14	0	0	0	0	0	0	64	36
	1.0	20		0	13	13	0	0	38	36
Cr⁺ + propanal	0.5	N.R.[c]								
	2.0	N.R.								
Cr⁺ + acetone	0.5	N.R.								
	2.0	N.R.								

[a] Product distributions are measured at 0.5 eV relative kinetic energy. [b] Reaction of Cr⁺ with trimethylene-*1,1,3,3-d₄* oxide yields Cr(C₂H₂D₂)⁺. Cr(CO)⁺ is not formed. [c] N.R. indicates no reaction observed.

be explained only by invoking rearrangement processes prior to cleavage. Therefore, cleavage of the double bond in 1-butene is nonspecific.

In comparing the reactivity of propene and 2-methylpropene to that of 1-butene and 2-butene, the reactions of CrO⁺ with both propene and 2-methylpropene yield CrOH⁺, while the reactions with 1-butene and *cis*-2-butene do not. Since both 1-butene and *cis*-2-butene have allylic hydrogens, they might be expected to react with CrO⁺ via the allylic oxidation pathway to form an allyl–hydroxy intermediate (**13** of Scheme II). However, a facile β-hydrogen transfer process, as shown in Scheme II, appears to be preferred to the loss of allyl radical in the reactions with 1-butene and *cis*-2-butene. The β-hydrogen transfer process is obviously not accessible for propene and 2-methylpropene. The water–butadiene ion complex (**14**) thus formed may lose either water or butadiene. Therefore, in the reactions of CrO⁺ with 1- and 2-butene, the allylic oxidation pathway leads to the products Cr(C₄H₆)⁺ and CrOH₂⁺.

Reactions of Cr⁺ with C₃H₆O Isomers. Reaction intermediates such as **2**, **3**, **8**, and **9** of Scheme I could resemble intermediates which might form in the reactions of Cr⁺ with C₃H₆O structural isomers. For this reason it is of interest to compare product distributions for such reactions with those observed for the reaction of CrO⁺ with propene. Reactions examined for this purpose are listed in Table IV for the C₃H₆O isomers trimethylene oxide, propylene oxide, allyl alcohol, propanal, and acetone. An important consideration in comparing these reactions is the heat of formation of the reactants (Figure 2). If common intermediates are formed, then product distributions are expected to be identical only at the same level of internal excitation. For this reason, it is desirable to compare product distributions at different collision energies as well as at the same collision energy when the reactants have considerably different heats of formation.

The reaction of Cr⁺ with allyl alcohol, which is expected to involve an intermediate similar to **3** in Scheme I, yields Cr(C₃H₄)⁺ and Cr(C₃H₄O)⁺ at low energy (Table IV). Cr(C₃H₄)⁺ is proposed in Scheme I as an allylic oxidation product in the reaction of CrO⁺ with propene. Formation of CrOH⁺ in the reaction of Cr⁺ with allyl alcohol is observed at higher energies (reaction 26), as expected from $D°(Cr⁺-OH) < D°(CH_2CHCH_2-OH) = 78$ kcal mol⁻¹ [17] (Table I). This demonstrates that the reaction of

$$Cr⁺ + \text{allyl alcohol} \rightarrow CrOH⁺ + CH_2CHCH_2 \quad (26)$$
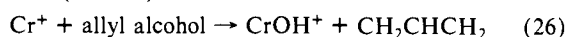
Cr⁺ with allyl alcohol, with excess translational energy, gives rise to all the allylic oxidation products proposed in Scheme I for the reaction of CrO⁺ with propene, namely, CrOH⁺ and Cr(C₃H₄)⁺. Considering that this system has less energy available to the reactants than the reaction of CrO⁺ with propene (Figure 2), these observations are consistent with the postulated intermediate **3** in Scheme I. We consider both **2** and **3** to be possible as an initial intermediate for the allylic oxidation process, since intermediates **2**, **3**, and **4** are expected to be easily interconvertible at the level of internal excitation provided when CrO⁺ abstracts allylic hydrogen from propene.

Reaction of Cr⁺ with propylene oxide yields products including CrOH₂⁺, Cr(C₂H₄)⁺ and/or Cr(CO)⁺, Cr(OCH₂)⁺, Cr(C₃H₄)⁺, and Cr(C₃H₄O)⁺ (Table IV and Figure 3b). Cr(OCH₂)⁺ is the major product from this reaction. Since this is also the major product from the reaction of CrO⁺ with propene, a common intermediate, the metallacycle **11** in Scheme I, may be implicated. The reaction of Cr⁺ with propylene oxide yields several additional products which are not observed in the reaction of CrO⁺ with propene, namely, CrOH₂⁺, Cr(C₂H₄)⁺ and/or Cr(CO)⁺, and Cr(C₃H₄O)⁺. This indicates the availability of several reaction pathways in addition to metallacycle formation.

As an additional point, reactions of Cr⁺ with trimethylene oxide, propylene oxide, and allyl alcohol give rise to very different product distributions. This indicates that three different intermediates may be formed in these reactions which are not easily interconverted. Propanal and acetone do not react with Cr⁺ in the energy ranges considered.

Bond Dissociation Energy of CrO⁺. An examination of the thermochemistry for the reactions generating CrO⁺ provides an estimate for the Cr⁺–O bond energy. Observation of CrO⁺ in the exothermic reaction of Cr⁺ with ethylene oxide (reaction 16) provides a lower limit for $D°(Cr⁺-O)$ of 84.0 kcal mol⁻¹ [5]. Reaction of Cr⁺ with propylene oxide, on the other hand, yields CrO⁺ as an endothermic product (reaction 27), providing an upper limit for $D°(Cr⁺-O)$ of 86.5 kcal mol⁻¹. Parts a and b of Figure 3 present experimental cross section data for these reactions, which

$$Cr⁺ + \text{propylene oxide} \rightarrow CrO⁺ + \text{propene} \quad (27)$$
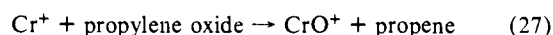
are consistent with exothermic and endothermic formation of CrO⁺ from the reaction of Cr⁺ with ethylene oxide (reaction 16) and propylene oxide (reaction 27), respectively. As shown in Figure 3b, reaction 27 is one of the many competing product channels in the reaction of Cr⁺ with propylene oxide. As a result, caution should be exercised in interpreting the experimental cross section for CrO⁺ formation as indicating an endothermic reaction, since the observed increase in cross section with increasing kinetic energy might be due to competition with processes which are more favorable at lower levels of excitation. This possible complication seems remote, however, considering the similarity between reactions with ethylene oxide (reaction 16) and propylene oxide (reaction 27). Hence, we choose to interpret the data in Figure 3b as indicating that reaction 27 is endothermic.

Using $D°(Cr⁺-O) = 85.3 \pm 1.3$ kcal mol⁻¹, the neutral Cr–O bond dissociation energy can be derived from the thermodynamic cycle implied by eq 28, which gives $D°(Cr-O) = 110 \pm 2$ kcal mol⁻¹. These values are compared with other literature values in Table V.

$$D°(Cr-O) = D°(Cr⁺-O) + IP(CrO) - IP(Cr) \quad (28)$$

Conclusion

Gas-phase CrO⁺ undergoes exothermic reactions with all of the alkenes considered in this study. CrO⁺ oxidizes ethene into acetaldehyde. Reactions with larger alkenes exhibit hydrogen

Table V. Cr⁺–O and Cr–O Bond Dissociation Energies[a]

bond energy	this study	lit
$D°(Cr^+–O)$	85.3 ± 1.3	76 ± 7[b]
		80 ± 3[c]
		86 ± 5[d]
$D°(Cr–O)$	110 ± 2	101 ± 7[b]

[a] In kcal mol⁻¹. [b] $D°(M^+–O) = D°(M–O) + IP(M) – IP(MO)$. $D°(Cr–O)$ from the following: Grimley, R. T.; Burns, R. P.; Inghram, M. G. *J. Chem. Phys.* **1961,** *34,* 664. [c] Table I. [d] Recent measurement by the following: Armentrout, P. B., et al., to be published.

abstraction, C–C bond cleavage, and formation of oxygen-containing products including aldehydes. An examination of reactions of Cr⁺ with C_3H_6O isomers provides useful information concerning reaction pathways involved in alkene oxidation by CrO⁺. The major pathways include allylic oxidation, which proceeds via abstraction of allylic hydrogen by CrO⁺, and formation of chemically activated metallacycle intermediates by cycloaddition of CrO⁺ and the double bond.

The present results exhibit interesting similarities to condensed-phase alkene oxidations by oxometal reagents. The observation of allylic hydrogen abstraction by CrO⁺ parallels several studies of alkene oxidation by heterogeneous metal oxide catalysts.[20,21] The formation of metallacycle intermediates has

analogies in the mechanism proposed for reactions of CrO_2Cl_2 with alkenes in solution.[22] In the gas phase, CrO⁺ oxidizes alkenes via both pathways, bridging the gap between the heterogeneous metal oxide catalysts and other solution-phase oxometal reagents. Observation of such varieties of oxidation pathways from a simple diatomic metal oxide ion is quite surprising and suggests that even mechanistically complex heterogeneous allylic oxidation processes might be interpreted in terms of rather simple reactions involving specific active sites.

Registry No. CrO_2Cl_2, 14977-61-8; CrO(+1), 56371-63-2; ethene, 74-85-1; propene, 115-07-1; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; 2-methylpropene, 115-11-7; trimethylene oxide, 503-30-0; propylene oxide, 75-56-9; allyl alcohol, 107-18-6; propanal, 123-38-6; acetone, 67-64-1.

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Reactions of Transition-Metal Ions with Methylsilanes in the Gas Phase. The Formation and Characteristics of Strong Transition Metal–Silylene Bonds

Heon Kang,[1] **Denley B. Jacobson,**[2a] **Seung Koo Shin,**[2a] **J. L. Beauchamp,**[*2a] **and M. T. Bowers**[2b]

Contribution No. 7322 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, and Department of Chemistry, University of California, Santa Barbara, California 93106. Received March 12, 1986

Abstract: Reactions of transition-metal ions (Ti⁺, V⁺, Cr⁺, Fe⁺, Co⁺, and Ni⁺) with organosilanes are investigated in the gas phase with an ion beam apparatus. Co⁺ and Ni⁺ react with silane to yield metal silylenes as exothermic products. Collision-induced dissociation studies of the product $CoSiH_2^+$ and nascent $CoSiH_4^+$ adducts provide additional information concerning the product structure and reaction mechanisms. Reactions with methylsilanes lead to formation of metal silylenes as major reaction channels, along with several other processes including hydride abstraction, dehydrogenation, and methane loss. Reactions with hexamethyldisilane are also investigated, with major products indicating Si–Si bond cleavage. An examination of the reaction enthalpies for the observed metal silylene products provides estimates for metal ion–silylene bond energies, which include $D°(M^+ – SiH_2) = 67 ± 6$ kcal mol⁻¹ (M = Co, Ni). Correlation between the metal ion–silylene bond energies and the electronic structure of the metal ions supports a bonding scheme in which silylene donates its nonbonding lone pair electrons to an empty 4s orbital of the metal center. For Co⁺ and Ni⁺, back-donation of paired 3d electrons from the metal into the empty 3p orbital on silicon is suggested to account for the stronger bond deduced for these metals.

Studies of molecular transformations involving the reactions of silicon compounds at transition-metal centers are numerous. Hydrosilation, for example, which results in the addition of Si–H bonds to unsaturated hydrocarbons, is catalyzed by transition-metal complexes.[3–5] However, catalytic hydrosilations are often very complex, and their mechanisms are not well understood. Oxidative addition of a Si–H bond to the metal center is presumed to be an obligatory step in the hydrosilation process, and direct evidence for this reaction is provided by several spectroscopic studies at low temperatures.[6,7] Nevertheless, relatively little is known about the nature, strengths, and specific reactions leading to the formation and rupture of single and multiple bonds between transition metals and silicon.

Recent studies of the reactions of transition-metal ions with small organic molecules in the gas phase have been very successful

(1) Present address: Department of Chemistry, University of Houston, 4800 Calhoun Road, Houston, Texas 77004.

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*To whom correspondence should be addressed.