J. Am. Chem. Soc. **1986**, *108*, 7502-7509

Gas-Phase Studies of Alkane Oxidation by Transition-Metal Oxides. Selective Oxidation by CrO^+

H. Kang and J. L. Beauchamp*

Contribution No. 7319 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.

Received February 24, 1986

Abstract: The gas-phase reactions of CrO^+ with alkanes have been studied by using ion beam reactive scattering techniques. CrO^+ undergoes facile reactions with alkanes larger than methane. CrO^+ selectively oxidizes ethane to form ethanol. In addition to the possibility of alcohol formation, reactions with larger alkanes are more complex, yielding products in which dehydrogenation and loss of alkenes and alkanes occur. In reactions with cyclic alkanes, cyclopropane and cyclobutane yield products characteristic of C–C bond cleavage. In contrast, reactions with cyclopentane and cyclohexane mainly involve dehydrogenation and elimination of H_2O. A series of hydrogen abstraction reactions are examined to determine the bond dissociation energy $D°(CrO^+–H) = 89 \pm 5$ kcal mol^{-1}. This bond energy has implications for the reaction mechanisms of CrO^+ with alkanes, leading to the suggestion of a multicenter reaction intermediate, in which alkyl C–H bonds add *across* the $Cr^+–O$ bond as an initial step. This is supported by an examination of the reactions of Cr^+ with alcohols.

The development of new reagents and catalysts for the selective oxidation of saturated hydrocarbons remains an active area of interest among chemists. Desirable targets include such possibilities as the activation of methane and terminal oxidation of an alkane chain.[1,2] However, there is an intrinsic need for better understanding of the mechanisms of oxidation processes with particular emphasis being placed on elucidation of elementary processes. Of particular interest is the question as to whether or not oxidations of organic substrates involve intermediates with metal–carbon bonds. In the absence of any M–C bond formation, radical intermediates formed by hydrogen atom abstraction are likely to be the mode of hydrocarbon oxidation,[2-4] a route which is not well-designed for selectivity in general. On the other hand, reaction intermediates in which M–C bonds are formed offer the possibility of using the expanding body of knowledge in organometallic chemistry to design more selective alkane oxidation systems. The question of possible organometallic intermediates has been raised in a number of cases but seldom answered unequivocally in condensed phase studies. In this paper, we report gas-phase studies of simplified alkane oxidation systems which permit detailed examination of the reaction energetics as well as mechanisms.

Table I. Reaction Enthalpies Used in Text

reaction		$\Delta H°$ rxn, kcal mol^{-1} [a]
O (^3P) + H_2	H_2O	−116.8
O + CH_4	CH_3OH	−89.2
	$CH_2O + H_2$	−67.1
	$H_2O + CH_2$	−5.2[b]
O + C_2H_6	$CH_4 + CH_2O$	−82.7
	CH_3CH_2OH	−95.0
	CH_3OCH_3	−82.8
	$C_2H_4 + H_2O$	−84.1
	$CH_3OH + CH_2$	−6.9
O + $CH_3CH_2CH_3$	1-propanol	−95.3
	2-propanol	−99.3
	$CH_3OC_2H_5$	−85.9
	$CH_3OH + C_2H_4$	−69.8
	H_2 + allyl alcohol	−63.8
	H_2 + propanol	−79.8
	H_2 + acetone	−86.2
	cyclopropane + H_2O	−79.3
	propene + H_2O	−87.1
	$C_2H_6 + CH_2O$	−80.4
	$CH_4 + CH_3CHO$	−91.8

[a] Reference 10. [b] Reference 31.

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

ion	low-lying states	energy, eV	yield[c] %	vib freq $\bar{\omega}_e$, cm^{-1}
CrO^+ [a]	$X^4\Sigma^-$	0	97	640 ± 30
	$^4\Pi$	0.65	3	
Cr^+ [b]	X^6S	0	>99.9	
	^6D	1.52	0	
	^4D	2.46	0	

[a] Reference 16. Energies are results of ab initio SCF + CI calculations. [b] Reference 32. [c] Ion beam composition at 1300 K.

In a previous study from our laboratory,[4] arguments based on energetic considerations were presented which suggested that CrO^+ is an ideal reagent for studies of gas-phase oxidation processes. The conjecture that this species would be both reactive and selective was generally supported by studies of alkene oxidation. In our earlier study, the bond dissociation energy $D°(Cr^+–O) = 85.3 \pm 1.3$ kcal mol^{-1} was determined. With this value, the general oxidation process indicated in reaction 1 will typically be exothermic by 10–15 kcal mol^{-1} when RH is a saturated hydrocarbon (Table I).

$$CrO^+ + RH \rightarrow Cr^+ + ROH \qquad (1)$$

It would be naive to believe that the criterion of reaction exothermicity alone can be used to identify processes deserving of further study. However, Freiser et al. have shown that FeO^+ reacts readily with saturated hydrocarbons.[5] These results, along with our study of alkene oxidation by CrO^+, lend support to the expectation that CrO^+ will also oxidize saturated hydrocarbons. The present study demonstrates that this contention is indeed correct. Ion beam studies of the reactions of CrO^+ with alkanes are reported in which the oxidation of alkanes to alcohols (reaction 1) is observed along with other reaction pathways. To better characterize the energetics of these reactions, the CrO^+–H bond dissociation energy is determined by examining a series of hydrogen atom abstraction reactions. The value determined for this bond energy implicates an intermediate in which alkyl C–H bonds add *across* the Cr^+–O bond as an initial oxidation step. Reaction mechanisms are investigated by using deuterium labeled alkanes. In addition, reactions of Cr^+ with alcohols are investigated in an attempt to further elucidate the potential energy

---

(1) Report of the International Workshop on "Activation of Dioxygen Species and Homogeneous Catalytic Oxidations"; Collins, T. J., Ed., Galzignano, Italy, 1984.

(2) Sheldon, R. A.; Kochi, J. A. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

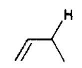
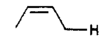
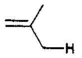
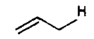
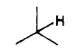
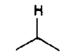
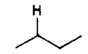
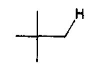
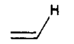
(3) Martir, W.; Lunsford, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 3728. Schultz, J. C.; Beauchamp, J. L. *J. Phys. Chem.* **1983**, *87*, 3587.

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

(5) Jackson, T. C.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1252.

0002-7863/86/1508-7502$01.50/0

Table III. Reactions Providing Limits for the Bond Dissociation Energies $D°(CrO^+-H)$ and $D°(CrO^+-H^-)$[a]

R-H	tot. cross sectn, Å²	Langevin cross sectn, Å²	$D°(R-H)$[b] kcal mol^{-1}	$D°(R^+-H^-)$[c] kcal mol	prod, % of tot. yield		
					$CrOH^+$	$CrOH_2^+$	CrOH
	88	67	82.5 ± 1.3	241	0	5	0
	140	67	85.6 ± 1.5	244	0	7	0
	52	67	~86	250	34	0	0
	70	58	86.3 ± 1.5	256	12	0	0
$C_6H_5CH_2-H$	17	83	88.0 ± 1	238	0	0	100
	110	68	93.2 ± 2	233	0	0	0
	14	60	95.1 ± 1	252	0	13	0
	100	68	~95	248	0	11	0
	70	75	100 ± 2	264	0	0	0
	8	49	110 ± 2	287	0	0	0
C_6H_5-H	no reactn		110.9 ± 2	282			

[a] At 0.5 eV relative kinetic energy. [b] Reference 7. [c] Reference 8.

surfaces for these reactions and provide support for proposed reaction mechanisms.

Experimental Section

The experimental techniques employed in the present study are the same as those described in ref 4, except that the Cr^+ beam is generated by using both electron impact ionization and surface ionization sources. The surface ionization source produces a Cr^+ beam which is almost entirely in the ground electronic state (>99.9%, Table II) by thermal decomposition of CrO_2Cl_2 and ionization of Cr on the hot filament surface (~1300 K). The electron impact ionization source is used to generate Cr^+ from $Cr(CO)_6$, a process which is known to yield a significant fraction of the Cr^+ beam in excited electronic states.[6] The CrO^+ beam, produced from CrO_2Cl_2 with the surface ionization source, is predominantly in the electronic ground state (>97%), with 51% in the vibrational ground state, 25% in $v = 1$ state, 12% in $v = 2$ state, and the rest in higher vibrational states (Table II). These distributions are calculated assuming that the ion is in thermal equilibrium with the surface. The ions are collimated, mass and energy selected, and allowed to react with the target gas in a collision chamber. Product ions scattered in the forward direction are detected by using a quadrupole mass spectrometer. Neutral products are not detected in these experiments.

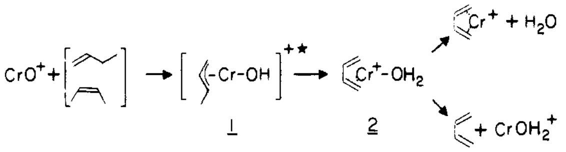
Results and Discussion

Determination of the CrO^+–H Bond Dissociation Energy. The CrO^+–H bond dissociation energy is an important quantity in characterizing the reactivity of CrO^+ toward alkanes. Hence, the determination of $D°(CrO^+-H)$ will be presented first in order to permit logical development of discussions in later sections. $D°(CrO^+-H)$ can be obtained by examining hydrogen atom abstraction reactions (reaction 2) with a series of hydrocarbons of

$$CrO^+ + RH \rightarrow CrOH^+ + R \tag{2}$$

varying bond energies[7,8] (Table III). The results for alkenes are taken from ref 4. Hydrogen abstraction is observed from propene and 2-methylpropene, which have allylic C–H bond dissociation energies ~86 kcal mol^{-1}.[7] 1-Butene and *cis*-2-butene also have allylic C–H bonds with comparable bond dissociation energies, but they do not yield $CrOH^+$. The study in ref 4 suggested a mechanism in which hydrogen atom abstraction from these molecules results in the formation of $CrOH_2^+$ rather than $CrOH^+$ (Scheme I). Briefly, both 1-butene and *cis*-2-butene undergo H abstraction to form an allyl–hydroxy ion complex **1** followed by a facile β-H transfer from the allyl substituent to the Cr center to form a water–butadiene ion complex **2**, which may lose either butadiene or H_2O. Hence, H abstractions from 1-butene and *cis*-2-butene are considered to yield $CrOH_2^+$. The analogous β-H transfer pathway is not available in the reactions of propene and 2-methylpropene, rendering generation of $CrOH^+$ a major process. The H abstraction reactions from propene and 2-methylpropene exhibit the typical cross section behavior of an exothermic process.[4] The exothermic hydrogen abstraction from propene provides a lower limit for $D°(CrO^+-H)$ of 86.3 kcal mol^{-1}.[7] No hydrogen abstraction reaction is observed from the hydrocarbons with alkyl, vinyl, and phenyl C–H groups, which provides an upper limit of 93.2 kcal mol^{-1} for the bond energy. Since failure to observe a reaction does not *necessarily* imply that a reaction is endothermic, the upper limit on the bond strength is less rigorous than the lower limit.

Scheme I



Reaction with toluene gives rise to $C_7H_7^+$ and CrOH, representing a formal hydride abstraction from toluene.[9] Hydride abstraction is not observed from the other hydrocarbons. The hydride abstraction from toluene provides a lower limit for the bond energy, $D°(CrO^+-H^-) > D°(C_6H_5CH_2^+-H^-) = 233$ kcal mol^{-1}.[9] The reaction with 2-methylpropene, which yields $CrOH^+$ and a neutral product 2-methylpropenyl radical, suggests IP(CrOH) < IP[$CH_2{=}C(CH_3)CH_2$] = 7.90 eV.[1] This value, combined with $D°(CrO^+-H)$, yields an upper limit for $D°(CrO^+-H^-)$ of 253 kcal mol^{-1} from the thermodynamic cycle depicted by eq 3.

$$D°(CrO^+-H^-) = D(CrO^+-H) + IP(CrOH) - EA(H) \tag{3}$$

---

[6] Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962.

[7] McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

[8] Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917.

[9] The product $C_7H_7^+$ can be either benzyl or cycloheptatrienyl cation. $D°(C_6H_5CH_2^+-H^-) = \Delta H°_f(C_7H_7^+) + \Delta H°_f(H^-) - \Delta H°_f(C_6H_5CH_3)$ is used to calculate the bond dissociation energy, which gives 233 kcal mol^{-1} when the product is cycloheptatrienyl cation. For the formation of benzyl cation, it gives 237 kcal mol^{-1} for the bond energy.

Table IV. Summary of Thermochemical Data[a]

$D^\circ(\mathrm{CrO^+{-}H})$	89 ± 5	$D^\circ(\mathrm{FeO^+{-}H})$	106 ± 4[e]
$D^\circ(\mathrm{Cr^+{-}OH})$	73 ± 5	$D^\circ(\mathrm{Fe^+{-}OH})$	73 ± 3[d]
PA(CrO)	221 ± 5	$D^\circ(\mathrm{CoO^+{-}H})$	107 ± 4[e]
$D^\circ(\mathrm{Cr^+{-}O})$	85.3 ± 1.3[b]	$D^\circ(\mathrm{Co^+{-}OH})$	71 ± 3[d]
$D^\circ(\mathrm{CrO{-}H})$	>67, <90		
$D^\circ(\mathrm{Cr{-}OH})$	>76, <99		
$D^\circ(\mathrm{CrO^+{-}H^-})$	>231, <253		
$D^\circ(\mathrm{Cr^+{-}OH^-})$	>189, <212[c]		
IP(CrOH)	>6.9, <7.9		

[a] Bond energies in kcal mol^{-1}, IP's in eV. [b] Reference 4. [c] Derived from $D^\circ(\mathrm{Cr^+{-}OH^-}) = D^\circ(\mathrm{Cr{-}OH}) + \mathrm{IP(Cr)} - \mathrm{EA(OH)}$. [d] Reference 33. [e] Derived from $D^\circ(\mathrm{MO^+{-}H}) = D^\circ(\mathrm{M^+{-}OH}) - D^\circ(\mathrm{M^+{-}O}) + D^\circ(\mathrm{O{-}H})$.

Table V. Product Distribution for the Exothermic Reactions of CrO^+ with Linear and Branched Alkanes[a]

alkane	tot. cross sectn, Å^2	neutral loss	ion prod.	% of tot.
H_2	<0.7	N.R.	N.R.	
methane	<0.7	N.R.	N.R.	
ethane	8	C_2H_5OH	Cr^+	100
propane	14	H_2	$Cr(C_3H_6O)^+$	47
		C_2H_4	$Cr(CH_4O)^+$	20
		C_3H_6	$CrOH_2^+$	13
		C_3H_8O	Cr^+	20
butane	100	H_2	$Cr(C_4H_8O)^+$	10
		CH_4	$Cr(C_3H_6O)^+$	10
		H_2O, H_2	$Cr(C_4H_6)^+$	34
		C_2H_4	$Cr(C_2H_6O)^+$	32
		C_4H_8	$CrOH_2^+$	11
		$C_4H_{10}O$	Cr^+	3
2-methylpropane	110	H_2	$Cr(C_4H_8O)^+$	58
		CH_4	$Cr(C_3H_6O)^+$	22
		H_2O, H_2	$Cr(C_4H_6)^+$	11
		$C_4H_{10}O$	Cr^+	9
2,2-dimethylpropane	70	$^{\bullet}CH_3$	$Cr(C_4H_9O)^+$	11
		CH_4	$Cr(C_4H_8O)^+$	57
		H_2O, H_2	$Cr(C_5H_8)^+$	4
		CH_4, H_2O	$Cr(C_4H_6)^+$	3
		$CrOCH_3$	$C(CH_3)_3^+$	4
		$C_5H_{12}O$	Cr^+	21

[a] Measured at 0.5 eV relative kinetic energy.

In the examination of the above hydrogen atom and hydride abstraction reactions, it is important to consider the internal excitation of the CrO^+ beam. The total cross section for the reactions with propene is 70 A^2 at 0.5 eV relative kinetic energy. For comparison, a theoretical cross section σ_r can be calculated by using the Langevin–Gioumousis–Stevenson analysis for ion–molecule reactions (eq 4),[13,14] where α is the angle-averaged

$$\sigma_r = \pi(2\alpha e^2/E_t)^{1/2} \tag{4}$$

polarizability of the neutral reactant, e is the ion charge, and E_t is the relative kinetic energy. The calculated cross section at the same energy is 58 A^2 for propene. The process of hydrogen atom abstraction from propene exhibits a cross section of 8 A^2, which corresponds to 12% of the observed total cross section and 14% of the calculated Langevin cross section. For 2-methylpropene, the reaction cross section for hydrogen abstraction corresponds to 34% of the observed total cross section and 25% of the Langevin cross section. Therefore, the observed hydrogen abstraction reactions cannot be attributed to electronically excited CrO^+ which comprises 3% of the beam. Possible complications due to the presence of vibrationally excited CrO^+ also deserves consideration. The second vibrationally excited state ($v = 2$) of CrO^+, being only 12% of the total beam population, is unlikely to give rise to the observed cross sections for hydrogen atom abstraction. Hence, we may consider that only the $v = 0$ and $v = 1$ states are responsible for the reactions. For the possible participation of the $v = 1$ state, we may add uncertainty of 1.8 kcal mol^{-1} to the lower limits derived for $D^\circ(\mathrm{CrO^+{-}H})$ and $D^\circ(\mathrm{CrO^+{-}H^-})$. The resulting estimates for these quantities (Table II) are $D^\circ(\mathrm{CrO^+{-}H}) = 89 \pm 5$ kcal mol^{-1} and 253 kcal mol^{-1} > $D^\circ(\mathrm{CrO^+{-}H^-})$ > 231 kcal mol^{-1}.

By using the value for $D^\circ(\mathrm{CrO^+{-}H})$, the Cr^+OH bond dissociation energy can be calculated by using eq 5, which gives $D^\circ(\mathrm{Cr^+{-}OH}) = 73 \pm 5$ kcal mol^{-1}.[15] The proton affinity of CrO is calculated by using eq 6, which gives PA(CrO) = 221 ± 5 kcal mol^{-1}.

$$D^\circ(\mathrm{Cr^+{-}OH}) = D^\circ(\mathrm{CrO^+{-}H}) + D^\circ(\mathrm{Cr^+{-}O}) - D^\circ(\mathrm{O{-}H}) \tag{5}$$

$$\mathrm{PA(CrO)} = D^\circ(\mathrm{CrO^+{-}H}) + \mathrm{IP(H)} - \mathrm{IP(CrO)} \tag{6}$$

The lower limit for $D^\circ(\mathrm{CrO^+{-}H^-})$, obtained from the exothermic hydride abstraction from toluene, can be used to derive a lower limit for IP(CrOH) from eq 3. In turn, neutral bond dissociation energies $D^\circ(\mathrm{CrO{-}H})$ and $D^\circ(\mathrm{Cr{-}OH})$ can be derived by combining these values with IP(CrO) and IP(Cr) and by using eq 7 and 8.[16] Derived thermochemical data are summarized in

$$D^\circ(\mathrm{CrO{-}H}) = D^\circ(\mathrm{CrO^+{-}H}) + \mathrm{IP(CrOH)} - \mathrm{IP(CrO)} \tag{7}$$

$$D^\circ(\mathrm{Cr{-}OH}) = D^\circ(\mathrm{Cr^+{-}OH}) + \mathrm{IP(CrOH)} - \mathrm{IP(Cr)} \tag{8}$$

Table IV. The limits $67 \leq D^\circ(\mathrm{CrO{-}H}) \leq 90$ suggest that the CrO–H bond is stronger than a typical metal–hydrogen bond. As a result, the species CrOH is likely to be more stable than the isomer HCrO, and we have chosen this as the favored product.

The measured CrO^+–H bond dissociation energy is ~18 kcal mol^{-1} *less* than the corresponding FeO^+–H and CoO^+–H bond dissociation energies (Table IV). Abstraction of a hydrogen atom from an alkyl C–H bond by CrO^+ is *slightly endothermic.* Thus, unlike CoO^+ and FeO^+, reactions of CrO^+ with alkanes cannot yield radical products directly by hydrogen abstraction. Abstraction of hydrogen by CrO^+ *may still occur* within the collision complex and not give rise to free $CrOH^+$. As a result, reaction energetics require that any exothermic process which might involve hydrogen atom transfer from C–H bonds of alkanes to CrO^+ as a first step must proceed via a multicenter mechanism. The analogous hydrogen abstraction reactions involving FeO^+ or CoO^+ are exothermic processes. Reactions of these metal oxide ions with alkanes lead to radical products, as illustrated by recent studies of the reactions of FeO^+ with alkanes.[5]

Similarly, hydride abstraction from primary C–H bonds of alkanes by CrO^+ is slightly endothermic. Direct hydride abstractions from secondary and tertiary alkyl C–H bonds are not observed even though the range estimated for the CrO^+–H^- heterolytic bond dissociation energy overlaps with their R^+–H^- bond dissociation energies. This implies that the hydride transfer, if it occurs as a first step in a complex reaction, may also involve a multicenter transition state.

Reactions of CrO^+ with Linear and Branched Alkanes. CrO^+ undergoes facile reactions with linear and branched alkanes larger than methane at low energies. The product distributions measured at 0.5 eV relative kinetic energy are summarized in Table V.

Neither H_2 nor CH_4 are observed to react with CrO^+, although processes involving formation of Cr^+ and H_2O in the reaction with H_2 (reaction 9) and formation of Cr^+ and methanol in the reaction with methane (reaction 10) are estimated to be exothermic by

---

(10) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(11) In the dissociation of such a charged intermediate, the preferred ionic product is the fragment having the lower ionization potential (IP). Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. IP's are from ref 12.

(12) Schultz, J. C. Ph.D. Thesis, California Institute of Technology, 1984.

(13) Polarizabilities of hydrocarbons are from Chan, S. C.; Rabinovitch, B. S.; Bryant, J. T.; Spicer, L. D.; Fujimoto, T.; Lin, Y. N.; Pavlou, S. P. *J. Phys. Chem.* **1970**, *74*, 3160.

(14) Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics*; Oxford University Press: 1974.

(15) $D^\circ(\mathrm{O{-}H})$ = 101.3 kcal mol^{-1} from Kuber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.

(16) IP(Cr) = 6.76 eV and IP (CrO) = 7.85 ± 0.02 eV. Dyke, J. M.; Gravenor, B. W. J.; Lewis, R. A.; Morris, A. *J. Chem. Soc., Faraday Trans. 2*, **1983**, *79*, 1083.

Table VI. Product Distributions for the Reactions CrO^+ + Propane, Cr^+ + 1-Propanol, and Cr^+ + 2-Propanol[a]

reaction	rel kinetic energy, eV	tot. cross sectn, Å^2	product yield (% of total cross section)						
			Cr^+	$Cr(OH)^+$	$Cr(OH_2)^+$	$Cr(CH_4O)^+$	$Cr(C_3H_6)^+$	$Cr(C_2H_4O)^+$	$Cr(C_3H_6O)^+$
(H) CrO^+ + propane	0.5	14	20	0	13	20	0	0	47
(I) Cr^+ + 1-propanol	0.5	0.6	*b*	0	0	0	0	55	45
	1.0	0.06		0	0	0	0	70	30
	2.0	0.12		40	0	0	0	50	10
(J) Cr^+ + 2-propanol	0.5	7		0	54	0	46	0	0
	1.0	3		0	57	0	43	0	0
	2.0	0.2		0	100	0	0	0	0

[a] Measured at 0.5 eV relative kinetic energy. [b] Product cannot be distinguished from reactant beam.

32 kcal mol^{-1} and 4 kcal mol^{-1}, respectively (Table I).

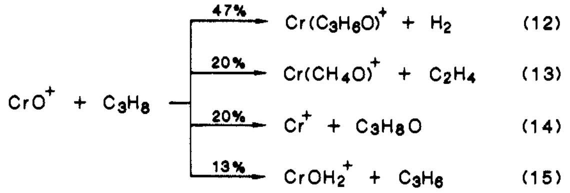
Ethane reacts with CrO^+ to yield Cr^+ and C_2H_6O (reaction 11). The product C_2H_6O can only be ethanol, since the other feasible products including dimethyl ether, H_2O and ethene, and CH_2O and CH_4 are expected to involve slightly endothermic processes (Table I).

$$CrO^+ + H_2 \nrightarrow Cr^+ + H_2O \qquad (9)$$

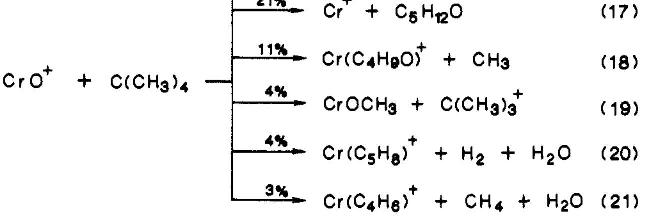
$$CrO^+ + CH_4 \nrightarrow Cr^+ + CH_3OH \qquad (10)$$

$$CrO^+ + C_2H_6 \rightarrow Cr^+ + C_2H_6O \qquad (11)$$

Reaction of CrO^+ with propane leads to the formation of several products in processes which appear to be exothermic, including dehydrogenation and elimination of ethene, propene, and C_3H_8O (reactions 12–15). The structure of C_3H_8O may be inferred from the reaction thermochemistry presented in Table I. If the structure of C_3H_8O in reaction 14 involved fragmented molecules, the adducts of the fragment with Cr^+ would also have appreciable yields. Only the products CH_4 and CH_3CHO can be formed in a significantly exothermic process ($\Delta H°$ = −6.5 kcal mol^{-1}). The absence of $Cr(C_2H_4O)^+$ as a product suggests that C_3H_8O formed in reaction 14 is either a propanol or ethyl methyl ether.



Reaction 13 is of interest since loss of ethene requires the cleavage of a C–C bond in the alkane. Products involving C–C bond cleavage become even more prevalent with larger alkanes. For example, in the reaction of CrO^+ with 2,2-dimethylpropane, the most prominent reaction pathway involves loss of methane (reactions 16–21). Reactions 18, 19, and 21 also involve C–C bond cleavage.



Reactions of CrO^+ with alkanes to yield alcohols (reactions 11, 14, 17) are exothermic by 10–15 kcal mol^{-1} for the formation of ground electronic state $Cr^+(^6S)$. Formation of electronically excited Cr^+ requires an extra energy of at least 35 kcal mol^{-1} (Table II), and hence the product Cr^+ must be in the ground state. Since CrO^+ ($^4\Sigma^-$ electronic ground state) and $Cr^+(^6S)$ have different spin states, reactions of CrO^+ with alkanes occur via a quartet–sextet surface crossing. The fact that these processes are only slightly exothermic suggests that activation barriers for the surface crossing may not be significant in the interactions of CrO^+ with alkanes.[17]

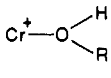
Formation of ethanol in the reaction with ethane (reaction 11) indicates that *primary C–H bonds in saturated alkanes can react with CrO^+*. The reactivity of primary C–H bonds is further illustrated by the fact that the reaction with 2,2-dimethylpropane, which has only primary C–H bonds, exhibits loss of H_2 and H_2O (reaction 20). Reactions in which C–C bonds are cleaved by CrO^+ to yield smaller alkanes have extensive analogies in studies of the reactions of atomic transition-metal ions with alkanes.[11,18-20] Although definitive proof is lacking, the loss of alkanes has been rationalized in these studies by a mechanism involving a first step in which the atomic metal ion inserts into a C–C bond.

Of particular interest is the structure of an intermediate which is formed when CrO^+ attacks an alkyl C–H or C–C bond. Studies of the gas-phase reactions of CrO^+ with alkenes[4] have suggested an initial reaction step in which CrO^+ abstracts an allylic H from the alkene to form $CrOH^+$ (e.g., reaction 22). An analogous pathway may be considered for the reactions of CrO^+ with alkanes, which is the transfer of alkyl H to CrO^+. The mechanism involving alkyl hydrogen transfer is supported by the formation of ethanol in the reaction of CrO^+ with ethane (reaction 11), which suggests that an intermediate is formed in which either H or C_2H_5 is initially bonded to oxygen. An examination of the reaction energetics in the previous section has illustrated that while the hydrogen transfer from allylic C–H bonds to CrO^+ is exothermic, the analogous process involving alkyl C–H bonds requires a multicenter intermediate. These arguments suggest an initial reaction intermediate in which CrO^+ is inserted into a C–H bond, with **3** and **4** being considered the most viable candidates. Addition of a C–H bond at the metal center is regarded as unlikely due to the weakness of Cr–H and Cr–alkyl bonds. The possibility of initial insertion into alkyl C–C bonds is not ruled out. In the case of ethane this process would be nonproductive. With larger alkanes, however, product formation involving cleavage of C–C bonds may be better explained by insertion into alkyl C–C bonds.

$$CrO^+ + CH_3CHCH_2 \rightarrow CrOH^+ + CH_2CHCH_2 \qquad (22)$$

$R\text{-}Cr^+\text{-}OH$

3



4

Reactions of Ground- and Excited-State Cr^+ with Alcohols. Intermediates involved in the reaction of CrO^+ with alkanes could resemble intermediates which might form in the reactions of Cr^+ with alcohols, making it interesting to compare product distributions between these reactions. In this section, reactions of ground- and excited-state Cr^+ with 1-propanol and 2-propanol are examined to explore the viability of the intermediates **3** and

---

[17] This may be compared with an activation energy of 25 kcal mol^{-1} measured in the reaction of Cr^+ with N_2O forming CrO^+ and N_2. Armentrout, P. B.; Halle, L. R.; Beauchamp, J. L. *J. Chem. Phys.* **1982**, *76*, 2449.

[18] Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963 and references therein.

[19] Byrd, G. D.; Brunier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565.

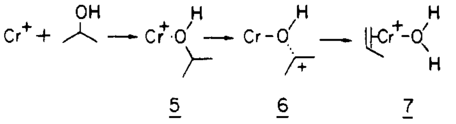
[20] Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912 and references therein.

Table VII. Product Distributions for the Reactions of Cr^+ with Alcohols Using the Electron Impact Source[a]

reaction	electron impact energy, eV	tot. cross sectn Å²	product yield (% of total cross section)									
			$C_3H_7^+$	CrO^+	$Cr(OH)^+$	$Cr(OH_2)^+$	Cr-$(CH_4O)^+$	Cr-$(C_3H_4)^+$	Cr-$(C_3H_6)^+$	Cr-$(C_2H_4O)^+$	Cr-$(C_2H_5O)^+$	Cr-$(C_3H_6O)^+$
Cr^+ + 1-propanol	16	9	5	0	5	40	19	4	0	3	3	21
	30	17	12	8	52	9	6	3	0	1	3	7
	70	30	7	8	60	8	5	3	0	0	2	7
	SI	0.6	0	0	0	0	0	0	0	55	0	45
Cr^+ + 2-propanol	16	18	6	0	6	21	13	9	21	0	10	14
	18	25	9	0	13	30	14	8	9	0	4	13
	70	64	21	8	41	13	8	1	1	0	2	5
	SI	7	0	0	0	54	0	0	46	0	0	0

[a] Measured at 0.5 eV relative kinetic energy.

Scheme II



4, which might be formed in the reaction of CrO^+ with propane. Initial association of Cr^+ and propanol leads to an ion–molecule adduct with a structure analogous to the intermediate **4**. Therefore, the adducts of 1-propanol and 2-propanol with Cr^+ could represent oxidative addition of primary and secondary C–H bonds of propane across an oxygen atom of CrO^+, respectively. Reaction of Cr^+ with 2-propanol yields $Cr(OH_2)^+$ and $Cr(C_3H_6)^+$ (Table VI). In order to rationalize these products, a mechanism which involves an initial attack of the metal ion at the oxygen center and *heterolytic cleavage* of the i-$C_3H_7^+$–OH^- bond may be postulated as shown in Scheme II. Cr^+ is envisioned to act as a Lewis acid, binding to the oxygen center of 1-propanol **5**. The hydroxide anion is transferred to the metal, generating 2-propyl cation **6**, which then undergoes proton transfer to the oxygen atom forming intermediate **7**.[21] Competitive loss of H_2O and propene from **7** gives rise to the observed products. For comparison, analogous mechanisms which involve heterolytic cleavage of polar R–X bonds have been proposed in earlier studies[22] of reactions of metal ions (Li^+, Na^+, Fe^+, Co^+, and Ni^+) with alkyl halides and alcohols. The mechanism proposed in Scheme II for the reaction with 2-propanol, which involves heterolytic cleavage of the R–OH bond, suggests that the different reactivity of 1-propanol might result from the energetically more demanding heterolytic bond cleavage with 1-propanol [$D°(n\text{-}C_3H_7^+\text{–}OH^-)$ = 237 kcal mol^{-1}] compared to 2-propanol [$D°(s\text{-}C_3H_7^+\text{–}OH^-)$ = 220 kcal mol^{-1}].[23] The products from the reaction with 1-propanol exhibit small reaction cross sections but certainly exclude the possibility of an excited state Cr^+ reaction.

No combination of the product distributions for reactions of Cr^+ with propanols resembles that of reaction of CrO^+ with propane. Most significantly, $Cr(C_3H_6)^+$ and $Cr(C_2H_4O)^+$ are not formed in the reaction of CrO^+ with propane. When we consider the higher heats of formation of the reactants in the interaction of CrO^+ with propane than in the interaction of Cr^+ with propanols (Figure 1), a common intermediate for these reactions should allow the reaction of CrO^+ with propane to yield products which include those from the reactions of Cr^+ with propanols. The failure to observe $Cr(C_2H_4O)^+$ and $Cr(C_3H_6)^+$ in the reaction of CrO^+ with propane thus contradicts the assumption of a common intermediate. This rules out the possibility of an initial C–H bond addition across an oxygen atom in **4** and leaves the addition across the Cr^+–O bond in **3** as a feasible *initial* step in the reaction of CrO^+ with propane.

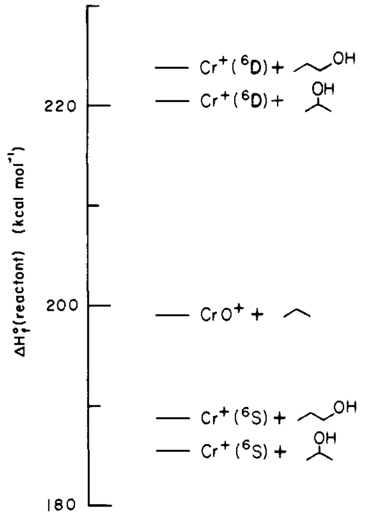


Figure 1. Heats of formation of reactants for the reactions Cr^+ + propanol and CrO^+ + propane. Values from ref 10 and 34.

It is of further interest to examine the reactions of Cr^+ with propanols at different levels of total reactant energy. Two methods are employed to control the available reactant energy. One is to change the collision energy, and the other is to generate Cr^+ in electronically excited states. As expected, the total reaction cross section decreases as the collision energy is increased. However, the overall product distribution does not change significantly compared with that of the low-energy reaction (Table VI). In contrast, Cr^+ generated by electron impact from $Cr(CO)_6$ reacts with propanols to yield a variety of products in addition to those from the reaction of ground electronic state Cr^+ (Table VII). These additional products undoubtedly result from the reaction of electronically excited Cr^+, which constitutes a significant fraction of the beam when it is formed by using electron impact ionization. For example, formation of $CrOH^+$ in the reactions of Cr^+ with propanols (reaction 23) must involve electronically

$$Cr^+ + \text{propanol} \rightarrow CrOH^+ + C_3H_7 \qquad (23)$$

excited Cr^+, since this process is endothermic by 18–20 kcal mol^{-1} for the ground state. This product exhibits an experimental cross section which increases with increasing electron impact energy, representing an increasing fraction of excited state Cr^+ in the beam [Figure 2a]. $CrOH^+$ is observed as a product only when electron impact energy exceeds 16.5 ± 0.5 eV, indicating that formation of the excited electronic state Cr^+ occurs above this threshold energy. The product $CrOH_2^+$ exhibits an apparent reaction cross section which is constant at low electron energies and starts to increase around the same threshold energy recorded for $CrOH^+$ [Figure 2b], indicating that this product results from the reactions of both ground- and excited-state Cr^+. Since the threshold energy lies ca. 1–2 eV above the appearance potential of Cr^+,[25] this may

---

[21] PA($CH_2CH{=}CH_2$) = 184.9 kcal mol^{-1} from Aue, D. H.; Bowers, M. T. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, Chapter 9.

[22] Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. Tsarbopoulos, A.; Allison, J. *J. Am. Chem. Soc.* **1985**, *107*, 5085.

[23] $D°(R^+\text{–}OH^-)$ is calculated by using $D°(R^+\text{–}OH^-) = D°(R\text{–}OH) + IP(R\cdot) - EA(OH)$. $D°(R\text{–}H)$ is from ref 20. $IP(n\text{-}C_3H_7\cdot)$ = 8.15 eV and $IP(i\text{-}C_3H_7\cdot)$ = 7.36 eV from ref 9. EA(OH) = 1.825 eV from Janousek and Brauman (Janousek, B. K.; Brauman, J. I. Chapter 10 of ref 21).

[24] $D°(i\text{-}C_3H_7OH)$ = 92.8 kcal mol^{-1} and $D(n\text{-}C_3H_7\text{–}OH)$ = 91.6 kcal mol^{-1} from ref 7 and 10.

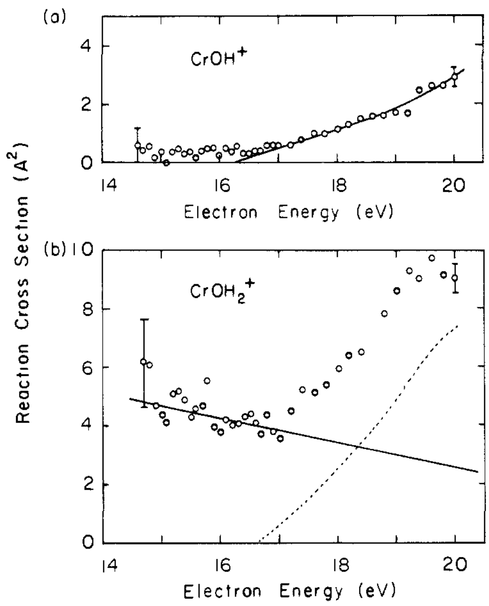


Figure 2. Variation in experimental cross section as a function of electron impact ionization energy for reactions of Cr$^+$ [derived from Cr(CO)$_6$] with 2-propanol at a relative kinetic energy of 0.5 eV. (a) Formation of CrOH$^+$ exhibits a threshold at 16.5 ± 0.5 eV. The cross section increases with the electron impact energy representing an increasing portion of excited state Cr$^+$ in the beam. (b) Formation of CrOH$_2^+$ results from the reactions of both ground-state (solid line) and excited-state (dotted line) Cr$^+$.

Table VIII. Isotopic Product Distributions for Neutral Lost in the Exothermic Reactions of Deuterated Alkanes with CrO$^+$

alkane	totl cross sectn, Å^2	neutral loss (% of tot.)
propane-*2,2-d*$_2$[a]	22	H_2 (25), HD (24), C_2H_3D (10), $C_2H_2D_2$ (13), $C_3H_4D_2$ (11), $C_3H_6D_2O$ (17)
2-methylpropane-*2-d*$_1$[b]	150	H (23), HD (23), CH_4 (29), H_2O + H_2 (13), HDO + H_2 and H_2O + HD (5), C_4H_9DO (7)
butane-*1,1,1,4,4,4-d*$_6$[a]	110	H_2 (5), HD (5), CD_4 (10), H_2O + H_2 (27), HDO + H_2 and H_2O + HD (7), $C_2H_2D_2$ (23), C_2HD_3 (9), $C_4H_4D_4$ (5), $C_4H_3D_5$ (6), $C_4H_4D_6O$ (3)

[a] Measured at 0.5 eV relative kinetic energy. [b] Measured at 0.25 eV relative kinetic energy.

suggest that the first excited electronic state (^{6}D) of Cr$^+$ (Table II), which is located 1.52 eV above the ground electronic state (^{6}S), can give rise to these products. The ^{6}D state of Cr$^+$ should have a relatively long lifetime and persist in the beam on a microsecond time scale. Interestingly, the observed products in the reaction of Cr$^+$(^{6}D) with propanol *include* those from the reaction of CrO$^+$ with propane. Since Cr$^+$(^{6}D) can provide much more energy to reaction intermediates than the ground-state Cr$^+$ (Figure 1), this might imply that intermediate **4**, generated in the reaction of Cr$^+$(^{6}D) with propanol, could rearrange to **3**, yielding products of the reaction of CrO$^+$ with propane.

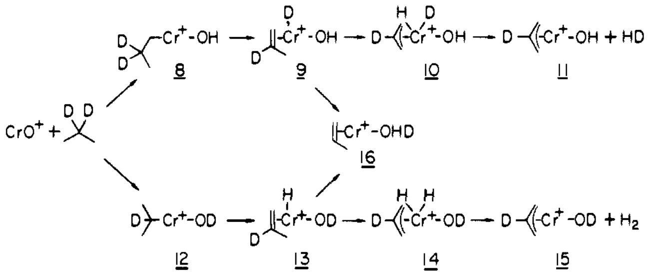
Reactions of CrO$^+$ with Deuterium-Labeled Alkanes. Product distributions measured in the reaction of CrO$^+$ with several deuterium-labeled alkanes, including propane-2,2-*d*$_2$, 2-methylpropane-2-*d*$_1$, and butane-1,1,1,4,4,4-*d*$_6$, are listed in Table VIII. In studying reactions of deuterium-labeled compounds, scrambling processes sometimes result in products with a statistical distribution of hydrogen and deuterium. For example, if isotope effects are ignored, complete scrambling in the reaction with butane-1,1,1,4,4,4-*d*$_6$ would yield dehydrogenation products in the ratio of H_2:HD:D_2 = 2:8:5 (Table IX). This is very different from the observed isotopic product distribution for this reaction (H_2:HD:D_2 = 1:1:0) suggesting a specific process in which H_2 loss occurs mainly across the central C–C bond. Product formation involving loss of HD in the reaction with 2-methylpropane-2-*d*$_1$ is more favored (HD/H_2 = 1) than the statistical ratio (HD/H_2 = 0.25), indicating that 1,2-dehydrogenation occurs preferentially. CH_4 loss in this reaction is highly specific. These observations, along with the proposed initial intermediate **3**, provide a guide to investigate plausible mechanisms for the reaction of CrO$^+$ with alkanes.

Table IX. Isotopic Distribution of Dehydrogenation Products in the Reactions of CrO$^+$ with Deuterated Alkanes (H_2:HD:D_2)

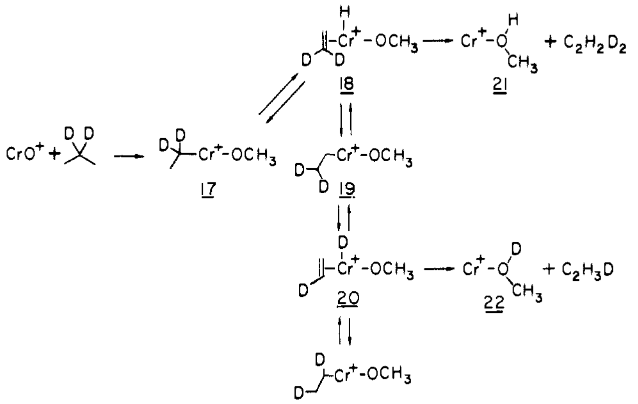
alkane	loss of H_2:HD:D_2	
	statistcl ratio	obsd ratio
propane-*2,2-d*$_2$[a]	15:12:1	1:1:0
2-methylpropane-*2-d*$_1$[b]	4:1:0	1:1:0
n-butane-*1,1,1,4,4,4-d*$_6$[a]	2:8:5	1:1:0

[a] Measured at 0.5 eV relative kinetic energy. [b] Measured at 0.25 eV relative kinetic energy.

Scheme III



Scheme IV

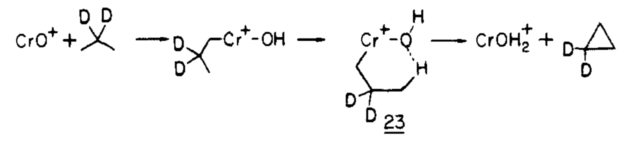


Scheme III presents a postulated mechanism for the dehydrogenation of propane, which is the major product channel in the reaction of CrO$^+$ with propane-2,2-*d*$_2$. The first step is insertion of CrO$^+$ into either a primary C–H or secondary C–D bond. The orientation of CrO after insertion is chosen to reflect the initial tendency of this species to abstract hydrogen atoms at the oxygen center. The C–H insertion intermediate **8** undergoes *β*-D transfer to the Cr center to generate **9** and in turn **10** by another *β*-H transfer, which reductively eliminates HD to yield an allyl–hydroxy complex **11**. Insertion into a secondary C–D bond in **12** follows an analogous process to eliminate H_2 in **15**. The overall mechanism is consistent with the fact that D_2 loss is not observed in the reaction. Formation of allyl–hydroxy complexes has been postulated in the previous study of the reactions of CrO$^+$ with alkenes (**1** of Scheme I).[4] We assume that the preferred pathway for rearrangement of intermediate **9** is the *β*-H transfer which leads to **10** and **11**, rather than the transfer of D to the oxygen center to generate **16**. In general, loss of H_2 is observed without loss of H_2O in the reactions with alkanes.

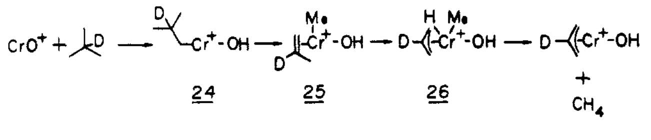
---

(25) AP(Cr$^+$) from Cr(CO)$_6$ is measured by using our ion beam instrument to be 15.0 ± 0.2 eV. Several other measurements include 14.7 ± 0.1 eV (Foffani, A.; Pignataro, S.; Cantone, B.; Grasso, F. *Z. Phys. Chem. (Frankfurt)* **1965**, *45*, 79) and 15.2 ± 0.2 eV (Bidinosti, D. R.; McIntyre, N. S. *Can. J. Chem.* **1967**, *45*, 641).

Scheme V



Scheme VI



However, loss of H_2O is always accompanied by loss of H_2. This may suggest that loss of H_2 precedes loss of H_2O, supporting the argument that the conversion of **9** to **10** prevails. In the case of propane-2,2-d_2, if intermediate **16** were formed, loss of either C_3H_5D or HDO would be expected. Exclusive $C_3H_4D_2$ loss in this reaction thus contradicts the possible formation intermediate **16**, supporting the proposed mechanism.

Scheme IV presents a mechanism which invokes initial insertion of CrO^+ into a C–C bond in order to provide a possible explanation for the processes leading to ethene loss in the reaction with propane-2,2-d_2. The C–C insertion intermediate **17** undergoes β-H transfer to form **18**, which may assume an equilibrium with **20** via reversible ethene insertion into the Cr^+–H bond. The analogous reversible olefin insertion into a M^+–H bond (M = Fe, Co, Ni, and Rh) has been suggested in several studies.[26,27] The intermediates **18** and **20** result in loss of $C_2H_2D_2$ and C_2H_3D, respectively.

The process of propene loss in the reaction with propane shows unique features. Despite the fact that the corresponding ionic product $CrOH_2^+$ is most likely a chromium–water complex, loss of H_2O is not observed from this reaction. Intermediate **16** of Scheme III might be expected to account for the propene loss, as we postulated for the reaction of Cr^+ with 2-propanol (**7** of Scheme II). This is not supported, however, by either the absence of H_2O loss, which might be expected from the competitive bond cleavage of intermediate **16**[28] or the arguments leading to the mechanism proposed in Scheme III. Moreover, the observed isotopic product distribution for the reaction using propane-2,2-d_2 shows exclusive 1,3-dehydrogenation from propane. A mechanism involving the cyclic intermediate **23** provides a plausible explanation, which is shown in Scheme V. Initial insertion into a C–H bond leads to a six-membered cyclic intermediate **23**, which permits hydrogen transfer from the terminal C–H bonds of propane to the oxygen atom, and in turn, dissociation of $C_3H_4D_2$. The preferential loss of $C_3H_4D_2$ compared with H_2O loss suggests that the neutral product in this reaction might be cyclopropane, since cyclopropane is expected to bind less strongly than H_2O to Cr^+. Alternatively, the terminal C–H bond in **23** might add to the metal center to yield $HCrOH^+$ as the ionic product. If the binding energy of H_2O to Cr^+ is estimated as 31 kcal mol^{-1},[28] then $D[CrOH^+–H] \simeq 77$ kcal mol^{-1}. Since this is much stronger than a typical metal–hydrogen bond, the thermodynamically formed product is $CrOH_2^+$ rather than $HCrOH^+$.

Table X. Product Distributions for the Exothermic Reactions of CrO^+ with Cyclic Alkanes and Propene[a]

reactant	tot. cross sectn, Å^2	neutral lost	ion prod.	% of tot.
cyclopropane	48	H_2	$Cr(C_3H_4O)^+$	5
(propene)[b]	(70)	H_2O	$Cr(C_3H_4)^+$	6 (7)
		C_2H_4	$CrOCH_2^+$	25 (39)
		$\cdot C_3H_5$	$CrOH^+$	20 (12)
		C_3H_6O	Cr^+	44 (44)
cyclobutane	90	C_2H_4	$Cr(C_2H_4O)^+$	78
		C_4H_8O	Cr^+	22
cyclopentane	80	$2H_2$	$Cr(C_5H_6O)^+$	91
		$C_5H_{10}O$	Cr^+	9
cyclohexane	80	$2H_2$	$Cr(C_6H_8O)^+$	10
		$3H_2$	$Cr(C_6H_6O)^+$	14
		H_2O	$Cr(C_6H_{10})^+$	5
		H_2O, H_2	$Cr(C_6H_8)^+$	25
		H_2O, $2H_2$	$Cr(C_6H_6)^+$	18
		$C_6H_{12}O$	Cr^+	28

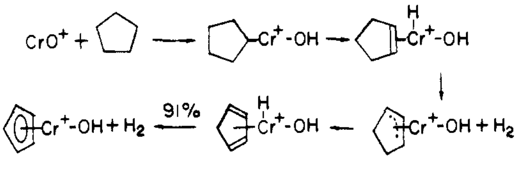
[a] Measured at 0.5 eV relative kinetic energy. [b] These data are taken from ref 4.

Table XI. C–H and C–C Bond Energies of Cyclic Alkanes

alkane	bond energies, kcal mol^{-1}	
	C–H[a]	C–C[b]
cyclopropane	106.3 ± 0.3	54
cyclobutane	96.5 ± 1	55
cyclopentane	94.5 ± 1	75
cyclohexane	95.5 ± 1	81

[a] Reference 7. [b] Estimated values from ring strain energies: ref 33.

Scheme VII



A major product channel common in the reactions of CrO^+ with 2-methylpropane, 2,2-dimethylpropane, and butane is the loss of methane. In order to rationalize these processes, mechanisms which involve initial C–H insertion and β-Me group transfer may be postulated, with an example being shown in Scheme VI for the reaction with 2-methylpropane-2-d_1. The initial C–H insertion intermediate **24** undergoes β-Me transfer to form **25**, and β-H transfer to form **26**, which then eliminates CH_4. This mechanism is consistent with the isotopic product distribution, which shows exclusive loss of CH_4. There are precedents for β-methyl shifts in the gas-phase metal ion literature.[29]

Reactions of CrO^+ with Cyclic Alkanes. Reactions of CrO^+ with cyclic alkanes and propene are summarized in Table X. Interaction of CrO^+ with cyclopropane yields $CrOH^+$ as a major product (reaction 24), representing formal hydrogen atom abstraction from cyclopropane.

$$CrO^+ + c\text{-}C_3H_6 \rightarrow CrOH^+ + C_3H_5 \qquad (24)$$

Since cyclopropyl C–H bonds are stronger than the CrO^+–H bond (Table XI), the hydrogen abstraction implies that the neutral lost in reaction 24 is an allyl rather than cyclopropyl radical. If this rearrangement occurs in the reaction intermediate prior to dissociation, then similar results might be expected in comparing the reactions of cyclopropane and propene. The nearly identical product distributions support this argument. The additional product $Cr(C_3H_4O)^+$ observed in the reaction with cyclopropane can be rationalized by the fact that cyclopropane has a higher heat of formation than propene.[30] Reaction with cyclobutane is highly specific yielding $Cr(C_2H_4O)^+$ as the only product in addition to Cr^+. The loss of C_2H_4 in the

---

(26) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

(27) Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.

(28) Binding energies of propene and H_2O to metal ions may be estimated by using a correlation scheme between binding energies of molecules to $CpNi^+$ (Cp = cyclopentadienyl) and proton. Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998. We estimate $D°(CpNi^+–OH_2) \sim 31$ kcal mol^{-1} and $D[CpNi^+–(CH_3CH{=}CH_2)] \geq 44$ kcal mol^{-1} from this correlation.

(29) See, for example: Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. For a more thorough discussion see: Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.*, in press.

(30) $\Delta H°_f$(cyclopropane) = 12.73 kcal mol^{-1} and $\Delta H°_f$(propene) = 4.88 kcal mol^{-1} from ref 10.

(31) $\Delta H°_f(CH_2)$ = 93.7 kcal mol^{-1} from ref 7.

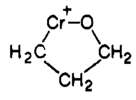
(32) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards, Washington, DC, 1971.

(33) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176.

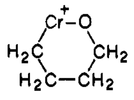
(34) Benson, S. *Thermochemical Kinetics*; Wiley: New York, 1968.

(35) $\Delta H°_f(Cr^+)$ = 250.3 kcal mol^{-1} from Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl.* **1977**, 6.

reactions of CrO^+ with cyclopropane and cyclobutane may result from rearrangement and decomposition of the intermediates **27** and **28**, respectively, formed by insertion of CrO^+ in the strained C–C bonds of these cycloalkanes.

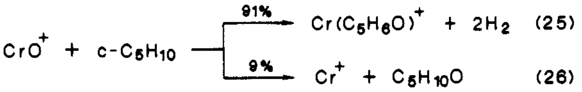


27



28

Reaction with cyclopentane eliminates two molecules of H_2 to yield $Cr(C_5H_6O)^+$ exclusively (reaction 25). This multiple dehydrogenation product can be rationalized by a mechanism analogous to Scheme III, which involves initial insertion into a C–H bond followed by successive β-H transfers to the Cr center to eliminate H_2 (Scheme VII). This mechanism suggests a structure of (C_5H_5)–Cr^+–OH for the double dehydrogenation product. Cyclohexane yields products resulting from dehydrogenation and elimination of H_2O in various intermediate steps.



$$CrO^+ + c\text{-}C_6H_{10} \xrightarrow{91\%} Cr(C_5H_6O)^+ + 2H_2 \quad (25)$$

$$CrO^+ + c\text{-}C_6H_{10} \xrightarrow{9\%} Cr^+ + C_6H_{10}O \quad (26)$$

Summary

1. A single bimolecular encounter between CrO^+ and an alkane provides energetically facile pathways for alkane oxidation. CrO^+ undergoes exothermic reaction with ethane to oxidize ethane into ethanol selectively. In addition to the possibility of alcohol formation, reactions of CrO^+ with larger alkanes provide a variety of product channels for alkane oxidation, which include dehydrogenation and loss of alkenes and smaller alkanes.

2. Reactions of CrO^+ with cyclopropane and cyclobutane yield products characteristic of C–C bond cleavages. Reaction of CrO^+ with cyclopropane is unique, exhibiting a product distribution which closely resembles that of the reaction with propene. In contrast, reactions with cyclopentane and cyclohexane exhibit multiple dehydrogenation and H_2O loss.

3. A CrO^+–H bond dissociation energy of 89 kcal mol^{-1}, determined by examining a series of hydrogen abstraction reactions, implies that the reaction between CrO^+ and an alkyl C–H bond involves multicenter intermediates. This argument, supported by an examination of the reactions of Cr^+ with alcohols, suggests an initial intermediate in which a C–H bond adds across the Cr^+–O bond.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation under Grant CHE-8407857. Graduate fellowship support by the Korean Government (H.K 1980–1984) is gratefully acknowledged.

Registry No. H_2, 1333-74-0; CrO_2Cl_2, 14977-61-8; Cr, 7440-47-3; $Cr(CO)_6$, 13007-92-6; $Cr(OH)^+$, 68566-23-4; CrO^+, 56371-63-2; $H_2C{=}CHCH_2CH_3$, 106-98-9; *cis*-$H_3CCH{=}CHCH_3$, 590-18-1; $H_2C{=}C(CH_3)_2$, 115-11-7; $H_2C{=}CHCH_3$, 115-07-1; $C_6H_5CH_3$, 108-88-3; $(H_3C)_3CH$, 75-28-5; $H_3CCH_2CH_3$, 74-98-6; $H_3C(CH_2)_2CH_3$, 106-97-8; $(H_3C)_3CCH_3$, 463-82-1; $H_2C{=}CH_2$, 74-85-1; C_6H_6, 71-43-2; $Fe(OH)^+$, 15092-05-4; $Co(OH)^+$, 12323-82-9; CrO, 12018-00-7; CrOH, 36011-51-5; CH_4, 74-82-8; CH_3CH_3, 74-84-0; $HO(CH_2)_2CH_3$, 71-23-8; $H_3CCH(OH)CH_3$, 67-63-0; $H_3CCD_2CH_3$, 2875-95-8; $(H_3C)_2CDCH_3$, 13183-68-1; $D_3C(CH_2)_2CD_3$, 13183-67-0; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7.

Mechanistic and Kinetic Study of Alkane Activation by Ti^+ and V^+ in the Gas Phase. Lifetimes of Reaction Intermediates

M. A. Tolbert and J. L. Beauchamp*

Contribution No. 7394 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125.
Received May 14, 1986

Abstract: The reactions of Ti^+ and V^+ with several deuterium-labeled alkanes are studied by using an ion beam apparatus. The dominant reactions observed for both of these metal ions are single and double dehydrogenations. Alkane loss reactions are also observed for Ti^+ but may be due to electronically excited states. The dehydrogenation mechanisms are investigated by using partially deuterated alkanes. The results are consistent with 1,2-eliminations for both V^+ and Ti^+, where deuterium scrambling may occur in the latter case. It is proposed that some 1,3-elimination of hydrogen also occurs in the reaction of Ti^+ with *n*-butane. Although the dehydrogenation reactions of V^+ and Ti^+ appear to be similar to those of Ru^+ and Rh^+, there are some important differences in the reactivity of V^+. Extensive adduct formation and large deuterium isotope effects are consistent with reaction intermediates which are relatively long-lived for V^+ in comparison to Ti^+, Ru^+, and Rh^+. Collisional stabilization studies are used to estimate dissociation rates of reaction intermediates formed when Ti^+ and V^+ interact with *n*-butane. The measured upper limits to the unimolecular decomposition rates are 1.47×10^5 s^{-1} and 1.23×10^7 s^{-1} for V^+ and Ti^+, respectively. Model RRKM calculations are able to reproduce these rates and provide an explanation of isotope effects observed when *n*-butane-d_{10} is employed as the neutral reactant. The slower rate for V^+ is suggested to arise from the inability of V^+ to form two strong σ bonds due to the $3d^4$ electronic configuration of the ground-state ion. This renders C–H bond insertion energetically much less favorable for V^+ than for the other metal ions and limits the excitation energy of reaction intermediates.

Recent studies have indicated that a wide variety of transition-metal ions are capable of activating the bonds of totally saturated hydrocarbons.[1-6] These studies have revealed that, although groups of transition-metal ions exhibit similar reactivity (i.e., Ru^+, Rh^+; Fe^+, Co^+, Ni^+), there are also intriguing dif-

Table I. Bond Dissociation Energies[a]

	$D(M^+ - H)$		
M^+	exp	theory[b]	$D(M^+ - CH_3)$ exp
Ti^+	55[c]	55.0	56.5[c]
V^+	48[d]	44.5	50[d]

[a] All values in kcal/mol. [b] Reference 36. [c] Reference 7. [d] Reference 8.

---

(1) (a) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963. (b) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784. (c) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.

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

(3) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.

(4) Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5675.

0002-7863/86/1508-7509$01.50/0