these gas-phase metal ion reactions as a tool to determine the original label distribution in a molecule. For example, by looking at the product ratio for loss of methane to loss of ethane from butane in the reaction with nickel ions, we can determine the amount of ^{13}C at interior vs. exterior positions. Because mass spectrometry is used to detect the products, this technique could be quite useful for identifying isotopically labeled reactants when only small amounts of the compound are available.

Acknowledgment. We wish to thank Dr. Peter Armentrout for helpful discussions about this paper. This research was supported in part by the U.S. Department of Energy. Graduate fellowship support from Bell Laboratories, SOHIO, and EXXON (L.F.H.) is gratefully acknowledged.

Registry No. $FeCl_3$, 7705-08-0; $CoCl_2$, 7646-79-9; $NiCl_2$, 7718-54-9; Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; propane, 74-98-6; 2-methylpropane, 75-28-5; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; 2,2-dimethylpentane, 590-35-2; heptane, 142-82-5; 2-methylhexane, 591-76-4; octane, 111-65-9; cyclobutane, 287-23-0; cyclopentane, 287-92-3; methylcyclopentane, 96-37-7; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2.

Fluorine Substituent Effects on Metal–Carbene Bond Dissociation Energies. Implications for Metathesis Reactions of Fluorinated Olefins[†]

L. F. Halle, P. B. Armentrout,[1] and J. L. Beauchamp*

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,
Pasadena, California 91125

Received June 21, 1983

The reactions of singly charged atomic nickel ions with ethylene oxide, cyclopropane, ethene, and several fluorinated hydrocarbons are examined by using an ion beam apparatus. Analysis of the thresholds for endothermic processes leading to the formation of nickel ion carbene species yields the bond dissociation energies $D^0(Ni^+–CH_2) = 86 \pm 6$ kcal/mol and $D^0(Ni^+–CF_2) = 47 \pm 7$ kcal/mol. Although fluorine substitution results in a substantially weakened bond, the difluorocarbene is, in fact, more stable as judged by several criteria. For example, the reaction of $NiCH_2^+$ with C_2F_4 to yield $NiCF_2^+$ and CH_2CF_2 is exothermic by 20 kcal/mol. The implications of these carbene bond strengths for the metathesis of various fluorinated olefins is discussed.

Introduction

Metal carbenes are considered to be propagating intermediates in reactions such as olefin metathesis[2] and possibly olefin polymerization.[3] Little is known about the strength of the metal–carbene bond. Estimates of the relative strengths of π bonds in these species are sometimes derived from measured rotational barriers.[4] This analysis may lead to erroneous conclusions for metal systems in which more than a single d orbital is available for π bonding.[5] Theoretical calculations for model metal carbene systems have provided some estimates of bond strengths.[6,7] Where comparison with experiment has been possible, the agreement is sufficiently poor to suggest that caution must be used in regarding the calculated bond strengths as useful estimates.[7-9] In our laboratory, we have developed experimental methods to directly measure carbene bond strengths to metal ions in the gas phase.[9,11] The present study reports the results of ion beam reactions of Ni^+ with various organic compounds which yield the metal carbene ions $NiCH_2^+$ and $NiCF_2^+$. Bond energies are derived from an examination of thresholds of endothermic reactions using theoretical techniques described previously. These bond strengths can be used to assess fluorine substituent effects on carbene stability and evaluate the energetics of gas-phase metathesis reactions of fluorinated olefins with $NiCH_2^+$ and $NiCF_2^+$ as the propagating intermediates.

Experimental Section

The ion beam apparatus is described in detail elsewhere.[10] Ions from a surface ionization source are accelerated and focused into a 60° sector magnet for mass separation. The mass selected beam is decelerated to a chosen 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

---

[†] Contribution No. 6816.

(1) Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

(2) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

(3) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.

(4) Kiel, W. A.; Lin, G. Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. See also: Kegley, S. E.; Brookhart, M. *Organometallics* **1982**, *1*, 760.

(5) Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hehre, W. J., submitted for publication in *Organometallics*.

(6) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1977**, *99*, 3966.

(7) (a) Brooks, B. R.; Schaefer, H. F., III *Mol. Phys.* **1977**, *34*, 193. (b) Vincent, M. A.; Yoshioka, Y.; Schaefer, H. F., III *J. Phys. Chem.* **1982**, *86*, 3905.

(8) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449.

(9) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501.

(10) Armentrout, P. B.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *75*, 2819.

(11) Stevens, A. E.; Berman, D. W.; Beauchamp, J. L. submitted for publication in *J. Am. Chem. Soc.*

0276-7333/83/2302-1829$01.50/0

in a pulse counting mode. Ion signal intensities are corrected for the mass discrimination of the quadrupole mass filter.

The ion source, previously described, is comprised of a tubular stainless steel oven attached to the side of a U-shaped repeller plate which surrounds a rhenium ionization filament. The oven is loaded with $NiCl_2 \cdot 6H_2O$ in these experiments. The filament generates sufficient heat to dehydrate the nickel complex and vaporize $NiCl_2$. This vapor is directed at the filament where dissociation and ionization of the resulting Ni occurs. At the filament temperature used, ~2500 K, it is estimated that over 98% of the nickel ions produced are in the ^2D ground state (derived from the $3d^9$ configuration), while less than 2% are in the first excited state, ^4F (derived from the $4s3d^8$ configuration), which lies 1.04 eV above the ground state.[12]

The nominal collision energy of the ion beam is taken as the difference in potential between the collision chamber and the center of the filament, the latter being determined by a resistive divider. This energy was verified by use of a retarding field energy analyzer. Agreement was always within 0.3 eV. The energy distribution of the Ni^+ beam was also obtained by using the retarding grid and was determined to be 0.7 eV (fwhm). In the center of mass frame, this introduces an uncertainty of less than ±0.23 eV for reactions in which bond energies were determined. No specific account of the energy distribution of the ion beam is taken in the treatment below. A more severe problem concerning the actual energy of interaction is the effect of the thermal motion of the reactant gas. This energy distribution effectively broadens any sharp features in the excitation function, including threshold. To account for this effect, the proposed excitation function is convoluted with this distribution before comparison with the data using the method outlined by Chantry.[13]

Reaction cross sections for a specific product, σ_i, are calculated from eq 1, where the sum is over all products and I_i refers to a

$$\sigma_i = \sigma I_i / \sum I_i \qquad (1)$$

particular measured product ion intensity. The total reaction cross section, σ, is evaluated by using eq 2, where I_0 is the

$$I_0 = (I_0 + \sum I_i) \exp(-n\sigma l) \qquad (2)$$

transmitted reactant ion beam intensity, n is the number density of the target gas, and l is the length of the interaction region. The pressure of the target gas, measured by using an MKS Baratron Model 90H1 capacitance manometer, is kept sufficiently low, (1–5) × 10^{-3} torr, that attenuation of the ion beam is minimal. The length of the interaction region is 5 mm and is uncorrected for entrance and exit aperture effects[14] (1.0 and 1.5 mm in diameter, respectively).

The greatest uncertainty in measurements of reaction cross sections is the ion detection efficiency. At laboratory energies below about 10 eV, a small field of 0.5 V is placed across the specially designed collision chamber[15] to extract low-energy ions. This field introduces an additional uncertainty in the energy of interaction. Relative cross sections are well reproduced, and we estimate that the absolute cross sections reported are accurate to a factor of 2.

In a previous paper,[10] a functional form for the energy-dependent cross section was suggested. The basic result used in examining the endothermic reactions presented here is given by eq 3, where E is the total energy of the reactants and E_0 is the

$$\sigma = 0 \quad E \le E_0$$

$$\sigma = \sigma_0[(E - E_0)/E]^n \quad E_0 < E < E_0 + D/a \qquad (3)$$

$$\sigma = \sigma_0(D/aE)^n \quad E \ge E_0 + D/a$$

endothermicity of the reaction, taken to be the difference between the bond energy of the ionic product, D, and the bond energy of the neutral reactant. The average fraction of the total internal energy of the products in the ionic fragment is given by a, and n is a variable exponent which equals 1 when using the line of centers model.[16] If the reaction involves a long-lived intermediate, n is large and may be a sizable fraction of the total number of vibrational degrees of freedom.[10] In fitting the data, the curves eq 3 describes are convoluted by using the method of Chantry[13] to account for the thermal motion of the reactant gas as discussed above. Often, within experimental error, several sets of parameters fit the data equally well and thus give a range of possible threshold energies. This is how the uncertainty in E_0 is determined.

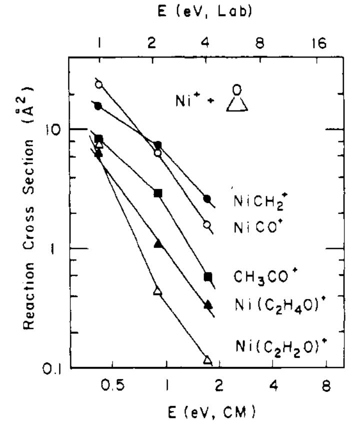
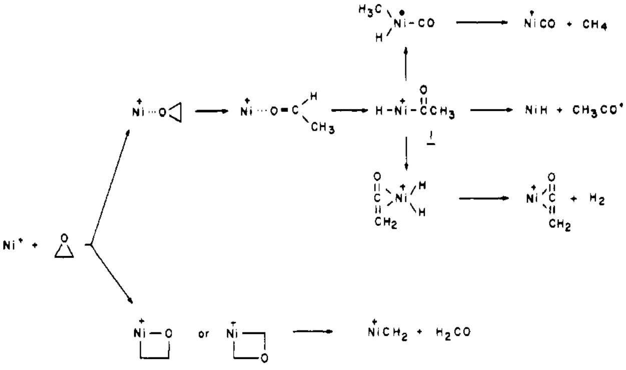


Figure 1. Variation in experimental cross section for the interaction of Ni^+ with ethylene oxide as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale).

Scheme I



It is important to point out that in these experiments neutral products are not detected. However, except at higher energies, the identity of these products can usually be inferred without ambiguity. In addition, these experiments provide no direct structural information about the ionic products. However, straightforward thermochemical arguments can often distinguish possibilities for isomeric structures.

Results

Nickel Carbene. Reaction of nickel ions with ethylene oxide at low energies yields a number of products having large cross sections which decrease with increasing energy (Figure 1). This behavior implies that these processes are exothermic. Scheme I outlines a possible mechanism for the production of these species. Initial interaction of Ni^+ with ethylene oxide may be associated with the basic oxygen center to produce a chemically activated species which can rearrange to acetaldehyde. A hydrido acyl compound, analogous to 1, is formed in the reaction of $Rh(PPh_3)_3Cl$ with ethylene oxide.[17] Moreover, this same

---

[12] Moore, C. E. "Atomic Energy Levels"; National Bureau of Standards: Washington, DC, 1949.

[13] Chantry, P. J. *J. Chem. Phys.* **1971**, *55*, 2746.

[14] Nenner, T.; Tien, H.; Fenn, J. B. *J. Chem. Phys.* **1975**, *63*, 5439.

[15] Armentrout, P. B.; Hodges, R. V.; Beauchamp, J. L. *J. Chem. Phys.* 1977, *66*, 4683.

[16] Levine, R. D.; Bernstein, R. B. "Molecular Reaction Dynamics"; Oxford University Press: New York, 1972.

[17] Milstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 5228. See also: Milstein, D.; Calabrese, J. C. *Ibid.* **1982**, *104*, 3773.

Table I. Thermochemical Data Used in This Study

species	$\Delta H_{f\,298}^{\circ}$, eV	$\Delta H_{f\,298}^{\circ}$, kcal/mol	ref
CH_2	4.01	92.4 ± 1.0	*a*
CF_2	−1.01	−44.0 ± 1.0	*b*
C_2H_4	0.534	12.45 ± 0.3	*c*
CH_2CF_2	−3.47	−80.1 ± 0.8	*c*
C_2F_4	−8.47	−157.9 ± 0.4	*c*
c-C_3H_6	0.552	12.7 ± 0.1	*c*
H_2CO	−1.13	−25.98 ± 0.2	*c*
CH_2CO	−0.494	−11.4 ± 0.6	*c*
c-C_2H_4O	−0.545	−12.6 ± 0.15	*c*
H^-	1.505	34.7	*d*
CH_3CO^+	7.167	157.0 ± 0.4	*e*
Ni^+	12.07	278.3	*f*

[a] Chase, M. W.; Curnett, J. L.; Prophet, H.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data, Suppl.* **1975**, *4*, No. 1. [b] Schug, K. P.; Wagner, H. G. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 719. [c] Pedley, J. B.; Rylance, J. "Sussex-N.P.L. Computer Analysed Thermo-Chemical Data: Organic and Organometallic Compounds"; Sussex University: Sussex, 1977. [d] EA(H) = 0.754 eV from: Wagman, D. D.; Evans, W. H.; Parker, V. B.; Halow, I.; Bailey, S. M.; Schumm, R. H. *NBS Tech. Note* **1968**, *No. 270-30*. [e] Traeger, J. C.; McLoughlin, R. G.; Nicholson, A. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5318. [f] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*, No. 1.

hydrido acyl is formed in the reaction of $Rh(PPh_3)_3Cl$ with acetaldehyde. Upon heating, methane is evolved.[18] In experiments using the technique of ion cyclotron resonance mass spectrometry, reaction of $(\eta^5\text{-}C_5H_5)Ni^+$ with CH_3CHO yielded only the $(\eta^5\text{-}C_5H_5)NiCO^+$ product.[19] Other studies have shown that $M(CO)^+$ (where M = Co, Fe) is the only exothermic product formed in the interaction of M^+ with acetaldehyde.[20,21] Ni^+ may also insert into the carbon–carbon or a carbon–oxygen bond of ethylene oxide as steps prior to formation of the carbene.

The exothermic formation of $C_2H_3O^+$ indicates that the bond energy for NiH must be greater than 1.98 eV (see Table I). This is consistent with Gaydon's value of 2.6 eV.[22] In order for the process forming $NiCH_2^+$ to be exothermic, the metal ion carbene bond energy must be greater than the enthalpy change, ΔH = 3.43 eV (see Table I for thermochemical data used), for reaction 4.

$$c\text{-}C_2H_4O \rightarrow CH_2O + CH_2 \qquad (4)$$

At low energies, the cross section for formation of $NiCH_2^+$ from the reaction of Ni^+ with cyclopropane, Figure 2, is small. As reaction energy is increased, the cross section reaches a maximum and then falls off. This is typical behavior for an endothermic process. Thus, the bond energy for $NiCH_2^+$ must be less than the enthalpy change, ΔH = 3.99 eV (see Table I), for reaction 5.[23] The

$$c\text{-}C_3H_6 \rightarrow C_2H_4 + CH_2 \qquad (5)$$

lines drawn in Figure 2 show three fits to the data using eq 3, giving rise to a range of threshold energies, E_0 = 0.48–0.60 eV. The fit chosen as the best description of the data uses $n = 5$, $\sigma_0 = 6.1$ Å^2, $E_0 = 0.55$ eV, and $a = 0.68$. In this case, the uncertainties set by the various good fits are small due to the low E_0 and do not accurately represent the uncertainty in the experimental data. From this last fit, a bond energy $D^0(Ni^+\text{–}CH_2) = 3.45 \pm 0.3$ eV is calculated.

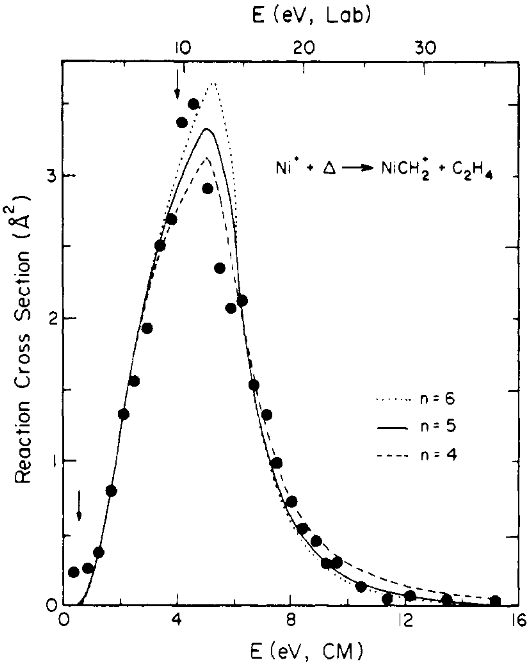


Figure 2. Variation in experimental cross section as a function of kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for the formation of $NiCH_2^+$ from reaction of Ni^+ with cyclopropane. Arrows mark the threshold at 0.55 eV and the energy needed to produce methylene and ethene from cyclopropane, 4.0 eV. The curves are the convoluted fits to the data as discussed in the text.

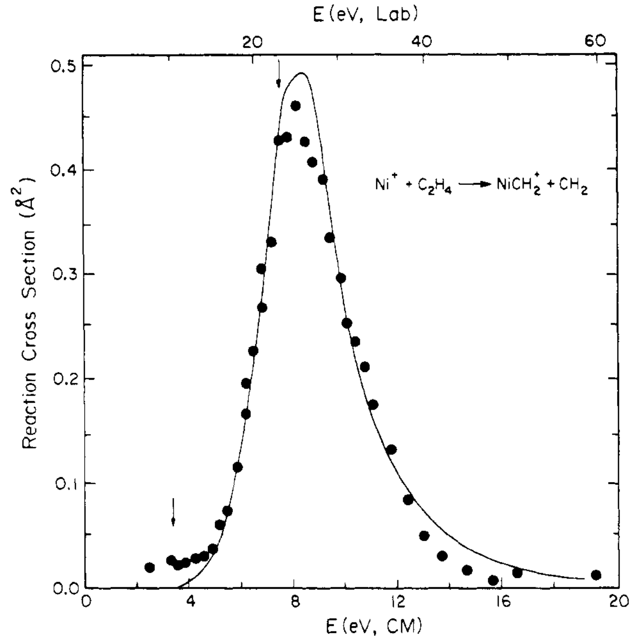


Figure 3. Variation in experimental cross section with kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for the formation of $NiCH_2^+$ from the reaction of Ni^+ with ethene. Arrows indicate the threshold energy for reaction, 3.4 eV, and the carbon–carbon bond energy of ethene, 7.47 eV. The curve is the fit to the data given in the text and convoluted as discussed.

---

(18) Milstein, D. *Organometallics* **1982**, *1*, 1549.

(19) Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 5700.

(20) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

(21) Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L., to be submitted for publication.

(22) Gaydon, A. G. "Dissociation Energies and Spectra of Diatomic Molecules"; Chapman and Hall: London, 1968.

(23) Data for the reaction of Co^+ with ethylene oxide are similar to that to Ni^+, indicating exothermic production of $CoCH_2^+$. The excitation function for the carbene product formed in the reaction of Co^+ with cyclopropane shows complications that are not observed in the Ni^+ reaction. See ref 10.

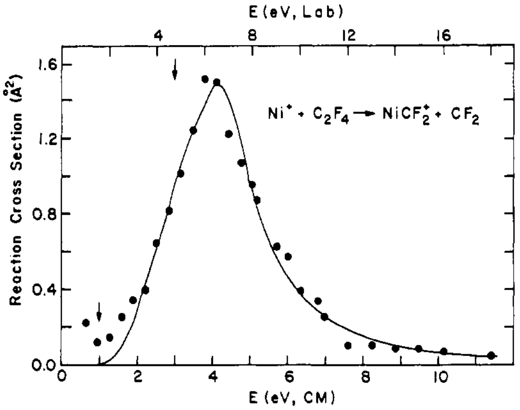


Figure 4. Variation in experimental cross section with kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for the formation of $NiCF_2^+$ from the reaction of Ni^+ with tetrafluoroethene. Arrows indicate the threshold energy for reaction, 1.0 eV, and the carbon–carbon bond energy of C_2F_4, 3.03 eV. The curve is the fit to the data given in the text and convoluted as discussed.

Results for reaction of Ni^+ with ethene to yield $NiCH_2^+$ are shown in Figure 3. The theoretical fit uses $n = 5$, $\sigma_0 = 8.5$ Å², $E_0 = 3.4$ eV, and $a = 0.81$. From this threshold, a bond strength of $D^0(Ni^+–CH_2) = 4.1 \pm 0.3$ eV is derived.

Nickel Fluorocarbenes. The products formed in the reaction of Ni^+ with C_2F_4 are given in eq 6–8. All of these

$$Ni^+ + C_2F_4 \rightarrow NiF^+ + C_2F_3 \quad (6)$$

$$Ni^+ + C_2F_4 \rightarrow NiCF_2^+ + CF_2 \quad (7)$$

$$Ni^+ + C_2F_4 \rightarrow NiC_2F_3^+ + F \quad (8)$$

products are formed in endothermic processes. The thresholds for reactions 6 and 8 were not examined. Detailed cross section data for reaction 7 are shown in Figure 4. The maximum cross section occurs at ~3.8 eV relative kinetic energy. At this energy, reaction 7 accounts for 80% of the products observed. At higher energies, NiF^+ becomes the dominant product ($\sigma[NiF^+] = 1$ Å² at 6.3 eV relative kinetic energy). The fit to the data shown in Figure 4 is given by eq 3 with $n = 4$, $\sigma_0 = 4.7$ Å², $E_0 = 1.0$ eV, and $a = 0.60$. Given the $F_2C–CF_2$ bond energy in tetrafluoroethene of 69.9 kcal/mol (see Table I), a bond energy of $D^0(Ni^+–CF_2) = 47 \pm 7$ kcal/mol (2.0 ± 0.3 eV) is calculated.

In unsuccessful attempts to find other sources for the fluorocarbenes, we briefly examined the reaction of Ni^+ with carbon tetrafluoride, 1,1-difluoroethene, and *cis*-1,2-difluoroethene. Only endothermic processes were observed, but no thresholds were derived. The lowest energy processes in the interaction of Ni^+ with CF_4 are given in reactions 9 and 10. At higher energies (>7 eV relative

$$Ni^+ + CF_4 \rightarrow NiF^+ + CF_3 \quad (9)$$

$$Ni^+ + CF_4 \rightarrow CF_3^+ + NiF \quad (10)$$

kinetic energy) small amounts of CF^+ and CF_2^+ appear. A small amount (<0.3 Å²) of $NiCH_2^+$ is formed in the reaction with 1,1-difluoroethene, but no $NiCF_2^+$ is observed. The largest product ($\sigma_{max} \approx 2$ Å² at 0.7 eV relative kinetic energy) is NiF^+, and some $C_2H_2F^+$ and NiC_2H^+ are also seen. These latter three products are the only ones observed in the reaction of Ni^+ with 1,2-difluoroethene.

Discussion

Table II. Experimental Results for $D^0(Ni^+–CH_2)$

reaction	$D^0(Ni^+–CH_2)$ eV	$D^0(Ni^+–CH_2)$ kcal/mol
$Ni^+ + C_2H_4O \rightarrow NiCH_2^+ + CH_2O$	>3.43	>79.0
$Ni^+ + C_3H_6 \rightarrow NiCH_2^+ + C_2H_4$	<3.99	<92.1
	3.45 ± 0.3[a]	79.6 ± 7
$Ni^+ + C_2H_4 \rightarrow NiCH_2^+ + CH_2$	4.1 ± 0.3[a]	95 ± 7

[a] Calculated from threshold for reaction using theory as described in text.

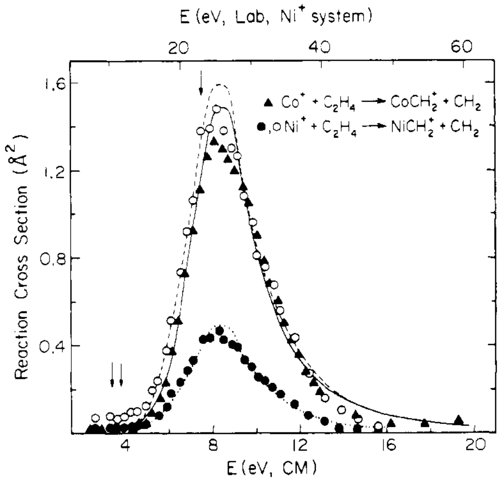


Figure 5. Variation in experimental cross section with kinetic energy in the center of mass frame (lower scale) and the laboratory frame (upper scale) for the formation of MCH_2^+ from the reaction of M^+ with ethene. The dotted line is the fit to the data for $M^+ = Ni^+$, and the dashed line is the same multiplied by 3.24. Solid curve is the fit to the data for $M^+ = Co^+$. Arrows indicate the threshold for the Ni^+ reaction, 3.4 eV, the threshold for the Co^+ reaction, 3.8 eV, and the carbon–carbon bond energy of ethene, 7.47 eV.

$NiCH_2^+$. Table II lists the thermochemical results obtained from the reactions of Ni^+ studied leading to formation of $NiCH_2^+$. The bond strength of the nickel carbene species is estimated to be $D^0(Ni^+–CH_2) = 3.75 \pm 0.25$ eV (86 ± 6 kcal/mol), an average value determined from the threshold of cyclopropane reaction and the limit set by the endothermicity of this reaction. The bond energy derived from the results with ethene, $D^0(Ni^+–CH_2) > 4$ eV, reflects the experimental errors as well as possible inaccuracies in the theoretical analysis.

It is useful to compare the results and analysis of reactions of Ni^+ with previous experiments in which the reactant ion was Co^+.[10] In particular, the comparison for Co^+ reacting with ethene to yield $CoCH_2^+$ is shown in Figure 5.[23] Also shown are the data for $NiCH_2^+$ from this system normalized to the corresponding $CoCH_2^+$ data, as well as the excitation function for $NiCH_2^+$ multiplied by this same normalization factor. The theoretical fits to the data for formation of $NiCH_2^+$ and $CoCH_2^+$ from reaction with ethene have very similar shapes and both use the same value of $n = 5$. The excitation function for the $CoCH_2^+$ product is displaced approximately 0.3 eV higher than that for $NiCH_2^+$. The threshold for formation of $CoCH_2^+$ from ethene is 3.8 eV,[10] which suggests that the $NiCH_2^+$ product should have a threshold of about 3.5 eV or a bond energy of about 4 eV. This value is in reasonable agreement with the threshold energy taken directly from Figure 3, $D_0 = 3.4 \pm 0.3$ eV, and is in slightly better agreement with the other determinations of this bond energy than the latter value. It is not clear why the maximum cross section for the metal carbene ion from reaction with ethene is 3 times larger for the Co^+ system compared to the Ni^+ system. The analogous reaction of Fe^+ has a maximum cross section of 1.8 Å².[24] A com-

Table III. Carbene Bond Energies[a]

ion	$D(\mathrm{Ni^+{-}CX_2})$	$D[\mathrm{(CO)_5Mn^+{-}CXY}]$[b]
$NiCH_2^+$	86 ± 6	
$NiCF_2^+$	47 ± 7	
$(CO)_5MnCH_2^+$		93 ± 8
$(CO)_5MnCHF^+$		91 ± 9
$(CO)_5MnCF_2^+$		79 ± 3

[a] All values in kcal/mol at 298 K. [b] Data from ref 11.

parison of metal ion carbene bond strengths is discussed elsewhere.[9,11] Briefly, we note that the group 8 metal ion bond energies are similar, with the iron system having a slightly higher bond strength: $D^0(\mathrm{Co^+{-}CH_2}) = 85 \pm 6$ kcal/mol and $D^0(\mathrm{Fe^+{-}CH_2}) = 96 \pm 5$ kcal/mol.

The results of these studies indicate that the $\mathrm{Ni^+{-}CH_2}$ bond (86 kcal/mol) is almost twice as strong as the $\mathrm{Ni^+{-}CF_2}$ bond (47 kcal/mol). A similar weakening of the metal carbene bond energies by successive fluorine substitution has been noted previously for the bond energies of $\mathrm{(CO)_5Mn^+{-}CXY}$ where X and Y = H or F.[11] The bond strengths for these systems were determined by photoionization mass spectrometry and are listed along with the present results in Table III. A difference of 14 kcal/mol between the bond strength of $\mathrm{(CO)_5Mn^+{-}CH_2}$ and $\mathrm{(CO)_5Mn^+{-}CF_2}$ is measured. This difference is smaller than that of the bare nickel ion, but still substantial.[25] It is interesting to note that the carbon–carbon bond energy in tetrafluoroethene is over 100 kcal/mol less than that of ethene.

The thermochemical data of the present study can be used to assess the enthalpy changes of the metathesis reactions (11) and (12). The enthalpy change for reaction

$$\mathrm{NiCH_2^+ + CF_2CF_2 \rightarrow NiCF_2^+ + CH_2CF_2} \qquad (11)$$

$$\mathrm{NiCH_2^+ + CH_2CF_2 \rightarrow NiCF_2^+ + CH_2CH_2} \qquad (12)$$

12 is calculated to be $\Delta H = -20$ kcal/mol, and that for reaction 11 is $\Delta H = -5$ kcal/mol (see Tables I and III). The exothermicity of these processes leading to $NiCF_2^+$ suggests that the weak $\mathrm{Ni^+{-}CF_2}$ bond should not be interpreted to imply a lack of stability of this species.

The thermochemistry determined above is also useful in judging whether these carbenes can act as catalytic intermediates in the olefin metathesis reaction 13. The

$$\mathrm{CH_2CH_2 + CF_2CF_2 \rightarrow 2CH_2CF_2} \qquad (13)$$

catalytic cycle is given by reaction 11 followed by the reverse of reaction 12. For both these steps to be exothermic in the general case, the inequalities shown in eq 14 must

$$43.9\ \mathrm{kcal/mol} < D^0(\mathrm{M{-}CH_2}) - D^0(\mathrm{M{-}CF_2}) < 58.6\ \mathrm{kcal/mol} \qquad (14)$$

hold. The limits depend only on the heats of formation of the olefins, given in Table I. The difference in carbene bond energies for the nickel ion system considered in the present study is 39 ± 9 kcal/mol (Table III). Thus, the nickel ion carbene and difluorocarbene may be only marginally able to catalyze reaction 13. Other systems may prove to be better candidates for this process.

Acknowledgment. This research was supported in part by the U.S. Department of Energy. Graduate fellowship support from Bell Laboratories, SOHIO, and the Shell Companies Foundation (L.F.H.) is gratefully acknowledged.

Registry No. $NiCH_2^+$, 87453-14-3; $NiCF_2^+$, 87453-15-4; $(CO)_5MnCH_2^+$, 72104-77-9; $(CO)_5MnCHF^+$, 87453-16-5; $(CO)_5MnCF_2^+$, 87453-17-6; Ni^+, 14903-34-5; C_2H_4O, 75-21-8; C_3H_6, 75-19-4; C_2H_4, 74-85-1; C_2F_4, 116-14-3.

---

(24) It is interesting to note that the maximum cross section for formation of MCH_3^+ from the reaction of M^+ with ethane is 2.1 Å^2 for Co^+ and Ni^+, but lower for Fe^+ (0.7 Å^2).

(25) Theoretical calculations (STO-3G level) for substituted titanium carbenes predict systems for which the monofluorocarbene bond to the metal may be stronger than the $\mathrm{M{-}CH_2}$ bond. The titanium–carbon bond distance decreases with fluorine substitution (on carbon) in the coordinatively unsaturated complexes $\mathrm{H_2Ti{=}CH_2}$ and $\mathrm{Cl_2Ti{=}CH_2}$ but increases with fluorine substitution in the more highly saturated system $\mathrm{Cp_2Ti{=}CH_2}$. The latter is undistorted while the methylidene hydrogen in the former two compounds has bent over in the direction of the metal. This distortion (which does not occur in any of the unsubstituted systems) probably accounts in whole or part for the observed metal–carbon bond shortening. See: Francl, M. M.; Pietro, W. J.; Hout, R. F., Jr.; Hebre, W. J. *Organometallics* **1983**, *2*, 281.