bromide, $[\alpha]^{25}{}_D$ 0.00. When (*R*)-(−)-α-deuteriobenzyl chloride was used under the same conditions, the recovered chloride was 90.2% racemic.

Benzylchloro-1,2-bis(diphenylphosphinoethane)palladium(II). To a stirred suspension of 3.5 g (5.0 mmol) of dichlorobis(triphenylphosphine)palladium(II) and 4.0 g (10 mmol) of 1,2-bis(diphenylphosphinoethane) in 100 mL of degassed ethanol was added 1.00 g (37.8 mmol) of sodium borohydride, and the suspension was stirred at 25 °C under argon until the gas evolution stopped (4 h). The yellow 1,2-bis(diphenylphosphinoethane)bis(triphenylphosphine)palladium(0),[23] isolated by filtration under argon, was washed with ethanol and dried in vacuo.

To a solution of this complex in 80 mL of degassed benzene under argon was added 3.04 g (24.0 mmol) of benzyl chloride. After being stirred at 25 °C for 36 h, the mixture was filtered and the solvent was removed by evaporation. Pentane–ether (2:1) was added, and the yellow benzylchloro-1,2-bis(diphenylphosphinoethane)palladium(II), isolated by filtration, was washed with pentane and dried in vacuo to give 2.00 g (63.5% based on dichlorobis(triphenylphosphine)palladium(II)) of product: mp 184–186 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.05–6.70 (m, 25 H, phenyls), 3.20 (d of d, $J = 4$ Hz, 2 H, $PhCH_2$), 2.50 (distorted d, $J = 3$ Hz, 4 H, $P-CH_2$); ^{13}C NMR ($CDCl_3$) δ 134.434–127.385 (m), 23.163 (s), 21.669 (s), 20.207 (s). Anal. ($C_{33}H_{31}ClP_2Pd$) C, H, Cl: calcd, 5.62; found, 6.17; P: calcd, 9.81; found, 10.94.

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Reactions of Atomic Metal Ions with Alkyl Halides and Alcohols in the Gas Phase

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Abstract: The chemistry of Li^+, Na^+, Fe^+, Co^+, and Ni^+ with alkyl halides and alcohols in the gas phase as elucidated by ion cyclotron resonance spectroscopy is described. The alkali metal ions induce dehydrohalogenation and dehydration of alkyl halides and alcohols, respectively. Reactivity of R-X decreases with increasing $D(R^+-X^-)$ indicating a mechanism involving charge generation at the carbon. A potential energy surface with a barrier associated with such a charge generation is proposed and discussed quantitatively. From halide transfer reactions of RX to alkali metal ions it is deduced that $\Delta H_f{}^\circ{}_{298}$(1-adamantyl cation) = 160.7 ± 3.0 kcal/mol and $\Delta H_f{}^\circ{}_{298}(C_7H_7^+) \leq 215.1 \pm 3.0$ kcal/mol. Fe^+, Co^+, and Ni^+, formed by electron impact on $Fe(CO)_5$, $Co(NO)(CO)_3$, and $Ni(CO)_4$, respectively, dehydrate alcohols and dehydrohalogenate alkyl halides by a mechanism completely different from the alkali metal ion reactions. Oxidative addition of M^+ to RX giving RMX^+ is postulated. In some cases MR^+ and MX^+ products are observed. Limits on several (M^+-X) bond strengths are deduced. It is deduced from observed reactions that the proton affinities of Fe and FeO are ≤203 and ≥227 kcal/mol, respectively. Reactions with the alcohols and alkyl halides of ions other than M^+ formed by electron impact on the carbonyls are also described. Reactions with the neutral metal carbonyls of a number of organic ions formed from the alkyl halides and alcohols are described.

The gas-phase chemistry of simple organic molecules with ions formed by electron impact on metal carbonyls has been the subject of several recent communications from our laboratory.[1-3] We have reported limits on metal to carbon bond strengths in simple transition-metal alkyls.[1] We have also reported direct evidence for metal insertion and β hydrogen shift mechanisms in the reactions of the atomic metal ions with alkyl halides and alcohols.[2] We provide here a more nearly complete description of the ion chemistry observed in gaseous mixtures of $Fe(CO)_5$, $Co(NO)(CO)_3$, and $Ni(CO)_4$ with simple alcohols and alkyl halides.

There have also been several reports on the gas-phase chemistry of alkyl halides with alkali metal ions.[1,4] We report here a mechanistic study of the alkali metal ion induced dehydrohalogenation of alkyl halides and the alkali metal ion induced dehydration of alcohols. An unusual generalization emerges from this study relating reaction rates to thermodynamic properties of the reactants.

The reactions of the transition-metal ions and the alkali-metal ions show superficial similarities. A closer examination reveals marked differences in the mechanism and energetics of the reactions of the two classes of metal ions. We attempt

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Table I. Reactions of Alkali Metal Ions

reaction		obsd[a]	ΔH,[b] kcal/mol	ΔH_{exch},[c] kcal/mol
$Na^+ + i\text{-}C_4H_9OH$	$\rightarrow Na(C_4H_8)^+ + H_2O$	no	<−12 (−14)	71.5
	$\rightarrow Na(OH_2)^+ + C_4H_8$	no	−18	
$Na^+ + n\text{-}C_4H_9OH$	$\rightarrow Na(C_4H_8)^+ + H_2O$	no	(−12)	71.3
	$\rightarrow Na(OH_2)^+ + C_4H_8$	no	−16	
$Na^+ + i\text{-}C_3H_7OH$	$\rightarrow Na(C_3H_6)^+ + H_2O$	no	(−4)	61.9
	$\rightarrow Na(OH_2)^+ + C_3H_6$	no	−12	
$Na^+ + C_2H_5Cl$	$\rightarrow Na(C_2H_4)^+ + HCl$	no	(+4)	58.1
	$\rightarrow Na(ClH)^+ + C_2H_4$	no	(<4)	
$Na^+ + n\text{-}C_3H_7Cl$	$\rightarrow Na(C_3H_6)^+ + HCl$	no	(+1)	50.4
	$\rightarrow Na(ClH)^+ + C_3H_6$	no	(<1)	
$Na^+ + t\text{-}C_4H_9OH$	$\rightarrow Na(C_4H_8)^+ + H_2O$	no	(−4)	50.1
	$\rightarrow Na(OH_2)^+ + C_4H_8$	no	−8	
$Na^+ + i\text{-}C_4H_9Cl$	$\rightarrow Na(C_4H_8)^+ + HCl$	no	(−8)	48.4
	$\rightarrow Na(ClH)^+ + C_4H_8$	no	(<−1)	
$Na^+ + n\text{-}C_4H_9Cl$	$\rightarrow Na(C_4H_8)^+ + HCl$	no	(−7)	47.5
	$\rightarrow Na(ClH)^+ + C_4H_8$	no	(<0)	
$Li^+ + i\text{-}C_4H_9OH$	$\rightarrow Li(C_4H_8)^+ + H_2O$	no	−22	44.4
	$\rightarrow Li(OH_2)^+ + C_4H_8$	no	−28	
$Li^+ + n\text{-}C_4H_9OH$	$\rightarrow Li(C_4H_8)^+ + H_2O$	no	(−20)	44.2
	$\rightarrow Li(OH_2)^+ + C_4H_8$	no	−26	
$Na^+ + i\text{-}C_3H_7Cl$	$\rightarrow Na(C_3H_6)^+ + HCl$	no	(+2)	38.3
	$\rightarrow Na(ClH)^+ + C_3H_6$	no	(<+5)	
$Li^+ + C_2H_5Cl$	$\rightarrow Li(C_2H_4)^+ + HCl$	no	(−1)	36.7
	$\rightarrow Li(ClH)^+ + C_2H_4$	no	<−1	
$Li^+ + i\text{-}C_3H_7OH$	$\rightarrow Li(C_3H_6)^+ + H_2O$	no	−11	34.8
	$\rightarrow Li(OH_2)^+ + C_3H_6$	no	−22	
$Li^+ + n\text{-}C_3H_7Cl$	$\rightarrow Li(C_3H_6)^+ + HCl$	yes	−9	29.0
	$\rightarrow Li(ClH)^+ + C_3H_6$	no	<−4	
$Li^+ + t\text{-}C_4H_9OH$	$\rightarrow Li(C_4H_8)^+ + H_2O$	yes (13%)	−12	24.5
	$\rightarrow Li(OH_2)^+ + C_4H_8$	yes (87%)	−18	
$Na^+ + t\text{-}C_4H_9Cl$	$\rightarrow Na(C_4H_8)^+ + HCl$	yes	<0 (−2)	23.1
	$\rightarrow Na(ClH)^+ + C_4H_8$	no	(<5)	
$Na^+ + CH_3COCl$	$\rightarrow Na(CH_2CO)^+ + HCl$	no	>0[d]	21.5
	$\rightarrow Na(ClH)^+ + CH_2CO$	no	(>9)	
$Na^+ + t\text{-}C_5H_{11}Cl$	$\rightarrow Na(C_5H_{10})^+ + HCl$	yes	(−5)	20.1
	$\rightarrow Na(ClH)^+ + C_5H_{10}$	no	(<3)	
$Li^+ + i\text{-}C_3H_7Cl$	$\rightarrow Li(C_3H_6)^+ + HCl$	yes (85%)	−5	16.9
	$\rightarrow Li(ClH)^+ + C_3H_6$	yes (15%)	<0	
$Li^+ + t\text{-}C_4H_9Cl$	$\rightarrow Li(C_4H_8)^+ + HCl$	yes	−10	1.7
	$\rightarrow Li(ClH)^+ + C_4H_8$	no	<0	
$Li^+ + t\text{-}C_5H_{11}Cl$	$\rightarrow Li(C_5H_{10})^+ + HCl$	yes	−12	−1.3
	$\rightarrow Li(ClH)^+ + C_5H_{10}$	no	<−2	
$Li^+ + CH_3COCl$	$\rightarrow Li(CH_2CO)^+ + HCl$	yes	<0[e]	−1.9
	$\rightarrow Li(ClH)^+ + CH_2CO$	no	<4	
$Li^+ + C_6H_5CH_2Cl$	$\rightarrow C_7H_7^+ + LiCl$	yes		<0[e]
Li^+ + 1-adamantyl chloride $\rightarrow$	$C_{10}H_{15}^+ + LiCl$	yes		<0[e]
Li^+ + 1-adamantyl bromide $\rightarrow$	$C_{10}H_{15}^+ + LiBr$	no		>0[e]

[a] We estimate rate constants for the observed processes to be in the range 2–10 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. The upper limit on rate constants for processes not observed is approximately 0.2 × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. [b] Based on heats of formation of neutrals in ref 12 and experimental values of $D(Li^+\text{-}OH_2)$ 34 kcal/mol and $D(Na^+\text{-}OH_2) = 24$ kcal/mol from S. K. Searles and P. Kebarle, *Can. J. Chem.*, **47**, 2619 (1969), and $D(Li^+\text{-}C_3H_6) = 23$ kcal/mol and $D(Li^+\text{-}i\text{-}C_4H_8) = 28$ kcal/mol from ref 13. The numbers in parentheses are estimates based on the following assumptions: $D(Li^+\text{-}i\text{-}C_4H_8) = D(Li^+\text{-}1\text{-}C_4H_8)$; $D(Li^+\text{-}i\text{-}C_4H_8) - D(Li^+\text{-}C_3H_6) = D(Li^+\text{-}C_3H_6) - D(Li^+\text{-}C_2H_4)$ and $D(Na^+\text{-}B) = D(Li^+\text{-}B) \times D(Na^+\text{-}H_2O)/D(Li^+\text{-}H_2O)$. Values of $D(Na^+\text{-}B)$ obtained from this last assumption are suggested to be accurate within ±2 kcal/mol by comparisons of $D(Li^+\text{-}B)$ (values referred to above) with $D(K^+\text{-}B)$ (from W. R. Davidson and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 6133 (1976)) for a series of bases, B. Except as noted the limits are based on observation of reactions 7 and 11. Limits in parentheses rely on unbracketed limits and the above assumptions. It is also assumed that $D(M^+\text{-}i\text{-}C_4H_8) = D(M^+\text{-}C_5H_{10})$. [c] $\Delta H_{exch} = D(R^+\text{-}X^-) - D(M^+\text{-}X^-)$. Except as noted based on gas-phase heats of formation $\Delta H_f{}^\circ{}_{298}(LiCl) = -46.8 \pm 3.0$, $\Delta H_f{}^\circ{}_{298}(NaCl) = -43.4 \pm 0.5$, $\Delta H_f{}^\circ{}_{298}(NaOH) = -50 \pm 5$, and $\Delta H_f{}^\circ{}_{298}(LiOH) = -59 \pm 4$ kcal/mol from D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **37**, (1971), and on heats of formation in ref 12. [d] Surmise discussed in text. [e] Deduced from present results. See text.

here to formulate generalizations governing the two kinds of reactivity and comment on the relationships between them. We also consider the relationship of this chemistry to chemistry observed in other systems. These systems include condensed phase homogeneous organometallic systems, dispersed heterogeneous systems (metal powders), and metal vapors.

In addition to the chemistry of metal-containing ions, we describe and discuss the chemistry of the neutral metal carbonyls with a variety of ions derived from alcohols and alkyl halides. Our observations lead us to a number of conclusions regarding heats of formation of organometallic and organic ions in the gas phase.

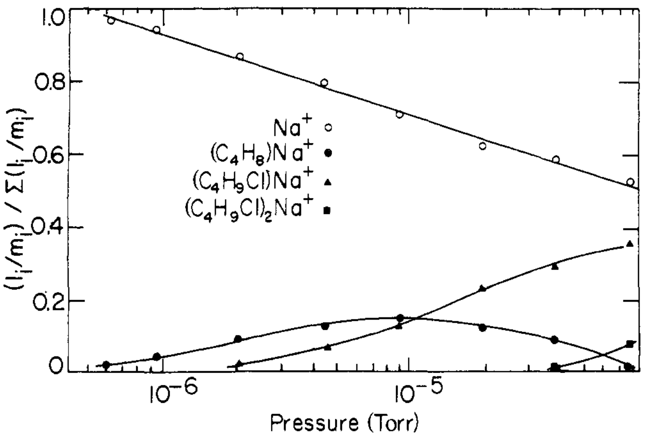


Figure 1. Variation of ion concentration with pressure in t-C_4H_9Cl reacting with the thermionically generated Na^+ ions. I_i/m_i is the ratio of the single resonance intensity of an ion to its mass and is approximately proportional to the relative abundance of the ion.[37]

Experimental Section

All experiments were performed on an ion cyclotron resonance spectrometer of conventional design built at Ford Scientific Research Laboratories and at the University of Delaware. The ICR cell is 1.1 × 2.5 × 11.5 cm. The source region is 1 cm long and the resonance region is 10.5 cm long. Experiments were carried out in the normal drift mode using trapping voltage modulation coupled with phase-sensitive detection.[5] The marginal oscillator detector was of solid-state design.[6] Double resonance experiments were performed using a Wavetek Model 144 HF sweep generator as the secondary oscillator. The signal amplitude for irradiation was between 25 and 500 mV cm^{-1}.

The ICR instrument has two sample inlet systems controlled by two Model 951-5700 Varian leak valves. The cell region is pumped by both a 4-in. diffusion pump and a 20 L/s ion pump. Approximate pressures may be obtained using ion pump current readings. Above 2×10^{-5} Torr pressure may be determined accurately using an MKS Baratron capacitance manometer.

Alkali metal ions were generated by thermionic emission. A platinum filament bearing a bead of β Eucryptite[7] was inserted into the cell in the source region. The bead emits when heated by passing current through the filament. Some K^+ and Na^+ emission was observed in addition to Li^+ emission which provided an opportunity to observe processes involving all three ions.

Experiments on the transition-metal systems were performed as follows. The metal carbonyl was first admitted to the system to a pressure of approximately 5×10^{-6} Torr. An equal amount of the organic substrate was then added. A mass spectrum was taken at this pressure, and at a series of higher pressures as the pumps were throttled to increase the total pressure of this 1:1 mixture. Spectra were taken up to m/z 330 in all mixtures. Double-resonance experiments were performed on all ions which increased in concentration as the pressure was increased.[5] All stoichiometrically possible precursors of each such ion were checked. Double-resonance experiments were also performed on ions formed by electron impact which might also be the product of a reaction. Where more than one precursor gave the same product the branching ratios were determined by ejecting each precursor with the double-resonance oscillator and observing the concomitant decrease in the product ion signal. Ions whose stoichiometries were ambiguous were characterized as completely as possible using deuterated reagents.

CD_3I, C_2D_5I, CD_3CH_2I, C_2D_5OD, CD_3OD, and i-C_4D_9OH were obtained from Stohler Isotopes and had a stated isotopic purity of 99 atom %. i-C_4D_9Cl was prepared by refluxing i-C_4D_9OH with dilute HCl. Hydrogen iodide was prepared by the dehydration of hydriodic acid with phosphorus pentoxide. The hydrogen iodide was collected in a trap at −78 °C.

Results

Alkali Metal Ion Reactions. Observed reactions of alkali metal ions are summarized in Table I. The products of these primary reactions in many instances react further with the substrate alkyl halide or alcohol. The reactions of Li^+ with t-C_4H_9Cl are typical. The reaction sequence is shown in eq 1-6. A similar but simpler sequence occurs in the reactions of Na^+ with t-C_4H_9Cl (eq 7-9). This sequence of reactions is illustrated in Figure 1. The initial product $Na(C_4H_8)^+$ disappears in favor of $Na(C_4H_9Cl)^+$ as the pressure is increased. At the highest pressures $Na(C_4H_9Cl)_2{}^+$, evidently the product of a termolecular association process, appears.

$$\mathrm{Li^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)^+ + HCl} \tag{1}$$

$$\mathrm{Li(C_4H_8)^+ + t\text{-}C_4H_9Cl} \rightarrow \begin{cases} \mathrm{Li(C_4H_9Cl)^+ + C_4H_8} & (2) \\ \mathrm{Li(C_4H_8)_2{}^+ + HCl} & (3) \end{cases}$$

$$\mathrm{Li(C_4H_9Cl)^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)(C_4H_9Cl)^+ + HCl} \tag{4}$$

$$\mathrm{Li(C_4H_8)_2{}^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)(C_4H_9Cl)^+ + C_4H_8} \tag{5}$$

$$\mathrm{Li(C_4H_8)(C_4H_9Cl)^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_9Cl)_2{}^+ + C_4H_8} \tag{6}$$

$$\mathrm{Na^+ + t\text{-}C_4H_9Cl \rightarrow Na(C_4H_8)^+ + HCl} \tag{7}$$

$$\mathrm{Na(C_4H_8)^+ + t\text{-}C_4H_9Cl \rightarrow Na(C_4H_9Cl)^+ + C_4H_8} \tag{8}$$

$$\mathrm{Na(C_4H_9Cl)^+ + t\text{-}C_4H_9Cl \xrightarrow[t\text{-}C_4H_9Cl]{} Na(C_4H_9Cl)_2{}^+} \tag{9}$$

Other alkyl chlorides follow a similar pattern, the reactivity generally increasing from primary to secondary to tertiary alkyl chlorides. None of the ethyl or methyl halides were observed to react at all, except to cluster with the metal ions at very high pressures. The i-C_3H_7Cl and n-C_4H_9Cl both react with Li^+, but not with Na^+. The reaction scheme in i-C_3H_7Cl, which has been previously reported,[4] is shown in eq 10-13. The reaction scheme in n-C_4H_9Cl is shown in eq 14 and 15. The reactions between Li^+ and *tert*-amyl chloride parallel reactions 1-6 between Li^+ and *tert*-butyl chloride. Similarly the reactions between Na^+ and *tert*-amyl chloride parallel reactions 7-9 between Na^+ and *tert*-butyl chloride.

$$\mathrm{Li^+ + i\text{-}C_3H_7Cl} \rightarrow \begin{cases} \mathrm{Li(C_3H_6)^+ + HCl} & (10) \\ \mathrm{Li(HCl)^+ + C_3H_6} & (11) \end{cases}$$

$$\mathrm{Li(HCl)^+ + i\text{-}C_3H_7Cl \rightarrow Li(C_3H_7Cl)^+ + HCl} \tag{12}$$

$$\mathrm{Li(C_3H_6)^+ + i\text{-}C_3H_7Cl \rightarrow Li(C_3H_7Cl)^+ + C_3H_6} \tag{13}$$

$$\mathrm{Li^+ + n\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)^+ + HCl} \tag{14}$$

$$\mathrm{Li(C_4H_8)^+ + n\text{-}C_4H_9Cl \rightarrow Li(C_4H_9Cl)^+ + C_4H_8} \tag{15}$$

In only two instances was halide abstraction observed. Li^+ reacts with benzyl chloride and 1-adamantyl chloride to produce benzyl and adamantyl cations, respectively.

Interest in the mechanism of reaction 4 led to the study of reactions of Li^+ in a mixture of *tert*-butyl chloride with *tert*-butyl-d_9 chloride. All of the expected ionic products are observed. Of particular interest are the products containing both deuterium atoms and hydrogen atoms. Double resonance identifies the precursors of two such ions to be those indicated in eq 16 and 17. The significance of these results is as follows. In the complex of the type $C_4H_9{}^{35}ClLi^{37}ClC_4D_9{}^+$, either loss of $H^{35}Cl$ or $D^{37}Cl$ may occur, but not $H^{37}Cl$ or $D^{35}Cl$. Note particularly that m/z 110 does not give m/z 164 and that m/z 101 does not give m/z 163.

$$\left.\begin{array}{l} \mathrm{LiC_4H_9{}^{35}Cl^+ (m/z\ 99) + t\text{-}C_4D_9Cl} \\ \mathrm{LiC_4D_9{}^{35}Cl^+ (m/z\ 108) + t\text{-}C_4H_9Cl} \\ \mathrm{LiC_4D_9{}^{37}Cl^+ (m/z\ 110) + t\text{-}C_4H_9Cl} \end{array}\right] \rightarrow \begin{array}{l} \mathrm{Li(C_4D_8)(C_4H_9{}^{35}Cl) + DCl} \\ \quad \mathrm{(m/z\ 163)} \end{array} \tag{16}$$

$$\left.\begin{array}{l} \mathrm{LiC_4H_9{}^{35}Cl^+ (m/z\ 99) + t\text{-}C_4D_9Cl} \\ \mathrm{LiC_4H_9{}^{37}Cl^+ (m/z\ 101) + t\text{-}C_4D_9Cl} \\ \mathrm{LiC_4D_9{}^{35}Cl^+ (m/z\ 108) + t\text{-}C_4H_9Cl} \end{array}\right] \rightarrow \begin{array}{l} \mathrm{Li(C_4H_8)(C_4D_9{}^{35}Cl) + HCl} \\ \quad \mathrm{(m/z\ 164)} \end{array} \tag{17}$$

Table II. Reactions of $Ni(CO)_4$ Forming Polynuclear Nickel Complexes

reactant ion[a]	product ions
Ni^+	$Ni_2(CO)_3^+$, $Ni_2(CO)_2^+$
$NiCO^+$	$Ni_2(CO)_4^+$, $Ni_2(CO)_3^+$, $Ni_2(CO)_2^+$
$Ni(CO)_2^+$	$Ni_2(CO)_5^+$, $Ni_2(CO)_4^+$, $Ni_2(CO)_3^+$, $Ni_2(CO)_2^+$
$Ni(CO)_3^+$	$Ni_2(CO)_6^+$, $Ni_2(CO)_5^+$, $Ni_2(CO)_4^+$, $Ni_2(CO)_3^+$, $Ni_2(CO)_2^+$
$Ni(CO)_4^+$	$Ni_2(CO)_7^+$, $Ni_2(CO)_6^+$, $Ni(CO)_3^+$

[a] Reactant neutral in all cases is $Ni(CO)_4$.

Analysis of the double-resonance responses arising from reaction 4 and its t-$C_5H_{11}Cl$ analogue provides supporting evidence regarding its mechanism. Since they may contain either ^{35}Cl or ^{37}Cl, both the reactant ion and the product ion of (4) will have two different masses. Each product ion may exhibit a double-resonance response to each of the two reactant ions. Examining the ratios of these responses reveals whether the chlorine atom eliminated from the ionic product originated with the ionic reactant or the neutral reactant. The observed ratios indicate the chlorine atom to be lost randomly from either the reactant ion or the reactant neutral. This suggests a transition state for the reaction which is symmetric with respect to the two chlorine atoms. This will enter our discussion again later.

Alcohols are less reactive than the alkyl halides. Ethanol and methanol are unreactive and isopropyl, isobutyl, and n-butyl alcohols cluster with Li^+ and Na^+ at higher pressures. Li^+ does react with t-C_4H_9OH according to eq 18–21. K^+ was not ob-

$$Li^+ + t\text{-}C_4H_9OH \rightarrow Li(H_2O)^+ + C_4H_8 \quad (18)$$

$$Li^+ + t\text{-}C_4H_9OH \rightarrow Li(C_4H_8)^+ + H_2O \quad (19)$$

$$Li(H_2O)^+ + t\text{-}C_4H_9OH \rightarrow Li(C_4H_9OH)^+ + H_2O \quad (20)$$

$$Li(C_4H_8)^+ + t\text{-}C_4H_9OH \rightarrow Li(C_4H_9OH)^+ + C_4H_8 \quad (21)$$

served to react with any of the alcohols or alkyl halides.

Transition Metal Carbonyl Reactions. Ions formed by electron impact on the metal carbonyls react with the neutral metal carbonyl to form ions containing two metal nuclei. The reaction between Ni^+ and $Ni(CO)_4$ is typical. Observations

$$Ni^+ + Ni(CO)_4 \rightarrow Ni_2(CO)_3^+ + CO$$

$$Ni^+ + Ni(CO)_4 \rightarrow Ni_2(CO)_2^+ + 2CO$$

of reactions of this general type are summarized in Table II. Similar reactions of $Fe(CO)_5$[8] and $Co(NO)(CO)_3$[9] have been described.

In addition to reactions forming polynuclear complexes, the following reactions are observed:

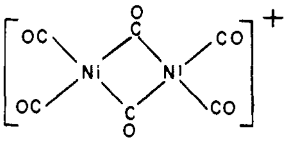
$$Ni^+ + Ni(CO)_4 \rightarrow Ni(CO)_4^+ + Ni$$

$$Ni^+ + Ni(CO)_4 \rightarrow Ni(CO)_3^+ + Ni(CO)$$

$$Ni(CO)^+ + Ni(CO)_4 \rightarrow Ni(CO)_3^+ + Ni(CO)_2$$

$$Ni(CO)_2^+ + Ni(CO)_4 \rightarrow Ni(CO)_3^+ + Ni(CO)_3$$

Double resonance on product ions containing various nickel isotopes indicates that in the Ni^+ and $Ni(CO)^+$ reactions the Ni in the product ion originates only with the reactant neutral. In the $Ni(CO)_2^+$ reaction, however, the Ni in the ionic product may originate with either reactant. This suggests that the reaction proceeds through a transition state symmetric with respect to the two metal atoms such as shown below.



Reactions in Mixtures of Transition-Metal Carbonyls with Alkyl Halides and Alcohols. For the purpose of presenting the results and for the purposes of discussion it is convenient to divide the primary reactant ions in these mixtures into three groups: (1) M^+, $M(CO)^+$, $Co(NO)^+$, and $Co(NO)(CO)^+$, (2) $M(CO)_n^+$ and $Co(NO)(CO)_n^+$ where $n \geq 2$, and (3) ions formed by electron impact on the alkyl halides and alcohols. The emphasis of the present report is on reactions of the first group of ions with neutral alkyl halides and alcohols, although we will consider briefly reactions of the other two categories of ions.

The reactions of M^+ and $M(CO)^+$ with alkyl halides CH_3I, CH_3Br, and C_2D_5I are summarized in Tables III and IV. Also summarized in Table IV are the reactions of CD_3CH_2I with Fe^+, Co^+, and Ni^+. The reactions of M^+, $M(CO)^+$, and $M(CO)_2^+$ with i-C_3H_7Cl are summarized in Table V. The reactions of M^+ and $M(CO)^+$ with CH_3OH and C_2H_5OH are summarized in Table VI and the reactions of those ions with i-C_3H_7OH are summarized in Table VII. The reactions of the second category of ions, $M(CO)_n^+$ ($n \geq 2$) and $Co(NO)(CO)_n^+$, are summarized in Table VIII. Nearly all of these reactions are of the type

$$M(CO)_n^+ + RX \rightarrow M(CO)_{n-1}(RX)^+ + CO$$

$$M(CO)_n^+ + RX \rightarrow M(CO)_{n-2}(RX)^+ + 2CO$$

Table VIII notes the number of carbonyls displaced in such reactions. There are several instances noted in Table VIII where products of the type $M(CO)_n(C_mH_{2m})^+$ or $M(CO)_nX^+$ are formed. The reactions with the neutral metal compounds of several ions formed by electron impact on the alkyl halides and alcohols are summarized in Table IX.

Table III. Reactions of M^+ and $M(CO)^+$ with CH_3I and CH_3Br

reaction		branching ratio,[a] % of total reaction		
		M = Fe	Co	Ni
$M^+ + CH_3I$	$\rightarrow MI^+ + CH_3$	50	73	100
	$\rightarrow MCH_3^+ + I$	50	27	
$M(CO)^+ + CH_3I$	$\rightarrow MI^+ + CH_3 + CO$	0	0	12
	$\rightarrow MCH_3I^+ + CO$	100	100	88
$MCH_3I^+ + CD_3I$	$\rightarrow MICD_3I^+ + CH_3$	100		
	$\rightarrow MICH_3I^+ + CD_3$	0		
$M^+ + CH_3Br$	$\rightarrow MBr^+ + CH_3$	100	100	100
	$\rightarrow MCH_3^+ + Br$			
$M(CO)^+ + CH_3Br$	$\rightarrow MCH_3Br^+ + CO$	100	100	100
$MCH_3Br^+ + CH_3Br$	$\rightarrow MBrCH_3Br^+ + CH_3$	100		

[a] A blank indicates that the product ion was not observed. A zero indicates that the product ion was observed but no double resonance was observed for the indicated reaction.

Table IV. Reactions of M^+ and $M(CO)^+$ with C_2D_5I

reaction		branching ratios,[a] % of total reaction M = Fe	Co	Ni
$M^+ + C_2D_5I$	→ $MI^+ + C_2D_5$	14	11	24
	→ $M(C_2D_4)^+ + DI$	86	78	32
	→ $MDI^+ + C_2D_4$		11	44
$M^+ + CD_3CH_2I$	→ $M(C_2H_2D_2)^+ + DI$	53	49	24
	→ $M(C_2HD_3)^+ + HI$	33	29	8
$M(CO)^+ + C_2D_5I$	→ $MI^+ + C_2D_5 + CO$	0	0	26
	→ $M(CO)(C_2D_4)^+ + DI$	25	38	10
	→ $M(C_2D_4)^+ + DI + CO$	0	27	26
	→ $MDI^+ + C_2D_4 + CO$		0	13
	→ $MC_2D_5I^+ + CO$	75	35	25
$Co(NO)^+ + C_2H_5I$	→ $Co(NO)(C_2D_4)^+ + DI$		100	
$MC_2D_5I^+ + C_2D_5I$	→ $MC_2D_4C_2D_5I^+ + DI$	100		100
$M(C_2D_4)^+ + C_2D_5I$	→ $MC_2D_5I^+ + C_2D_4$	10	41	31
	$M(C_2D_4)_2^+ + DI$	90	59	69

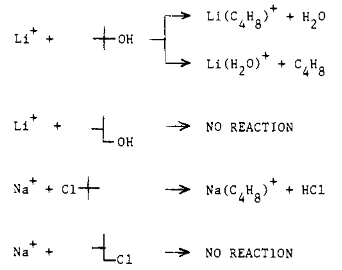
[a] A blank indicates that the product ion was not observed. A zero indicates that the product ion was observed but no double resonance was observed for the indicated reaction.

Table V. Reactions of M^+ and $M(CO)_n{}^+$ with $i\text{-}C_3H_7Cl$

reactions		branching ratios,[a] % of total reaction M = Fe	Co	Ni
$M^+ + C_3H_7Cl$	→ $C_3H_7{}^+ + MCl$	37	35	91
	→ $(C_3H_6)M^+ + HCl$	63	60	9
	→ $HClM^+ + C_3H_6$		5	
$M(CO)^+ + C_3H_7Cl$	→ $(C_3H_6)M(CO)^+ + HCl$	100	16	34
	→ $(C_3H_6)M^+ + CO + HCl$	0	67	66
	→ $HClM(CO)^+ + C_3H_6$		17	
$M(CO)_2{}^+ + C_3H_7Cl$	→ $(C_3H_6)M(CO)^+ + CO + HCl$	68	100	28
	→ $M(CO)C_3H_7Cl^+ + CO$	32		72
$Co(NO)(CO)^+ + C_3H_7Cl$	→ $(C_3H_6)Co(NO)^+ + CO + HCl$		53	
	→ $C_3H_7ClCo(NO)^+ + CO$		47	
$M(C_3H_6)^+ + C_3H_7Cl$	→ $M(C_3H_6)_2{}^+ + HCl$	100	100	
[b] $CoNOC_3H_7{}^{35}Cl^+ + C_3H_7{}^{37}Cl$	→ $CoNOC_3H_6C_3H_7{}^{37}Cl^+ + H^{35}Cl$		100	
	→ $CoNOC_3H_6C_3H_7{}^{35}Cl^+ + H^{37}Cl$		0	

[a] A blank indicates that the product ion was not observed. A zero indicates that the product ion was observed but no double resonance was observed for the indicated reaction. [b] The isotopic specificity of this reaction was discovered by examining the ratios of the double-resonance responses of the isotopic variants of the reactants.

Scheme I

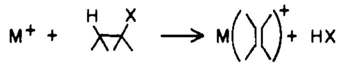


Reactions of M^+ with HI. Fe^+, Co^+, and Ni^+ all react with HI to form MI^+. No MH^+ was observed.

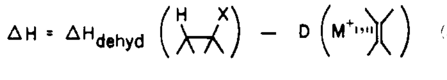
Discussion

Alkali Metal Ions. The first feature of the results meriting further discussion is the selective reactivity of the alkali metal ions illustrated by the observations in Scheme I. Dehydration of isobutyl alcohol is 10 kcal/mol more exothermic than dehydration of the tertiary alcohol (see Table I), yet only the tertiary alcohol reacts. Similarly, dehydrochlorination of isobutyl chloride is 6 kcal/mol more exothermic than dehydrochlorination of the tertiary chloride, yet only the tertiary chloride reacts.

The results in Table I suggest that in general the reactivity of alcohols and alkyl halides with Li^+ and Na^+ increases with extent of substitution from primary to secondary to tertiary. This is in spite of the fact that the energy required to remove HX from these species also increases with extent of substitution. The overall enthalpy change for the metal ion reactions, of course, depends not only on the dehydration or dehydrohalogenation enthalpy ($\Delta H_{\mathrm{dehyd}}$) of the neutral, but also on $D(M^+\text{- - -}C_2H_{2n})$. Specifically the enthalpy change for the process of eq 22 is given by eq 23. Table I lists ΔH determined



(22)



(23)

from $\Delta H_{\mathrm{dehyd}}$ and known or estimated values of $D(M^+\text{–}C_nH_{2n})$. Assumptions upon which these estimates are based are noted in the table. Even if there is considerable error in the

Table VI. Reactions of M^+ and $M(CO)^+$ with Ethanol and Methanol

reaction		branching ratios,[a] % of total reaction		
		M = Fe	Co	Ni
$M^+ + CH_3OH$	$\rightarrow MOH^+ + CH_3$	100		
$M(CO)^+ + CH_3OH$	$\rightarrow MCH_3OH^+ + CO$	100	100	100
$FeCD_3OH^+ + CH_3OH$	$\rightarrow FeOHCH_3OH^+ + CD_3$	100		
[b] $FeOHCH_3OH^+ + CH_3OH$	$\rightarrow FeCH_3OHCH_3O^+ + H_2O$	100		
$M^+ + C_2H_5OH$	$\rightarrow MC_2H_4^+ + H_2O$	100	87	79
	$\rightarrow MH_2O^+ + C_2H_4$		13	16
	$\rightarrow MC_2H_4O^+ + H_2$			5
$M(CO)^+ + C_2H_5OH$	$\rightarrow MC_2H_5OH^+ + CO$	100	100	46
	$\rightarrow MC_2H_4^+ + H_2O + CO$	0	0	36
	$\rightarrow MCOH_2O^+ + C_2H_4$			8
	$\rightarrow MH_2O^+ + C_2H_4 + CO$		0	7
	$\rightarrow MC_2H_4O^+ + H_2 + CO$			3
$M(NO)^+ + C_2H_5OH$	$\rightarrow M(NO)H_2O^+ + C_2H_4$		100	
$CoC_2D_4^+ + C_2D_5OD$	$\rightarrow CoC_2D_5OD^+ + C_2D_4$		100	
$MC_2H_5OH^+ + C_2H_5OH$	$\rightarrow MOHC_2H_5OH^+ + C_2H_5$	100	0	
	$\rightarrow M(C_2H_4)(C_2H_5OH) + H_2O$	0	100	
$FeOHC_2H_5OH^+ + C_2H_5OH$	$\rightarrow Fe\,C_2H_5O\,(C_2H_5OH)^+ + H_2O$	obsd		
	$\rightarrow Fe(C_2H_5OH)_2 + OH$	obsd		

[a] A blank indicates that the product ion was not observed. A zero indicates that the product ion was observed but no double resonance was observed for the indicated reaction. [b] See ref 2 for a discussion of this reaction.

Table VII. Reactions of M^+ and $M(CO)^+$ with 2-Propanol

reaction		branching ratios,[a] % of total reaction		
		M = Fe	Co	Ni
$M^+ + i\text{-}C_3H_7OH$	$\rightarrow C_3H_7^+ + MOH$	9	12	0
	$\rightarrow M(C_3H_6)^+ + H_2O$	49	48	33
	$\rightarrow MH_2O^+ + C_3H_6$	42	40	67
$M(CO)^+ + i\text{-}C_3H_7OH$	$\rightarrow M(CO)C_3H_6^+ + H_2O$		21	
	$\rightarrow M(C_3H_6)^+ + H_2O + CO$	0	21	30
	$\rightarrow MC_3H_7OH^+ + CO$	100	58	33
	$\rightarrow MH_2O^+ + C_3H_6 + CO$	0	0	37
$Co(NO)^+ + i\text{-}C_3H_7OH$	$\rightarrow Co(NO)H_2O^+ + C_3H_6$		84	
	$\rightarrow Co(NO)(C_3H_6)^+ + H_2O$		16	
$MH_2O^+ + C_3H_7OH$	$\rightarrow MC_3H_7OH^+ + H_2O$	0	100	100
$MC_3H_6^+ + C_3H_7OH$	$\rightarrow MC_3H_7OH^+ + C_3H_6$	0	100	100
$MC_3H_7OH^+ + C_3H_7OH$	$\rightarrow M(C_3H_6)C_3H_7OH^+ + H_2O$	100	100	

[a] A blank indicates that the product ion was not observed. A zero indicates that the product ion was observed but no double resonance was observed for the indicated reaction.

Table VIII. Number of Carbonyls Displaced from Metal Carbonyl Ions by RX

ion	RX						
	CH_3Br	CH_3I	C_2H_5I	C_3H_7Cl	CH_3OH	C_2H_5OH	$i\text{-}C_3H_7OH$
$Fe(CO)_5^+$	1	1	1, 2	g	1, 2	1, 2	1
$Fe(CO)_4^+$	1	1	1, 2	1, 2	1, 2	1, 2	1, 2
$Fe(CO)_3^+$	1	1[a]	1, 2	1	1, 2	1, 2	1, 2
$Fe(CO)_2^+$	1	1	1, 2	1[b]	1	1, 2	1
$Ni(CO)_4^+$	1, 2	g	1, 2	1, 2	1, 2	2	1
$Ni(CO)_3^+$	1, 2	1, 2[c]	1, 2	1, 2	1, 2	1, 2	1
$Ni(CO)_2^+$	1	1, 2	1, 2	1	1	1, 2	1
$Co(NO)(CO)_3^+$	1	1, 2	1, 2	1	1, 2	1, 2	2
$Co(NO)(CO)_2^+$	1	1, 2	2	1	1, 2	1, 2	1
$Co(NO)(CO)^+$	1	1	1	1[d]	1	1	1[e]
$Co(CO)_2^+$	1	1	1	f	1	1	1

[a] $Fe(CO)_3I^+$ product accounts for 82% of reaction. [b] $Fe(CO)C_3H_6^+$ product accounts for 68% of reaction. [c] $Ni(CO)_3I^+$ an additional product. [d] $Co(NO)C_3H_6^+$ product accounts for 53% of reaction. [e] $Co(NO)C_3H_6^+$ product accounts for 5% of reaction. [f] $Co(CO)C_3H_6^+$ product observed by double resonance. [g] No double resonance observed.

estimated values, it is evident that most of the unobserved reactions are as exothermic as the observed reactions.

A quantity more closely related to the reactivity of RX than overall exothermicity of reaction is $D(R^+\text{-}X^-)$. In fact, the important quantity seems to be $D(R^+\text{-}X^-) - D(M^+\text{-}X^-) = \Delta H_{\text{exch}}$. This quantity corresponds to the enthalpy change for the halide exchange process:

$$M^+ + RX \rightarrow R^+ + MX$$

Dehydration or dehydrohalogenation occurs in all cases (with

Table IX. Reactions of Metal Carbonyls with Organic Ions

reaction		branching ratios, % of total reaction[j] $ML(CO)_n$ = $Fe(CO)_5$[a]		
			$CoNO(CO)_3$[b]	$Ni(CO)_4$[c]
[d]$C_3H_7^+ + ML(CO)_n$	→ $ML(CO)_nH^+ + C_3H_6$	89	68	0
	→ $ML(CO)_{n-1}C_3H_7^+ + CO$	3	6	11
	→ $ML(CO)_{n-2}C_3H_7^+ + 2CO$		20	72
	→ $ML(CO)_{n-2}C_3H_5^+ + 2CO + H_2$	8	6	5
	→ $ML(CO)_{n-3}C_3H_5^+ + 3CO + H_2$			12
[e]$C_3H_5^+ + ML(CO)_n$	→ $ML(CO)_nH^+ + C_3H_4$	57		
	→ $ML(CO)_{n-2}C_3H_5^+ + 2CO$	16	27	30
	→ $ML(CO)_{n-3}C_3H_5^+ + 3CO$	26	73	70
[f]$CH_3O^+ + ML(CO)_n$	→ $ML(CO)_nH^+ + CH_2O$	54	58	23
	→ $ML(CO)_{n-1}H^+ + CH_2O + CO$	30	20	43
	→ $ML(CO)_{n-2}CH_3O^+ + 2CO$	13	22	21
	→ $ML(CO)_{n-3}CH_3O^+ + 3CO$	3		13
[g]$C_2H_5^+ + ML(CO)_n$	→ $ML(CO)_nH^+ + C_2H_4$	86	50	25
	→ $ML(CO)_{n-1}H^+ + C_2H_4 + CO$		6	4
	→ $ML(CO)_{n-1}C_2H_5^+ + CO$		9	
	→ $ML(CO)_{n-2}C_2H_5^+ + 2CO$	8	28	49
	→ $ML(CO)_{n-3}C_2H_5^+ + 3CO$	6	7	22
[h]$C_2H_3^+ + ML(CO)_n$	→ $ML(CO)_nH^+ + C_2H_2$	68	obsd	0
	→ $ML(CO)_{n-1}H^+ + C_2H_2 + CO$	32	obsd	100
	→ $ML(CO)_{n-2}C_2H_3^+ + 2CO$		obsd	
	→ $ML(CO)_{n-3}C_2H_3^+ + 3CO$		obsd	
[i]$CH_3OH_2^+ + ML(CO)_n$	→ $ML(CO)_nH^+ + CH_3OH$	obsd	obsd	obsd
[i]$C_2H_5OH_2 + ML(CO)_n$	→ $ML(CO)_nH^+ + C_2H_5OH$	obsd	obsd	obsd

[a] "ML" = Fe. [b] "ML" = CoNO. [c] "ML" = Ni. [d] $C_3H_7^+$ formed by electron impact on *i*-C_3H_7Cl. [e] $C_3H_5^+$ formed by electron impact on *i*-C_3H_7Cl. [f] CH_3O^+ formed by electron impact on C_2H_5OH. Results confirmed by examining reactions of CD_3O^+ formed by electron impact on C_2D_5OD. [g] $C_2H_5^+$ formed by electron impact on C_2H_5I. Results confirmed by examining reactions of $C_2D_5^+$ formed by electron impact on C_2D_5I. [h] $C_2H_3^+$ formed by electron impact on C_2H_5I. Results confirmed by examining reactions of $C_2D_3^+$ formed by electron impact on C_2D_5I. [i] Protonated alcohols formed by a variety of reactions of the alcohols with their electron impact fragments. [j] A blank indicates the product ion was not observed. A zero indicates the product ion was observed, but no double resonance was observed for the indicated reaction.

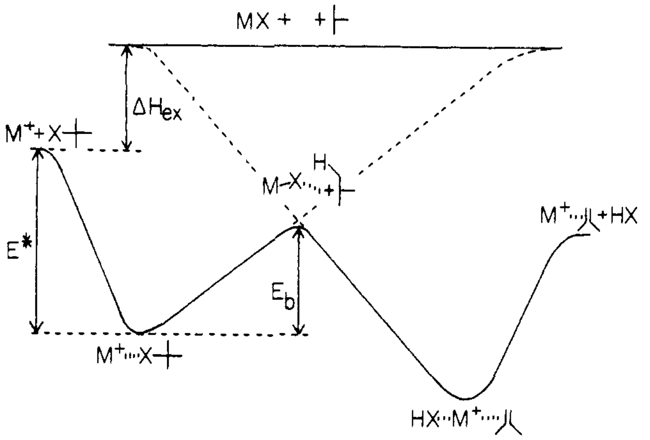
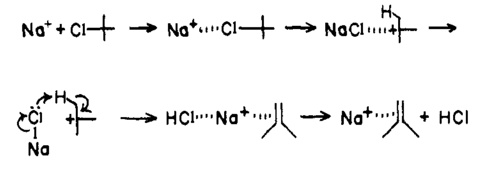


Figure 2. Schematic representation of the potential surface for the reaction of an alkali-metal ion with an alkyl halide.

one exception) for which $\Delta H_{\text{exch}} \leq 29.0$ kcal/mol and does not occur in all cases for which $\Delta H_{\text{exch}} \geq 34.8$ kcal/mol. The one exception is the case of Na^+ and CH_3COCl, for which ΔH_{exch} is 21.5 kcal/mol and for which no reaction is observed. It may be that the dehydrohalogenation reaction is endothermic in this case.[10] Also consistent with this pattern is the unreactivity of K^+. The lowest value of ΔH_{exch} for K^+ with any of the compounds examined is that with *t*-$C_5H_{11}Cl$, 33.5 kcal/mol.[11,12]

This connection between reactivity and ΔH_{exch} suggests a mechanism which involves transfer of the chloride to the metal cation and generation of charge at the carbon as suggested in Scheme II. After abstracting the chloride, the M^+ must interpose itself between the chloride and the incipient double bond while the chloride moves to facilitate forming a bond to the hydrogen atom. The energy necessary to move the chloride away from the charged carbon center is the source of the energetic barrier to reaction. This is best elucidated by means of a schematic representation of the potential energy surface for the proposed mechanism such as Figure 2. The important feature of this diagram is the presence of a barrier of height E_b. This barrier is a necessary consequence of the fact that the mechanism involves chloride abstraction and generation of charge at the carbon. More specifically, the barrier might be considered the result of the intersection of two potential surfaces. One of the intersecting surfaces is that for the formation of MX and *t*-$C_4H_9^+$ from the *t*-C_4H_9Cl-M^+ complex by transfer of a chloride and separation of the products. The other surface is for formation of the same products from the HX-Na^+-*i*-C_4H_8 complex by a proton transfer from the HX to the olefin and separation of the products. The intersection point

Scheme II



represents a partially separated M^+-X^--t-$C_4H_9^+$ complex which is common to both surfaces and is the transition state for conversion of t-C_4H_9X-M^+ into HX-M^+-i-C_4H_8. The diagram suggests that E_b increases as ΔH_{exch} increases. For reaction to occur E^*, the internal energy of the t-C_4H_9X-M^+ complex must be greater than E_b. If the complex is formed in a bimolecular collision between M^+ and t-C_4H_9X, then E^* will be simply $D(t\text{-}C_4H_9X\text{-}M^+)$ as suggested in Figure 2. Measured values of $D(RCl\text{-}Li^+)$ range from 25 (CH_3Cl) to 30 kcal/mol (i-C_3H_7Cl)[13] and decrease somewhat as ΔH_{exch} increases. Hence, as ΔH_{exch} increases, at some point E_b becomes greater than E^* and no reaction occurs. This rationalizes our experimental observation that systems with large ΔH_{exch} are unreactive.

It is of interest to consider the possibility of a quantitative relationship between E_b and the other energetic quantities in Figure 2. The simplest assumption is that E_b increases linearly with the sum of $D(RX\text{-}M^+)$ and ΔH_{exch}:

$$E_b = \alpha(D(RX\text{-}M^+) + \Delta H_{exch}) \tag{24}$$

This assumption is essentially the same as that commonly used to rationalize the linear free energy relationships observed in the kinetics of many common reactions.[14] The condition for reaction to occur then becomes

$$E^* > \alpha(D(RX\text{-}M^+) + \Delta H_{exch})$$

In the case of a bimolecular reaction between M^+ and RX where $E^* = D(RX\text{-}M^+)$ the condition for reaction to occur becomes $(1 - \alpha)D(RX\text{-}M^+) > \alpha\Delta H_{exch}$. Our observations suggest that for reactions of Li^+ and Na^+ with alkyl chlorides to occur ΔH_{exch} must be less than ~30 kcal/mol. The available data indicates that $D(RX\text{-}M^+)$ and hence E^* in these cases is 20-40 kcal/mol. The data are thus consistent with eq 24 if $\alpha \simeq 0.4$-0.5 This same value of α seems to apply both to alcohols and alkyl halides. A testable prediction of this relation is that Li^+ should dehydrate i-C_3H_7OH with an activation energy of less than 5 kcal/mol. Attempts to produce product from the $Li^+ + i\text{-}C_3H_7OH$ reaction by using the double-resonance oscillator to increase the translational energy of Li^+ were unsuccessful, however.

A further consequence of the proposed model has to do with the structure of species of the type RX-M^+. If such species are formed with relatively little internal energy (e.g., by a displacement reaction between C_nH_{2n}-M^+ and RX), then the barrier will prevent rearrangement of the complex into HX-M^+-C_nH_{2n}. That is, the RX-M^+ configuration of the complex is at least a local minimum in the potential surface and stable. An experimentally observed consequence of this fact is the isotopic composition of the products of the reaction (eq 25). The manner in which the isotopic distribution of

$$(t\text{-}C_4D_9{}^{35}Cl)Li^+ + t\text{-}C_4H_9{}^{37}Cl \begin{cases} \xrightarrow{50\%} (C_4D_9{}^{35}Cl)Li(C_4H_8)^+ + H^{37}Cl \\ \xrightarrow{50\%} (C_4H_9{}^{37}Cl)Li(C_4D_8)^+ + D^{35}Cl \end{cases} \tag{25}$$

products was determined is described in the Results section (see account following reactions 16 and 17). The transition state in the reaction must be symmetric with respect to the Cl atoms and the butyl groups. This suggests that the reactant complex has the indicated structure, $(t\text{-}C_4D_9{}^{35}Cl)Li^+$.

Another observation consistent with the proposed model is that dehydrohalogenation is the predominant reaction mode even at relatively high collision energies. This is indicated by the data in Table X.[15] The reaction pathway for dehydrohalogenation and that for halogen exchange are the same until MX and R^+ begin to separate. It might be expected that from this point on even energetic collisions would follow the low-energy dehydrohalogenation exit channel if the complex lives long enough for proton transfer from R^+ to MX to occur. The lifetime of the complex is probably much enhanced by the electrostatic attraction between R^+ and MCl (μ(LiCl) = 7.21 D) even at high collision energies.

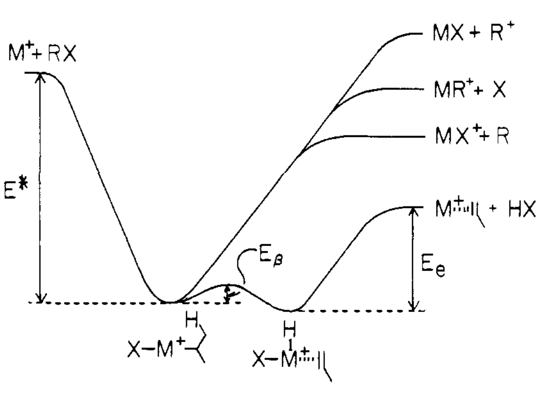


Figure 3. Schematic representation of the potential surface for the reaction of a transition-metal ion with an alkyl halide.

Table X. Variation of Product Distribution for t-C_4H_9Cl Reaction with Li^+ Energy

emitter bias,[a] V	$[C_4H_8Li^+]/[C_4H_9^+]$[b]
12	8.3
20	5.2
40	1.7

[a] The positive bias (relative to source potential) on a filament bearing a β-eucryptite (Li^+ emitter) bead inside the source of a Du Pont 110 mass spectrometer. The bead was 1 cm from the exit slit on the axis of the ion optics. The repeller was at source potential. [b] The ratio of the m/z 63 peak height to the m/z 57 peak height with a pressure of ~2 × 10^{-4} Torr of t-C_4H_9Cl in the source.

While not all exothermic reactions are observed, it may be assumed that all observed reactions are exothermic or thermoneutral. This is because in our system reactions will be observed only if their rate constants are within one or two orders of magnitude of the reactant collision frequencies. Limits on several ionic heats of formation may be deduced from reactions noted in Table 1. Of particular interest are the limits on the heat of formation of the 1-adamantyl cation deduced from reactions of Li^+ with adamantyl halides. If it is assumed that the observed chloride transfer from 1-adamantyl chloride is exothermic and the unobserved bromide transfer from 1-adamantyl bromide is endothermic, we arrive at $\Delta H_f{}^\circ{}_{298}$(1-adamantyl cation) = 160.7 ± 3.0 kcal/mol,[16,17] which compares favorably with $\Delta H_f{}^\circ{}_{298}$(1-adamantyl cation) = 160 kcal/mol[17,18] deduced from the appearance potential of $C_{10}H_{15}^+$ from 1-adamantyl bromide (9.79 eV).[18] A limit $\Delta H_f{}^\circ{}_{298}(C_7H_7^+) \leq 215.1 \pm 3.0$ kcal/mol may be deduced from the observation of chloride transfer from benzyl chloride to Li^+ and is consistent with a critically evaluated value $\Delta H_f{}^\circ{}_{298}(C_7H_7^+) = 214$ kcal/mol in the literature.[12]

Transition Metal Atomic Ions. The reactions of the transition metal atomic ions M^+ with alkyl halides and alcohols can be best accounted for by a metal insertion mechanism. The potential surface for this mechanism is schematically represented in Figure 3. The essential feature of this diagram is the absence of a barrier similar to that in Figure 2. The evidence indicates that in most instances species with the RMX^+ stoichiometry also have that structure. This, in turn, suggests that in most instances the RX-M^+ configuration is not a local minimum and that there is little, if any, energy barrier to the metal insertion. The formation of both MCH_3^+ and MI^+ products in reactions of CH_3I supports a CH_3MI^+ intermediate. The best evidence that RMX^+ is the lowest energy structure for ions of that stoichiometry, however, comes from the reactions of low-energy RMX^+ species such as (see Table VI):

$$FeCO^+ + CH_3OH \rightarrow FeCH_3OH^+ + CO$$

$$FeCH_3OH^+ + CD_3OH \rightarrow FeOHCD_3OH^+ + CH_3$$

Only CH_3 is lost in the second step, no CD_3, suggesting an activated complex asymmetric with respect to the methyl groups. Methanol attack on a $CH_3OH\text{-}Fe^+$ species would surely lead to a complex symmetric with respect to the methyl groups. Hence we propose that $FeCH_3OH^+$ is actually CH_3FeOH^+. Similar conclusions can be derived from the reactions of $FeCH_3I^+$ with CD_3I (see Table III). Note also that C_2H_5 is displaced from $FeC_2H_5OH^+$ by C_2H_5OH and OH is displaced from the resulting $Fe(OH)(C_2H_5OH)^+$ ion by C_2H_5OH (Table VI).

We can set a limit on the depth of the well, E^*, in Figure 2 in some cases. As noted above, if the reaction

$$MCO^+ + RX \rightarrow RMX^+ + CO$$

is observed it must be exothermic or thermoneutral since reactions must go at nearly the collision rate to be observed. In order for this reaction to be exothermic the following must be true:

$$E^* = \Delta H_f(M^+) + \Delta H_f(RX) - \Delta H_f(RMX)^+ > D(M^+\text{-}CO).$$

$D(Fe^+\text{-}CO)$ and $D(Ni^+\text{-}CO)$ have been reliably measured to be 62 and 48 kcal/mol, respectively.[19] Hence E^* is greater than 58 kcal/mol for Fe^+ reacting with CH_3I, CH_3Br, C_2H_5I, CH_3OH, C_2H_5OH, and $i\text{-}C_3H_7OH$. E^* is similarly greater than 48 kcal/mol for Ni^+ reacting with the same compounds.

In the presence of a β hydrogen atom, metal insertion can lead to dehydrohalogenation in the way shown in Scheme III. We suggest in Figure 2 that there is no energy barrier between **1** and **2**. The data supporting this are the product distributions observed for reactions between the metal ions and CD_3CH_2I. HI and DI are eliminated in approximately the statistical 2:3 ratio (see Table IV). This suggests that interconversion between **1** and **2** is very rapid in the excited complex. Such rapid interconversion scrambles the H atoms and the D atoms so that loss of HI or DI occurs statistically. The success with which the hydrogen atom shift competes with hydrogen iodide loss in the excited complex eliminates the possibility of any significant energy barrier between **1** and **2**.

Further evidence that the metal insertion and β-H atom shift occur without intermediate energy barriers comes from reactions of MRX^+ species formed by low-energy processes. Consider, for example, the following series of reactions (see Table V):

$$Co(NO)(CO)^+ + i\text{-}C_3H_7Cl \rightarrow Co(NO)C_3H_7Cl^+ + CO$$

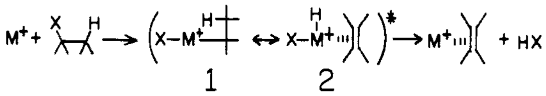
$$Co(NO)C_3H_7{}^{35}Cl + C_3H_7{}^{37}Cl \rightarrow C_3H_7{}^{37}ClCo(NO)(C_3H_6) + H^{35}Cl$$

Only the ^{37}Cl-containing ion is formed from the indicated isotopic variants of the reactants of the second reaction. This is in marked contrast to the stoichiometrically similar reaction of $t\text{-}C_4H_9ClLi^+$ with $t\text{-}C_4H_9Cl$. This suggests that the $Co(NO)C_3H_7Cl^+$ complex formed in the first step exists as $(Cl)Co(NO)(C_3H_7)^+$ or $(Cl)(H)Co(NO)(C_3H_6)^+$ rather than $Co(NO)(C_3H_7Cl)^+$. This complex has less energy, of course, than the same species formed by direct combination of $Co(NO)^+$ and $i\text{-}C_3H_7Cl$; nevertheless, the metal insertion and H atom shift appears to occur without hindrance. We note also that $Ni(CO)^+$ and $Co(CO)^+$ react according to (see Table IV)

$$M(CO)^+ + C_2D_5I \rightarrow M(C_2D_4)^+ + DI + CO$$

which again suggests that even relatively low energy complexes find the metal insertion hydrogen shift pathway quite accessible.

Scheme III



The isopropyl chloride (Table V) and isopropyl alcohol (Table VII) both react with the transition metal ions according to

$$M^+ + i\text{-}C_3H_7X \rightarrow C_3H_7^+ + MX.$$

This suggests the possibility of a mechanism similar to that of the alkali metal ion reactions: attack at X and heterolytic cleavage of the C-X bond. The products might just as readily result from a metal insertion process, however. The formation of $C_3H_7^+$ and MX rather than MX^+ and C_3H_7 may be dictated by the low ionization potential of $i\text{-}C_3H_7$ (7.36 eV).[20] If the $i\text{-}C_3H_7$ ionization potential is lower than that of MX, then $C_3H_7^+$ and MX are the lowest energy products of the decomposition of $C_3H_7MX^+$. The ionization potentials of the MX species are not known but the ionization potentials of the metal atoms Fe, Co, and Ni (7.87, 7.86, and 7.64 eV, respectively[12]) are slightly higher than that of $i\text{-}C_3H_7$. This is in contrast to the ionization potentials of methyl and ethyl radicals (9.84 and 8.38 eV, respectively[12]), which are considerably in excess of the metal ionization potentials. Methyl and ethyl cations, of course, are not observed to be products of any of the metal ion reactions.

In the reactions discussed so far, Ni^+ shows a notably different behavior than that of Fe^+ and Co^+. The metal tends to retain the halogen more often in Ni^+ reactions. In the reactions of M^+ with CH_3I, MI^+ is 50% of the product in the case of Fe^+, 73% in the case of Co^+, and 100% in the case of Ni^+ (Table III). In the reactions of M^+ with C_2D_5I, MI^+ and MDI^+ are 14% of product in the case of Fe^+, 22% in the case of Co^+, and 68% in the case of Ni^+ (Table IV). In the reactions of M^+ with $i\text{-}C_3H_7Cl$, MCl is 37% of the product in the case of Fe^+, 35% of the product in the case of Co^+, and 91% of the product in the case of Ni^+ (Table V). These data suggest that Ni^+ has a higher affinity for halogens and perhaps a lower affinity for alkyl groups than do Fe^+ and Co^+. This is perhaps related to the fact that the ionization potential of Ni (7.64 eV[12]) is slightly less than those of Co (7.86 eV[12]) and Fe (7.87 eV[12]). The difference is small, only 5 kcal/mol, but may be related to the difference in the bonding capabilities of the ions.

Limits on heats of formation deduced from the observed reactions of transition-metal ions are noted in Table XI. Very little thermodynamic information is available on species of the type MX and MX^+ and none on species of the type MR^+ where M is a transition metal. As we discuss elsewhere[1] the $Co^+\text{-}CH_3$ and $Fe^+\text{-}CH_3$ bonds are evidently somewhat stronger than the few transition metal carbon bonds for which bond strengths are in the literature. A value of $D(Ni\text{-}Cl) = 83 \pm 10$ kcal/mol has been reported[21] in good agreement with the limit we obtain. Values of $D(Ni\text{-}I) = 70$ kcal/mol[21] and $D(Mn\text{-}I) = 68$ kcal/mol[21] have also been reported and compare reasonably well for the limits we deduce for $D(M^+\text{-}I)$. Note that we deduce a lower limit on the proton affinity of FeO (PA(FeO) > 227 kcal/mol). Very little information is available on the basicity of metal oxides. The upper limit obtained on the proton affinity of atomic Fe (203 kcal/mol) is the proton affinity reported for $Fe(CO)_5$ (203 kcal/mol[8b]) and considerably less than our lower limit on PA(FeO).

Transition Metal Carbonyl Ions. As noted above and in Table VIII, metal-containing ions with two or more carbonyls generally undergo displacement reactions. In a few instances

Table XI. Thermochemical Inferences from Metal Ion Reactions

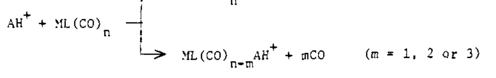
reaction		inferences,[a] kcal/mol
$M^+ + i\text{-}C_3H_7Cl \longrightarrow C_3H_7^+ + MCl$	M = Fe, Co, Ni	$D(M^+\text{-}Cl) > 168$,[b] $D(Fe\text{-}Cl) > 71$,[b] $D(Co\text{-}Cl) > 71$,[b] $D(Ni\text{-}Cl) > 76$[b]
$M^+ + i\text{-}C_3H_7OH \longrightarrow C_3H_7^+ + MOH$	M = Fe, Co	$D(M^+\text{-}OH^-) > 220$,[b] $D(Fe\text{-}OH) > 123$,[b] $D(Co\text{-}OH) > 123$,[b]
$M^+ + i\text{-}C_3H_7OH \not\longrightarrow C_3H_7^+ + NiOH$		$D(Ni^+\text{-}OH^-) < 220$,[b] $D(Ni\text{-}OH) < 128$[b]
$M^+ + CH_3I \longrightarrow MCH_3^+ + I$	M = Fe, Co	$D(M^+\text{-}CH_3) > 56$
$\longrightarrow MI^+ + CH_3$	M = Fe, Co, Ni	$D(M^+\text{-}I) > 56$
$Ni^+ + CH_3I \not\longrightarrow NiCH_3^+ + I$		$D(Ni^+\text{-}CH_3) < 56$
$M^+ + CH_3Br \not\longrightarrow MCH_3^+ + Br$	M = Fe, Co, Ni	$D(M^+\text{-}CH_3) < 69$
$\longrightarrow MBr^+ + CH_3$	M = Fe, Co, Ni	$D(M^+\text{-}Br) > 69$,
$Fe^+ + CH_3OH \longrightarrow FeOH^+ + CH_3$		$D(Fe^+\text{-}OH) > 91$, PA(FeO) ≥ 227[c]
$M^+ + CH_3OH \not\longrightarrow MOH^+ + CH_3$	M = Co, Ni	$D(M^+\text{-}OH) < 91$
$M^+ + HI \not\longrightarrow MH^+ + I$	M = Fe, Co, Ni	$D(M^+\text{-}H) < 71$, PA(Fe) < 203, PA(Co) < 203, PA(Ni) < 208
$\longrightarrow MI^+ + H$	M = Fe, Co, Ni	$D(M^+\text{-}I) > 71$

[a] Inferred by assuming reactions observed to be exothermic and reactions not observed to be endothermic. Except as noted additional heats of formation needed to calculate bond strengths obtained from ref 12. [b] $\Delta H_f{}^\circ{}_{298}(i\text{-}C_3H_7^+)$ which was determined to be 187 kcal/mol from IP(i-C_3H_7) = 7.36 eV (ref 20) and $\Delta H_f(i\text{-}C_3H_7)$ = 17.6 kcal/mol (ref 12). [c] Calculated using $\Delta H_f{}^\circ{}_{298}(FeO) = 60 \pm 5$ kcal/mol from citation in ref 11.

$M(CO)_2^+$ ions enter into dehydration or dehydrohalogenation reactions. Two trends emerge in the displacement reactions. First, alcohols tend to displace two carbonyls more than the halides do. This suggests that the alcohols bind the metals more strongly than the halides do. Second, the possibility that an alkyl halide will displace two carbonyls tends to increase with the size of the alkyl group. Such a trend is not clearly evident for the alcohols. This suggests that the binding energy between the metals and alkyl halides tends to increase with the size of the alkyl group.

The reactions of $Fe(CO)_3^+$ and $Ni(CO)_3^+$ (Table VIII) deviate from the general pattern. In addition to displacing a carbonyl, CH_3I reacts with these ions to form $Fe(CO)_3I^+$ and $Ni(CO)_3I^+$, respectively. This suggests that the metal carbonyl bonds in the $M(CO)_3I^+$ species are relatively stable or perhaps that the $CH_3\text{-}M(CO)_3I^+$ bonds are relatively unstable.

Alkyl Cations and Proton Transfer. The neutral metal carbonyls react with ions formed by electron impact on the alkyl halides and alcohols to give two sets of products (Table IX):



Proton transfer is sometimes accompanied by elimination of one CO. If A is a hydrocarbon, propensity to form a proton transfer product increases with the acidity of AH^+ (Table XII). $C_3H_5^+$, the weakest acid, transfers a proton only to $Fe(CO)_5$. $C_3H_7^+$, the next weakest acid, transfers a proton to $Fe(CO)_5$ and $Co(NO)(CO)_3$, and the remaining hydrocarbon ions transfer a proton to all three metal carbonyls. Observed proton transfer from $C_2H_5OH_2^+$ to all the metal carbonyls suggests that they all have proton affinities greater than that of ethanol (192 kcal/mol). This is consistent with the proton affinity of 203 kcal/mol reported for $Fe(CO)_5$ by Foster and Beauchamp.[8]

Table XII. Proton Affinities[a]

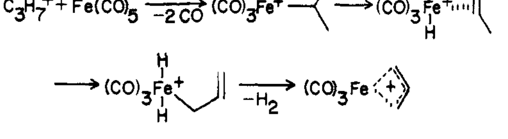
A	PA(A)[b]	A	PA(A)[b]
$Fe(CO)_5$[d]	203[c]	$CH_2{=}CHCH_3$	183[f]
$Ni(CO)_4$,[d] $Co(NO)(CO)_3$[d]		CH_2O	179[e]
C_2H_5OH	192[e]	C_2H_4	159
CH_3OH	187[e]	C_2H_2	153
$CH_2{=}C{=}CH_2$	185		

[a] PA = $-\Delta H$ for reaction $H^+ + A \rightarrow AH^+$. [b] Based on data from ref 12 except as noted. [c] Reference 8b. [d] Proton affinities surmised to be greater than PA(C_2H_5OH) on the basis of observed proton transfer reactions. [e] Based on PA(NH_3) − PA(CH_2O) = 26.5 kcal/mol, PA(NH_3) − PA(CH_3OH) = 20.1 kcal/mol, or PA(NH_3) − PA(C_2H_5OH) = 15.5 kcal/mol (J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and J. L. Taft, *J. Am. Chem. Soc.*, **99,** 5417 (1977)) and PA(NH_3) ≃ 207 kcal/mol. See Y. K. Lau, P. P. S. Sabuja, P. Kebarle, and R. W. Alder, *J. Am. Chem. Soc.*, **100,** 7328 (1978), for a discussion of this value. [f] A recently reported value of IP(i-$C_3H_7\cdot$) = 7.36 eV (ref 20) with $\Delta H_f{}^\circ{}_{298}(i\text{-}C_3H_7\cdot)$ = 17.6 kcal/mol (ref 12) gives PA(C_3H_6) = 183 kcal/mol.

The mechanism of the proton-transfer processes may be initiated by formation of a strong hydrogen bond between the metal and the proton to be transferred. The reactions involving carbonyl elimination probably result in metal alkyls which may tautomerize via a β hydrogen shift to metal hydrides complexed with olefins. This provides a particularly attractive rationalization for the reactions of $C_3H_7^+$ which result in the loss of H_2 (Scheme IV). The fact that H_2 elimination is always accompanied by elimination of two or three carbonyls lends credence to this mechanism which requires empty sites about the Fe. The formation of metal acyl moieties ($M(CO)_n$-$(RCO)^+$) in the reactions of the alkyl cations is a possibility which cannot be eliminated.

Parallels to Other Systems. Metal insertion mechanisms have been proposed for reactions of transition-metal ions with aryl halides[3] and hydrocarbons.[22] Several reactions of (η^5-C_5H_5)Ni^+ with organic compounds[23,24] including the decar-

Scheme IV



bonylation of acetaldehyde[23] are postulated to involve metal insertion. Hence this particular mechanism is quite general in the ion–molecule reactions of transition-metal species. Furthermore, metal insertion is believed to be important in a variety of condensed-phase processes.[25] Many of the reactions of transition-metal vapors[26,27] and finely divided powders[28] are postulated to involve metal insertion. Such mechanisms as multistep free radical processes which might explain some condensed-phase results are not possible in the reactions reported here. Klabunde and Roberts have suggested a caged free radical mechanism to account for the reactions of Pd atoms with alkyl halides in low-temperature matrices.[29] They support with considerable evidence the postulate that Pd–X–R species are formed at 77 K and that RPdX is formed on warmup by recombination of R and PdX radicals trapped in a matrix "cage". The results of the present study neither require nor allow such an explanation of formation of species of the type RMX^+. There is, of course, no matrix in the gas phase. The direct formation of MR^+ in a number of instances, the reactions of RMX^+ species, and other observations discussed above indicate that direct metal insertion occurs in the gas phase. This lends support to the possibility of metal insertion in other systems. It should be noted that direct insertion may not be the exclusive mode of reaction of the transition-metal ions. The propensity of Ni^+ to form NiX^+ may be the result of a tendency to attack on the X end of RX and displace a radical R.

Mechanisms involving an ion-induced charge separation are postulated to be important in the ion–molecule reactions of such species as $TiCl_3^+$,[30-33] $SiCl_3^+$,[32,33] and NO^+.[34,35] In the case of $TiCl_3^+$ and $SiCl_3^+$ there is a correlation between reactivity and chloride affinity[32,33] similar to that described here for the alkali metal ions. Both ionic and neutral Lewis acids catalyze a great variety of condensed-phase reactions by polarizing a critical bond in a reactant molecule.

Metal species whose reactions involve charge separation or ionic mechanisms are categorized as class "a" or hard.[36] Typically alkali metals and transition metals in higher oxidation states are hard. Metal species whose reactions involve covalent interactions are categorized as class "b" or soft.[36] Typically transition metals in lower oxidation states are soft. Clearly the reactivity of the alkali metals and transition metals in the gas phase fit into this general scheme which is based on a large body of condensed-phase results.

Summary and Conclusions

(1) Alkali metal ions induce the dehydrohalogenation of alkyl halides and the dehydration of alcohols in the gas phase. The mechanism of this process involves generating positive charge at the carbon atom bearing the halogen or hydroxide. There is an energetic barrier to reaction associated with this charge generation. The height of this barrier increases with the difference between $D(R^+\text{-}X^-)$ and $D(M^+\text{-}X^-)$. We suggest, in fact, that the barrier height is proportional to the energy required to separate the ground state $RX\text{-}M^+$ complex into R^+ and MX. This accounts for the fact that Li^+ is more reactive than Na^+ which is more reactive than K^+. It also accounts for the fact that tertiary compounds are more reactive than secondary compounds which are more reactive than primary compounds.

(2) From the halide transfer reactions of Li^+ with adamantyl halides we deduce that $\Delta H_f{}^\circ{}_{298}$(1-adamantyl cation) = 160.7 ± 3.0 kcal/mol. From the chloride transfer reaction of Li^+ with benzyl chloride we deduce that $\Delta H_f{}^\circ{}_{298}(C_7H_7^+) \leq 215.1 \pm 3.0$ kcal/mol.

(3) The transition-metal ions dehydrogenate alkyl halides and alcohols by a mechanism that involves metal insertion into the C–X bond and shift of a β hydrogen atom from the alkyl group to the metal. There is little, if any, energy barrier associated with this reaction. The RMX^+ structure is readily accessible to a complex containing M^+ and RX regardless of the internal energy in the complex.

(4) A trend clearly emerges in the reactions of the metal ions Fe^+, Co^+, and Ni^+. Ni^+ tends to form NiX^+ and $NiXH^+$ products in favor of NiR^+ and Ni(olefin)$^+$ products. The opposite tends to be true for Fe^+ and Co^+. This is possibly related to the slightly lower ionization potential of Ni.

(5) Lower limits on a number of bond strengths of the type D(M–X) and $D(M^+\text{-}X)$ where X is a methyl group, a halogen, an hydroxyl group, or a hydrogen atom are obtained.

(6) Ions of the type $M(CO)_n{}^+$ tend to react with RX to form $M(CO)_{n-1}RX^+$ and $M(CO)_{n-2}RX^+$. The results suggest that alcohols form stronger bonds to the metal complexes than alkyl halides and that the metal–alkyl halide bond increases in strength with the size of the alkyl group.

(7) Alkyl cations, R^+, generally react with metal carbonyls, $M(CO)_n$, to form $M(CO)_{n-1}R^+$. Proton transfer from R^+ to $M(CO)_n$ increases in importance as the acidity of R^+ increases.

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(10) The dehydrohalogenation reaction will be endothermic if $D(CH_2CO\text{-}Na^+) < 21.5$ kcal/mol, which is less than $D(H_2O\text{-}Na^+) = 24$ kcal/mol (S. K. Searles and P. Kebarle, *Can. J. Chem.*, **47**, 2619 (1969)). The dipole moment of CH_2CO (1.47 D) is low relative to that of H_2O (1.84 D) and its polarizable electron density is delocalized over the length of the CH_2CO molecule. This could result in a $D(CH_2CO\text{-}Na^+)$ value significantly less than $D(H_2O\text{-}Na^+)$. It is thus a reasonable conjecture that Na^+-induced dehydrohalogenation of CH_3COCl is endothermic.
(11) Based on $\Delta H_f(KCl) = -51.31 \pm 0.1$: D. R. Stuhl and H. Prophet, "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **37** (1971).
(12) Based on heats of formation in H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, **6** (1977).
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(17) Based on $\Delta H_f{}^\circ{}_{298}$(1-adamantyl chloride) = −48.2 kcal/mol and $\Delta H_f{}^\circ{}_{298}$(1-adamantyl bromide) = −38.8 kcal/mol estimated using group equivalents from S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas Phase Unimolecular Reactions", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **21** (1970).
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Coal Chemistry. 8. Reactions of Tetralin with Coal and with Some Carbon-14-Containing Model Compounds[1]

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Abstract: When coal was treated with tetralin-*1*-^{14}C at 400 °C, small yields of α- and β-methylnaphthalenes-^{14}C were observed. In order to determine the mechanism of the reaction, tetralin was heated with ^{14}C-labeled 1,3-diphenylpropanes (**1**), with 1,3-diphenylpropene (**2**), and with ^{14}C-labeled phenetoles (**3**). In each case methylnaphthalenes were observed, and the origins of the methyl groups were determined with carbon-14. In addition to the methylnaphthalenes, **1** and **2** also yielded toluene and ethylbenzene (after 19 h), whereas phenetole-β-^{14}C (**3**-β-^{14}C) yielded toluene (unlabeled) plus ethyl-^{14}C-benzene, benzene, phenol, and a mixture of α- and β-ethyl-^{14}C-naphthalenes. Crossover experiments with labeled phenetole and unlabeled ethyl *p*-tolyl ether proved the intramolecularity of the reaction phenetole → toluene + ethylbenzene, thus illustrating a 1,2-phenyl shift from oxygen to carbon.

Introduction

Tetralin was the original "hydrogen donor" in the Pott-Broche process[2] for the solvent extraction of coal, and, although it was later replaced with recycled oils, it is still employed in coal research as the archetypal donor solvent.[3]

We have already established[4,5] that Illinois No. 6 vitrain is a better hydrogen donor, for several receptors, than tetralin. In a later study[6] several coals and a series of organic compounds were tested as hydrogen donors for the reduction, at 400 °C, of benzophenone to diphenylmethane. Tetralin did not place very high as a hydrogen donor by this criterion, and, with the exception of anthracite, did not score as well as the several other coals tested. Further, solvent-refined coal often exhibits little or no increase in hydrogen content.[3] The results just mentioned raise several obvious questions concerning the role of tetralin in coal conversion processes. In order to gain more information on the subject, we prepared tetralin-*1*-^{14}C[7] and studied its reactions with Illinois No. 6 vitrain at 400 °C for various periods of time. In the recovered solvent we found traces of carbon-14-labeled α- and β-methylnaphthalenes, representing 3% by weight of the original coal sample. Since the product contained carbon-14, the naphthalene residue came from the tetralin-*1*-^{14}C. Tetralin alone, at 400 °C for 18 h, gives no observable trace of methylnaphthalenes; we presume, therefore, that the methyl carbons had their origin in coal. In order to test this possibility, we investigated the reactions of tetralin and of tetralin-*1*-^{14}C with several labeled and unlabeled model compounds.[4,5] We report here on the reactions, with tetralin at 400 °C, of (a) 1,3-diphenylpropane (**1**) and its isotope position isomers **1**-*1*-^{14}C and **1**-*2*-^{14}C; (b) 1,3-diphenylpropene (**2**), and (c) phenetole (**3**) and **3**-α-^{14}C and **3**-β-^{14}C.

$$\mathrm{Ph\overset{*}{C}H_2CH_2CH_2Ph} \qquad \mathrm{PhCH_2\overset{*}{C}H_2CH_2Ph}$$
1-*1*-^{14}C **1**-*2*-^{14}C

$$\mathrm{PhCH{=}CHCH_2PH} \qquad \mathrm{PhO\overset{*}{C}H_2CH_3} \qquad \mathrm{PhOCH_2\overset{*}{C}H_3}$$
2 **3**-α-^{14}C **3**-β-^{14}C

Methods and Results

The starting materials were prepared by standard methods (see Experimental Section). On prolonged heating (19 h) with tetralin, **1**, **2**, and **3** all undergo considerable reaction. Tetralin itself, under these conditions yields, in addition to naphthalene, small amounts of indan and methylindan, plus traces of other materials.[8] Given in Table I are the yields, expressed in mole percent, of the major products derived from **1**, **2**, and **3** (compounds derived from tetralin alone[8] are omitted). As is apparent from Table I, 1,3-diphenylpropane (**1**) and 1,3-diphenylpropene (**2**) react with tetralin to produce toluene, ethylbenzene, and α- and β-methylnaphthalenes. Phenetole, in addition, yields a mixture of α- and β-ethylnaphthalenes plus benzene and phenol; that the naphthalene moieties of these products come from the tetralin and the alkyl moieties from the 1,3-diphenylpropane and phenetole can be seen from the results of the experiments with labeled reactants, presented in Figures 1 and 2. The reactions were also carried out by heating **1** and **3** (unlabeled) with tetralin-*1*-^{14}C for 18 h at 400 °C; only the alkylnaphthalenes produced during these experiments contained carbon-14. Each product was isolated by preparative GC and identified by its NMR spectrum. The radioactivity distributions shown in Figures 1 and 2 were determined by GC combined with a carbon-14 monitor;[9] by comparing areas under the appropriate peaks, it could be determined that the toluene and ethylbenzene obtained from **1**-*1*-^{14}C contained half (±4%) the molar radioactivity of the reactant. Similar comparisons for the products of reaction of the two isotope position isomers of **3** were attempted, but consistent results could not be obtained. Consequently, the toluene and ethylbenzene fractions produced from **3**-β-^{14}C and **3**-α-^{14}C were isolated and their molar radioactivities or those of the benzoic acid samples obtained on oxidation were determined.[10] The results are shown in Figures 3 and 4, and require some comment. The errors in molar radioactivities of Figures 3 and 4 are beyond normal limits because of difficulties in combusting volatile liquids. The data show, nonetheless, that

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