currently obtained in GC-MS, but the LC-MS system substantially expands the range of samples for which combined chromatography-mass spectrometry is applicable.

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Copper(I) Chemical Ionization–Mass Spectrometric Analysis of Esters and Ketones

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The present work lays the foundation for the understanding and evaluation of atomic metal ions as a new class of chemical ionization reagent ions. In particular, a thorough study of the gas phase ion chemistry of Cu⁺, generated by laser ionization from the pure metal, with a series of oxygenated compounds is reported. Definite patterns of reactivity for different classes of oxygenated compounds are observed which, together with an understanding of the reaction mechanisms, provide the basis for predicting the Cu⁺ chemical ionization mass spectra of new compounds with analogous functional groups. The chemistry of Cu⁺ is found to be dramatically different from that of Ti⁺ and Li⁺ reported earlier providing a significant indication of the flexibility and selectivity afforded by atomic metal reagent ions.

Chemical ionization (CI) is a technique in which the sample is ionized by a reagent ion in an ion-molecule reaction. In general CI has the advantage of being a "soft" ionization technique in that, as a rule, far less energy is transferred to the sample than by conventional 70-eV electron impact. The sample ion is, therefore, less likely to fragment and greater information about the intact sample molecule may be obtained. An added dimension of this technique is that, unlike electron impact, different reagent ions may be chosen to be as selective or "universal" as desired because the ionization process, as the name of the technique implies, is coupled to a chemical reaction. Because of these advantages, the popularity of CI for analytical applications is likely to continue its rapid increase. The choice of reagent ions has remained remarkably limited to date, however, and future developments in the area call for exploring the utility of a wider range of CI reagent ions.

The reagent gas utilized has been mainly methane, and although an increasing amount of work is appearing in which the reagent gas is varied (ammonia, isobutane, and methanol are common), the majority of the reagent ions produced from these gases are protonating agents. Atomic metal ions hold promise as CI reagents by offering a significantly enlarged

flexibility of choice of Lewis acids and charge transfer agents. Ultimately, the application of metal ions as useful reagent ions will be determined only by studying the ion chemistry of various metal ions with various classes of molecules until patterns of reactivity can be identified useful in predicting the gas phase chemistry. Such work is under way in several laboratories. Ridge et al. (1-3) have been especially active in this area reporting the chemistry of Ni⁺, Co⁺, Fe⁺, Cr⁺, and Ti^+ with a variety of compounds. Studies involving $U^+(4)$, $Al^+(5, 6)$, and alkali ions (7–9) have also been reported. Of these latter ions, the alkalis have received the most attention since they can be readily generated by thermionic emission. Generation of transition metal ions has been mainly by electron impact on volatile inorganics such as carbonyl compounds.

Recently we reported the novel application of a pulsed laser source with an ion cyclotron resonance (ICR) spectrometer which demonstrated that virtually any atomic metal ion could be generated and its chemistry studied (10, 11). The laser source lends itself particularly well to ICR spectrometry and offers the advantage that a far wider variety of simple atomic metal ions can be generated and their chemistry studied without interference of reaction products from other fragment ions or reactions with the parent neutral complexes such as occur in the electron impact studies. We reported a brief study on the reactions of Ag^+ and Cu^+ with isopropyl chloride (11) and a comparison of the coordination chemistry of Cu⁺ in the gas phase and in solution (10).

In this paper, we report a study of the reactions of Cu⁺ with a series of esters and ketones in the gas phase. Particular emphasis is placed on determining the mechanisms of the reactions in order to permit the prediction and interpretation of Cu⁺ chemical ionization mass spectra from unknown samples having the same functional groups. Studies involving atomic metal ions are not only important for applications involving chemical ionization but also yield critical thermodynamic, kinetic, and mechanistic information about the intrinsic organometallic and coordination chemistry of metal ions in the absence of complicating solvent effects. In addition to elucidating the reactions to be expected of Cu⁺ with esters and ketones, our observations also yield information pertaining to metal-ligand bond energies in the gas phase. Finally, we discuss the significance of our results with those obtained from a number of related studies.

EXPERIMENTAL

The ion cyclotron resonance spectrometer used in this study is a modified V-5900 series manufactured by Varian Associates (12). The ICR cell is one which has been used extensively in our laboratory for studies of electron (13) and photon excitation (14, 15) processes, as well as for our previous studies utilizing laser ionization as described in detail elsewhere (10, 11). The output from an International Laser Corporation pulsed Nd-Yag laser at 1.06 μ m having a 100-mJ pulse intensity over a 20-ns flash was focused onto a copper endplate for ionization. This laser system was found to be as effective at producing large ion currents as the pulsed nitrogen laser (337 nm) employed in our earlier studies. The apparent wavelength independence of the ionization process is indicative of a plasma formation mechanism (16).

Following the ion formation laser pulse, the ions were trapped in the source region for times approaching 150 ms during which time ion-molecule reactions could occur in the presence of a neutral gas (in the pressure range $1-10 \times 10^{-7}$ torr). Reaction pathways were identified by observing changes in reactant and product ion signal intensities as a function of time and by the ion cyclotron double resonance technique (17, 18). Measured rate constants are good to $\pm 20\%$ owing to the inherent difficulties of measuring the pressure accurately.

The repetition rate of the laser was 5 Hz and the output of the laser had a peak-to-peak reproducibility of better than $\pm 10\%$. The signal was found to be quite sensitive to small changes in focusing and light intensity and achieved the greatest degree of stability after a period of approximately 1 h, suggesting perhaps an effect due to temperature or annealing of the surface. Refocusing was required periodically as the signal became unstable.

Each of the chemicals used was a commercial sample of high purity, with the exception of *tert*-butyl and neopentyl acetate which were prepared by reaction of acetyl chloride with the corresponding alcohols, and was used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases. Mass spectrometry revealed no detectable impurities.

RESULTS AND DISCUSSION

Esters. Dissociative attachment reactions of Cu⁺ with esters are summarized in Table I. (Some carboxylic acids are included with the esters.) With the exceptions of methyl formate, diketene, and γ -butyrolactone, the esters are observed to cleave either to alcohols and ketenes generalized by Equation 1 or to carboxylic acids and alkenes generalized by Equation 2.

$$Cu^{+} + RCO_{2}R' - Cu(R'OH)^{+} + ketene$$

$$Cu^{+} + R'OH$$
(1)

$$Cu^{+} + RCO_{2}R' - Cu(RCO_{2}H)^{+} + alkene$$

$$Cu^{+} + RCO_{2}R' - Cu(alkene)^{+} + RCO_{2}H$$
(2)

The products of these reactions react further with the substrate ester by ligand displacement. The reactions of Cu^+ with methyl acetate and ethyl acetate are typical of the generalized reactions 1 and 2, respectively. The reaction sequence for methyl acetate is given in Equations 3–6.

$$Cu^{+} + CH_{3}CO_{2}CH_{3} + Cu(CH_{3}OH)^{+} + CH_{2}CO$$
(3)

$$Cu(CH_{3}CO_{2}CH_{3})^{+} + CH_{3}OH$$
(5)
$$Cu(CH_{3}CO)^{+} + CH_{3}CO, CH_{3} \longrightarrow$$

$$Cu(CH_3CO_2CH_3)^+ + CH_2CO \quad (6)$$

This sequence of reactions is illustrated in Figure 1 which shows ion intensity as a function of time at a neutral gas



Figure 1. Variation of ion abundance with time following a 100-mJ, 20-ns laser pulse focused onto the copper end plate in the presence of 1×10^{-7} torr of methyl acetate. The repetition rate of the laser was 5 Hz and only the ⁶³Cu isotopes were monitored



Figure 2. Temporal variation of ion abundance for the Cu^+ -methyl acetate system taken from the data in Figure 1

pressure of CH₃CO₂CH₃ of ~1 × 10⁻⁷ torr. From a plot of the normalized intensities of the data taken from Figure 1 and shown in Figure 2, the overall rate constant for reactions 3 and 4 is 9 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ and the rate constants for ligand displacement reactions 5 and 6 are 5 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, respectively. The reaction sequence for ethyl acetate is given in Equations 7–10.

$$Cu^{+} + CH_{3}CO_{2}C_{2}H_{5}$$

 $Cu(CH_{3}CO_{2}H)^{+} + C_{2}H_{4}$ (7)

 $Cu(CH_3CO_2H)^+ + CH_3CO_2C_2H_5$

$$Cu(CH_{3}CO_{2}C_{2}H_{5})^{+} + CH_{3}CO_{2}H \quad (9)$$
$$Cu(C_{2}H_{4})^{+} + CH_{3}CO_{2}C_{3}H_{5} \longrightarrow$$

$$Cu(CH_{3}CO_{2}C_{2}H_{5})^{+} + C_{2}H_{4}$$
 (10)

Trapped ion studies again revealed that these reactions are quite facile with an overall rate constant for Equations 7 and 8 of approximately 1.1×10^{-9} cm³ molecule⁻¹ s⁻¹. For C₂H₅-

 $CO_2C_2H_5$ and $C_3H_7CO_2C_2H_5$ both reaction pathways 1 and 2 were observed (see Table I). Methyl formate and γ -butyrolactone were observed only to directly attach Cu⁺, and diketene was cleaved symetrically to form $Cu(CH_2CO)^+$ as might be expected. A competitive pathway observed was RCO₂⁻ abstraction to produce an alkyl ion. This process becomes evident as the stability of the alkyl ion increases. The butyl acetates, for example, yield butyl ion (m/e 57) with the greatest abundance observed for *tert*-butyl acetate.

Previous studies on gas phase atomic metal ion chemistry indicate the propensity of transition metal ions to insert into C-C, C-H, C-X (X = halogen), and C-O bonds, as well as their ability to cause hydrogen and alkyl migration within a molecule or onto the metal center (1-3). Our results on the dissociative attachment of Cu⁺ to esters may be explained by a hydrogen migration followed by dissociation of the resulting species, without the need to invoke an initial metal ion insertion. Following formation of the copper ion-ester activated complex, a hydrogen from the β position of one of the alkyl groups can migrate either through a five-centered intermediate onto Cu⁺ or onto the alkoxy oxygen directly through a fourcentered intermediate, the latter shown in Scheme I. The complex then cleaves at the alkoxy oxygen on the side from which the hydrogen originated. This process leaves two fragment molecules bound to Cu⁺ and competitive dissociation then occurs leading to products. The product ion consisting of the fragment molecule bound most strongly to Cu⁺ should predominate. Both mechanisms are consistent with the experimental results. The four-centered mechanism in Scheme I is attractive in that it requires fewer steps. The following discussion, however, is equally applicable to either mechanism. The mechanism(s) indicates that a β hydrogen on either side of the alkoxy oxygen is required for dissociative attachment to occur (Table I). For example, Cu⁺ does not undergo dissociative attachment to HCO₂H, Equation 11, but does with CH_3CO_2H , Equations 12 and 13.

$$cu^{+} + bD_{2}bh \rightarrow Cu(HCD_{2}bh^{+})$$
(11)

$$cu^{+} + CH_{3}CD_{2}H \rightarrow C_{0}CH \rightarrow C_{0}CH \rightarrow C_{0}CH_{2}CH \rightarrow C_{0}CH_{2}CH \rightarrow C_{0}CH_{2}CH_{2}CH \rightarrow C_{0}CH_{2}CH_{2}CH_{2}CH \rightarrow C_{0}CH_{2}COC_{0}CH_{2} \rightarrow C_{0}CH_{2}CH_$$

Similarly, HCO_2CH_3 only attaches Cu⁺, Equation 14,

$$Cu^+ + HCO_2CH_3 \rightarrow Cu(HCO_2CH_3)^+$$
 (14)
dissociative attachment occurs for CH CO CH. Equa

(1A)

while dissociative attachment occurs for CH₃CO₂CH₃, Equations 15 and 16, and $HCO_2C_2H_5$, Equations 17 and 18.



In order to observe dissociative addition of Cu⁺ to a substrate molecule, the Cu⁺- molecule bond energy of the fragment neutral must be greater than the dissociation energy required to divide the substrate neutral into two fragments. This relationship is obvious from Equation 19,

substrate
$$\rightarrow A + B$$
 $\Delta H_{\text{dissociation}}$
 $\underline{Cu^{*} + A \rightarrow CuA^{*}}_{\text{substrate}} -D(Cu^{*} - A)$ (19)
 $\underline{Substrate} + Cu^{*} \rightarrow CuA^{*} + B$
 $\Delta H_{\text{rxn}} = \Delta H_{\text{dissociation}} - D(Cu^{*} - A)$

where $\Delta H_{\rm rxn} < 0$ requires $\Delta H_{\rm dissociation} - D({\rm Cu}^+ - {\rm A}) < 0$ or that $D(Cu^+ - A) > \Delta H_{dissociation}$ and is useful for explaining the product ions observed. In addition, $D(Cu^+ - A) > \Delta H_{dissociation}$ yields lower limits on $D(Cu^+ - A)$. Table II lists dissociation energies, observed pathways, and thermodynamic implications. From a perusal of Table II, it is concluded that if both alkyl groups have a β hydrogen, Cu⁺ bound to the fragment molecules from the lowest energy dissociation pathway of the free ester will occur preferentially with the exception of pathways leading to aldehyde products. Observation of aldehyde products would require a metal insertion mechanism as discussed below.

Formic acid again provides an interesting example in that it fails to react even though it requires only 6 kcal/mol to dissociate HCO_2H to H_2O and CO, the lowest energy process listed in Table II. From our results on CH₂CO₂H in Table II, we know $D(Cu^{+} - H_2O) > 31 \text{ kcal/mol.} D(Cu^{+} - CO)$ is undoubtedly also greater than 6 kcal/mol considering previously reported values of $D(Fe^+ - CO) = 62 \text{ kcal/mol and}$ $D(Ni^{+} - CO) = 48 \text{ kcal/mol} (21)$. This reinforces the necessity, therefore, of having a β hydrogen. Similarly, the data on methyl formate argue in favor of a mechanism requiring a β hydrogen. The only exception to this rule in Table II is neopentyl acetate which proceeds by a hydrogen shift from the neopentyl group despite the fact that the neopentyl group has no β hydrogen. This suggests the possibility that the Cu⁺-neopentyl acetate complex rearranges to a Cu⁺-secondary pentyl acetate complex prior to dissociation.

The results on methyl formate, together with those for methyl acetate and ethyl propionate provide evidence that Cu⁺ insertion does not occur. If Cu⁺ insertion were important, then fragmentation to aldehydes would be expected to be

	$Cu^+ + CH, CO, CH, CH, CH,$	
ociative Attachment Reactions of Cu ⁺ with Esters and Carboxylic Acids	$h^{+} + HCO, H - hC$	
Di	0	(



able II. Neutral Products of Reacti	ions of Copper Metal Ion	s with Esters and Carboxy	dic Acids		
compounds	đ	roducts	observed	$\Delta H_{ m diss}{}^a$	implication
НСО,Н	Н,0	00	No	6.3	
CH ₃ CO ₂ H	CH,CO	Н,О	Yes	31	$D(Cu^+ - CH, CO), D(Cu^+ - H, O) > 31$
•	CH,OH	CÕ	No	29	
$C_2H_5CO_2H$	CH ₃ CHCO ^e	H_2O	Yes	28	$D(Cu^+ - CH_3CHCO), D(Cu^+ - H_3O) > 28$
1	C,H,OH	CŌ	No	26	
n-C,H,CO,H	C,H,CHCO	Н,О	Yes	27	$D(Cu^{+} - C, H, CHCO), D(Cu^{+} - H, O) > 27$
	<i>n</i> -C,H,OH	CŌ	No	24	
HCO,CH,	CH,OH	00	No	9.3	
2	CH,O	CH,O	No	28	
HCO,C,H,	C,H,OH	, OO	No	6.1	
5 4 9	Ċ,H,	HCO,H	Yes	11	$D(Cu^{+} - C, H,), D(HCO, H) > 11$
	CH,CHO	CH,Ó	No	21	
CH ₃ CO ₂ CH ₃	CH, CO	CHOH	Yes	35	$D(Cu^{+} - CH, CO), D(Cu^{+} - CH, OH) > 35$
	CH,	CH,CO,H	No	88	
	CH,CHO	CH,O	No	30	
CH,CO,CHCH,	CH,CO	CH,CHO	Yes	21	$D(Cu^{+} - CH, CO), D(Cu^{+} - CH, CHO) > 21$
a 1	C,H,	CH,CO,H	No	26	
$CH_{s}CO_{2}C_{2}H_{s}$	ĊĤ,ĈO	C, H, OH	No	35	
	$\mathbf{C}_2 \mathbf{H}_4$	CH,CO,H	Yes	15	$D(\mathrm{Cu}^{+}-\mathrm{C},\mathrm{H}_{*}), D(\mathrm{Cu}^{+}-\mathrm{CH},\mathrm{CO},\mathrm{H}) > 15$
	CH,CHO	CH,CHO	No	26	
CH ₃ CO ₂ C(CH ₃)CH ₂ ^c	CH,CO	CH, COCH,	Ves	17	$D(Cu^+ - CH, CO), D(Cu^+ - CH, COCH,) > 17$
	CH, CCH,	CH,CO,H	No	27	
CH.CO.CH CHCH 6	CHICO	CH CHCH OH P	No	33	

	CH ₂ CCH ₂ CH ₂ CHCHO [€]	CH ₃ CO ₂ H CH ₃ CHO	Yes No	$22 \\ 41$	$D(\mathrm{Cu}^{+}-\mathrm{CH}_{2}\mathrm{CCH}_{2}), D(\mathrm{Cu}^{+}-\mathrm{CH}_{3}\mathrm{CO}_{2}\mathrm{H})>22$
CH ₂ CHCO ₂ C ₂ H ₅ ^c	$CH_{2}CCO^{d}$	C, H, OH	No	¢.	
5. N N	C,H ₄	CH, CHCO, H ^c	Yes	28	$D(Cu^+ - C_2H_4), D(Cu^+ - CH_2CHCO_2H) > 28$
	CH, CHCHO ^b	CH _i CHO	No	17	
C ₂ H ₅ CO ₂ C ₂ H ₅	CH _i CHCO ^e	C, H, OH	Yes	23	$D(Cu^+ - CH_3CHCO)$, $D(Cu^+ - C_2H_5OH) > 23$
	$\mathbf{C}_2 \check{\mathbf{H}}_4$	C ₂ H ₅ CO ₂ H	Yes	5.8	$D(\mathrm{Cu}^{+}-\mathrm{C_{2}H_{4}}), D(\mathrm{Cu}^{+}-\mathrm{C_{2}H_{5}CO_{2}H}) > 5.8$
	C, H, CHO	CH,CHO	No	16	
CH, CO, CH, CH, CH, b	CH, CO	C,H,OH	No	37	
5 8 8	C ₃ H	CH ₃ CO ₂ H	$\mathbf{Y}_{\mathbf{es}}$	14	$D(Cu^{+} - C_{3}H_{6}), D(Cu^{+} - CH_{3}CO_{2}H) > 14$
	CH, CHO	C ₂ H ₅ CHO	No	27	
$n-C_3H_7CO_2CH_3b$	CH, CH, CHCO	CH ₃ OH	Yes	33	$D(Cu^+ - CH_3CH_2CHCO)$, $D(Cu^+ - CH_3OH) > 33$
	n-C ₃ H ₇ ĊHO	CH ₂ O	No	34	
	n-C,H,CO,H	CH	No	92	
CH3 CO, CH, CH, CH, CH,	CH,CO	$n-C_AH_OH$	No	36	
	1-C ¹ H	CH,CÓ,H	Yes	13	$D(Cu^{\bullet} - 1-C_{a}H_{s}), D(Cu^{+} - CH_{3}CO_{2}H) > 13$
$CH_{3}CO, CH, CH(CH_{3}), b$	CH, CÔ	i-CAHOÌH	No	39	
	<i>i</i> -C ₄ H ₈	СН,СО,Н	Yes	14	$D(Cu^{+} - i-C_{4}H_{s}), D(Cu^{+} - CH_{3}CO_{2}H) > 14$
CH ₃ CO, CH(CH ₃)CH, CH ₂ ^b	CH, CO	s-CaH,OHb	No	35	
5 a	$2 \cdot C_{A}H_{s}$	CH,CO,H	Yes	7	$D(Cu^+ - 2 - C_4H_8), D(Cu^+ - CH_3CO_2H) > 7$
$CH_3CO_2C(CH_3)_3c$	CH,CO	t-C ₄ H ₆ OH	No	27	
	i-C.H.	CH,CO,H	Y_{es}	12	$D(Cu^{+} - i - C_{4}H_{s}), D(Cu^{+} - CH_{3}CO_{2}H) > 12$
n-C,H,CO,C,H, c	CH, CH, CHCO ^e	C, H, OĤ	Yes	31	$D(Cu^{+} - C_2H_5CHCO), D(Cu^{+} - C_2H_5OH) > 31$
- - -	<i>n</i> -C,H,ĊHO	CH,CHO	No	26	
	$n-C_3H_3CO_3H$	C_2H_4	Yes	15	$D(Cu^{+} - n - C_{3}H, CO_{2}H), D(Cu^{+} - C_{2}H_{4}) > 15$
$CH_1CO_2CH_2C(CH_3)_3c$	CH,CO	neo-C ₄ H ₁₁ OH	No	33	
	CH, CHC(CH,)2	CH ₃ CO ₂ H	\mathbf{Yes}	10	$D(Cu^{+} - CH_{3}CH(CH_{3})_{2}), D(Cu^{+} - CH_{3}CO_{2}H) > 10$
CH ₃ CO ₂ C ₆ H ₅ ^e	CH ₂ CO	C ₆ H ₅ OH	$\mathbf{Y}_{\mathbf{es}}$	30	$D(Cu^{+} - CH_{2}CO), D(Cu^{+} - C_{6}H_{5}OH) > 30$
	C ₆ H ₄	CH,CO,H	No	129	
CH ₃ CO ₂ CH ₂ COCH ₃ ^c	CH,CO	CH ₃ COCH ₂ OH ⁶	$\mathbf{Y}_{\mathbf{es}}$	33	$D(Cu - CH_2 CO), D(Cu^+ - CH_3 COCH_2 OH) > 33$
$(CH_2CO)_2 d$	CH,CO	CH,CO	$\mathbf{Y}_{\mathbf{es}}$	ċ	
	CH ₂ COCH ₂	- CO	No	ċ	
a Based on heats of formation of neutrals	in Raf 19 Eorovala	nation of AH (krallm	nd) see text	b Heat of fo	rmation obtained from Bef 20^{-c} Heat of formation ob-
ained hy group equivalents from Ref 90	d Heat of formation n	ot available	101) acc	TTCAL OF TO	
amon of Broad equitations more than a	TICAN OF TOTTINANO	UI avanaviu.			

ANALYTICAL CHEMISTRY, VOL. 52, NO. 11, SEPTEMBER 1980 • 1645





observed as generalized by equations $20 \ {\rm and} \ 21$ but this does not occur.

 $\begin{array}{c} O \\ \parallel \\ RCOCH_2R' + Cu^+ \longrightarrow RCCu^+OCH_2R' \longrightarrow RCCu^+OCHR' \\ H \\ \end{array} \\ \begin{array}{c} H \\ H \\ \hline \\ H \\ \hline \\ H \\ \hline \\ Cu(RCHO)^+ + R'CHO (20) \\ \hline \\ Cu(R'CHO)^+ + RCHO (21) \end{array}$

Taking methyl acetate as a specific example, Cu⁺ insertion would lead to the species $CH_3COCu^+OCH_3$. Since $D(H - CH_3)$ CH_2O = 24.5 kcal/mol (19) and $D(H - CH_2CO)$ = 42.8 kcal/mol (19), Cu⁺ might be expected to preferentially abstract H. from the methoxy moiety leading to Cu⁺ bound to either formaldehyde or acetaldehyde. In addition, aldehyde formation is the lowest energy dissociation pathway for methyl acetate as shown in Table II and yet Cu⁺-aldehyde is not observed. In methyl formate, while D(H - CO) = 59 kcal/molmay be prohibitive, Cu⁺ may certainly abstract H. from the methoxy moiety to generate $Cu(H_2CO)^+$. Finally, with ethyl propionate, no Cu⁺-aldehyde species are observed despite the fact that hydrogen abstraction from C₂H₅O requires less energy than from C_2H_5CO and that less energy is required to generate C₂H₅CHO and CH₃CHO from the substrate ester than CH_3CHCO and C_2H_5OH . Further evidence for the lack of metal ion insertion is that reaction of the Cu⁺-ester species with the parent neutral ester only leads to formation of the ester dimer. If insertion were occurring, intermediate mass ions would be expected to be observed corresponding to Cu⁺ bound to one ester and a fragment molecule. Finally as a footnote to this argument, Ridge et al. (3) report reactions 22 and 23 as evidence for metal ion insertion.

$$Fe^+ + CH_3OH \rightarrow FeOH^+ + CH_3$$
 (22)

$$Fe(CH_3OH)^+ + CD_3OH \rightarrow FeOHCD_3OH^+ + CH_3$$
 (23)

Neither of these reactions are observed with Cu⁺.

Ketones. Observed dissociative attachment reactions of Cu^+ with ketones are summarized in Table III. (Some aldehydes are included with the ketones.) With the exceptions of acetone, cyclopentanone, cyclohexanone, and 3,3-dimethyl-2-butanone, ketones, like esters, are observed to be cleaved by Cu^+ followed by a competitive loss of a neutral fragment. Ketones may be cleaved to form H_2O and a diene generalized in Equation 24.

$$Cu^{+} + RCR' - Cu(H_2O)^{+} + diene$$

$$Cu^{+} + RCR' - Cu(diene)^{+} + H_2O$$
(24)

 H_2O is not effective at competing with the diene, however, and $Cu(H_2O)^+$ is not observed. Alternatively, ketones may



be cleaved to an alkene and an enol species generalized in Equation 25.

$$Cu^{+} + RCR' \xrightarrow{\qquad \qquad } Cu(enol)^{+} + alkene$$

$$Cu^{+} + RCR' \xrightarrow{\qquad \qquad } Cu(alkene)^{+} + enol$$
(25)

Although the enol probably rearranges to a ketone, a few transition metal complexes of Fe and Pt containing the vinyl alcohol moiety π bonded to the metal have been reported (22). The specific reactions of Cu⁺ with 3-pentanone and 2-pentanone provide an interesting illustration of the two pathways generalized in Equations 24 and 25. The reaction observed for 3-pentanone follows pathway 24 and is given in Equation 26.

$$Cu^{+} + CH_{3}CH_{2}CCH_{2}CH_{3} \longrightarrow Cu(C_{5}H_{8})^{+} + H_{2}O \quad (26)$$

For 2-pentanone both reaction types 24 and 25 are observed as written in the reaction sequence 27-29.

$$Cu^{+} + CH_{3}CCH_{2}CH_{2}CH_{3} \longrightarrow Cu(C_{3}H_{6}O)^{+} + C_{2}H_{4}$$
(28)

$$\smile \operatorname{Cu}(\operatorname{C}_{2}\operatorname{H}_{4})^{*} + \operatorname{C}_{3}\operatorname{H}_{6}\operatorname{O}$$
 (29)

All of the product ions react further by ligand displacement with the parent ketone. Acetone, cyclopentanone, and cyclohexanone were observed only to directly attach Cu^+ and 3,3-dimethyl-2-butanone was observed to react predominently by CH_3^- abstraction. Direct attachment as well as CH_3^- abstraction compete with dissociative attachment.

The major mechanism for dissociative attachment of Cu⁺ to ketones seems to involve the metal-induced enolization of the ketone (Scheme II). This is similar to that proposed by Ridge et al. (2) for reactions of $TiCl_3^+$ with ketones. The mechanism involves as one step a β hydrogen or β alkyl migration. Acetone cannot undergo dissociative attachment since it has no β hydrogen. Cyclopentanone and cyclohexanone's β hydrogens are apparently inaccessible and no reaction occurs. The 3-pentanone shows only products involving retention or elimination of water whereas 2-pentanone also exhibits products involving retention and elimination of ethylene, since 3-pentanone has no β -methyl group. The 2-pentanone and 3-hexanone yield similar products since both have a β methyl group. Propionaldehyde does not react and butyraldehyde reacts only slowly because both lack the α hydrogen necessary for the last mechanistic step, although H⁻ abstraction which is observed may be kinetically favored. Another important test of the mechanism was provided by 3,3-dimethyl-2-butanone which, as predicted, was not observed to react by dissociative attachment since it lacks the α hydrogen necessary for the first step. These results are somewhat tempered by the observation of a large peak due to CH₃⁻ abstraction which might be kinetically favored. Nevertheless, both CH_3^- abstraction and dissociative attachment were observed for 4,4dimethyl-2-pentanone where the mechanism predicts reaction can occur. While H⁻ abstraction from aldehydes is somewhat expected and also observed as a primary reaction pathway with ethers (23), abstraction of CH_3^- is quite unexpected with only a few other examples of it in the literature (24, 25).

Table IV lists dissociation energies, observed pathways, and thermodynamic implications for the ketones studied. Metal ion insertion is again ruled out for a number of reasons. In acetone, for example, direct metal insertion would have been expected to lead to products of Cu⁺ bound to CO and C₂H₆ or CH₂CO and CH₄, neither of which were observed. A number of other examples of low energy pathways in Table IV which would be observed if metal ion insertion were occurring, such as Cu⁺ bound to CH₃CHCO and C₂H₆ from 3-pentanone, are not seen. In addition fragment molecules are not observed to be displaced from the Cu⁺-parent ketone complex by neutral parent ketone.

Unlike the esters, the products observed from the ketones cannot be said to always follow the lowest energy dissociative pathway of the parent ketone. The energy differences given in Table IV for the ketones are somewhat smaller than that for the esters, and Cu^+ affinities may play a larger role in determining the observed pathways.

Thermochemical Implications. From the previous discussion it is evident that thermodynamics may play a dominant role in determining the final products of reaction. Obtaining thermochemical information, therefore, is not only of fundamental importance but can provide an aid in predicting and interpreting metal ion CI spectra. Relative metal-ligand binding energies may be obtained by determining the preferred direction of reaction 30.

$$Cu^{+}L + L' \rightleftharpoons Cu^{+}L' + L \qquad (30)$$

Reactions such as 5, 6, 9, and 10 in which the parent neutral ester or ketone displaces a fragment molecule have been prevalent in this study. From any of these reactions, one can conclude that a particular parent neutral has a greater affinity for Cu⁺ than the fragment molecule. From a limited study we have also determined a binding energy order of $i-C_4H_8 > CH_3CO_2H > C_3H_6 \gtrsim C_2H_5OH > CH_3OH$. The data in Table I on methyl acetate indicate that $D(Cu^+ - CH_3OH) > 35$ kcal/mol. A complete study on this topic is currently under way in our laboratory and will be presented elsewhere.

Observation of H^- abstraction from propional dehyde, reaction 31,

$$Cu^+ + CH_3CH_2CHO \rightarrow CH_3CH_2CO^+ + CuH$$
 (31)

and not from acetaldehyde yields values for $D(Cu^+ - H^-)$ of 224 kcal/mol, D(Cu - H) = 64 kcal/mol, and $\Delta H_f(CuH)$ of 69 kcal/mol. The latter value is in agreement with the literature value of 70 kcal/mol (26).

The highest energy CH_3^- abstraction observed for Cu^+ was from acetone, reaction 32,

$$\begin{array}{c} O \\ \parallel \\ Cu^{+} + CH_{3}CCH_{3} \longrightarrow CH_{3}CO^{+} + CuCH_{3} \end{array}$$
(32)

which provides a lower limit of $D(\text{Cu}^+ - \text{CH}_3^-) > 235 \text{ kcal/mol}$ from which $\Delta H_f(\text{CuCH}_3) < 56 \text{ kcal/mol}$ and $D(\text{Cu} - \text{CH}_3) > 59 \text{ kcal/mol}$ are derived. Interestingly, only in the Cu(I) state does copper form Cu-C bonds in solution (27).

Finally, observation of $CH_3CO_2^-$ abstraction from neopentyl acetate indicates $D(Cu^+ - CH_3CO_2^-) > 199 \text{ kcal/mol}$ and thus $\Delta H_f(CuO_2CCH_3) < -60 \text{ kcal/mol}$ and $D(Cu - CH_3CO_2) > 96 \text{ kcal/mol}$. These values were derived using $\Delta H_f(CH_3CO_2^-) = -120 \text{ kcal/mol}$ obtained from $\Delta H^\circ_d = -349 \text{ kcal/mol}$ (28) and using $\Delta H_f(CH_3CO_2^-) = -45 \text{ kcal/mol}$ (29).

Comparison of Results to Those from Related Studies. Relatively little information about the chemical ionization of esters and ketones by metal ions is presently available. Studies on Li⁺ (7–9) and TiCl_n^+ (n = 0 to 3) (2) have been reported and provide a limited but interesting comparison. Extensive experimental and theoretical studies on gas phase Li⁺ have shown that it reacts only by attachment to carbonyl compounds (8) and that the bond formed is an electrostatic rather than a covalent one (30). Ti⁺ and TiCl⁺ extract an oxygen atom from smaller carbonyl compounds forming TiO⁺ and TiClO⁺ but are not observed to react with carbonyl compounds with more than five carbons (2). $TiCl_2^+$ and $TiCl_3^+$ combine with smaller carbonyl compounds to eliminate HCl but with carbonyl compounds containing four or more carbons, TiCl2+ and TiCl₃⁺ undergo dissociative additions similar to those observed with Cu^+ (2). Reactions 33 and 34 of $TiCl_3^+$ with 2-butanone, for example, are analogous to that observed for Cu⁺ (Table III).

$$\operatorname{TiCl}_{3}^{+} + \operatorname{CH}_{3}\operatorname{CCH}_{2}\operatorname{CH}_{3} \xrightarrow{} \operatorname{TiCl}_{3}(\operatorname{H}_{2}\operatorname{O})^{+} + \operatorname{C}_{4}\operatorname{H}_{6} \quad (33)$$
$$\xrightarrow{} \operatorname{TiCl}_{3}(\operatorname{C}_{4}\operatorname{H}_{6})^{+} + \operatorname{H}_{2}\operatorname{O} \quad (34)$$

To summarize these results, the titanium-oxygen bond strengths are very high indicating that Ti^+ and $TiCl^+$ are readily oxidized. $TiCl_2^+$ and $TiCl_3^+$ are more difficult to oxidize and exhibit a chemistry similar to Cu^+ . The necessity of covalent bonding to assist in dissociative attachment can be deduced from the failure of Li⁺ to react in this manner.

A number of systematic studies on the unimolecular chemistry of protonated compounds have appeared in the literature (31, 32) permitting another interesting comparison with the results from the current study on Cu⁺. Table V lists the neutral moieties lost from the activated protonated compounds and analogous Cu⁺ complexes. Observation of alkane loss from the protonated species in Table V arises from the presence of the proton and is, therefore, not observed for Cu⁺. Taking this difference into account and noting that the internal energy of the Cu⁺ complexes is on the order of 1 to 3 eV and that for the protonated species may be up to about 10 eV, the agreement in this limited comparison is quite good, supporting the suggestion that Cu⁺, like H⁺, is covalently rather than electrostatically bonded to the molecule. Studies involving other metal ions as well as collision induced dissociation on the Cu⁺ complexes will provide further insight into these conclusions.

compounds	products		observed	$\Delta H_{ m diss}{}^a$	implication
CH ₃ CHO	$C_2 H_2$ CH	H_2O	No No	36 -4.6	
c ₂ H ₅ CHO	H, CH,CCH ₂ C,H, C,H,	СН,СО Н,О СО СН О	o o o o X X X X	25 34 -0.76 30	
ı-С ₃ Н,СНО	CH CH CH CH CH CH	сн, со 1, со со со со со со со со со со со со со с	N N N N	13 31 - 2.2	
2H,cocH,	сли, сли, сли, сп, ссп,	CH ₂ C CH ₂ CO H ₂ O CO	No No No No	$\begin{array}{c} 22\\40\\5\end{array}$	$D(\mathrm{Cu}^{+}-\mathrm{C_2H_4}), D(\mathrm{Cu}^{+}-\mathrm{CH_3CHO}) > 22$
C ₂ H ₅ COCH ₃	СН 1,3-С4н С,Н,	CH,CO H,O CH,CO	No Yes No	19 25 22	$D({ m Cu}^+-1, 3{ m -C_4}{ m H_6})>25$
1-C ₃ H ₇ COCH ₃	стн, сн, ссн,)снсн, с, н,	CH ₁ CHO H ₂ O CH ₂ CO	No Yes No	30 22 22	$D(\mathrm{Cu}^+ - \mathrm{CH}_2\mathrm{C}(\mathrm{CH}_3)\mathrm{CH}\mathrm{CH}_2) > 22$
C ₂ H,COC ₂ H,	C ₃ H, C ₂ H, 1,3-C ₅ H, <i>n</i> -C ₄ H, C H,	CH,CHO CH,COCH, H,O CO CH CHCO ^b	No Yes No No	$\begin{array}{c} 27\\23\\5\\19\end{array}$	$D(Cu^{+} - C_2H_4), D(Cu^{+} - CH_3COCH_3) > 22$ $D(Cu^{+} - 1, 3 \cdot C_5H_8) > 23$
CH ₃ COC(CH ₃) ₃	C,Ht CH(CH,) CH(CH,), CH,C(CH,),	C,H,CHO CH,CO CH,CO CH,CHO	o o o o Z Z Z Z	28 23 8 29 3 8 29 3 8	
CH ₃ COCH ₁ CH ₂ CH ₂ ^b	1,3,5-C,H,6 1-C,H, C,H,	Н,0 СН,СО СН,СО	No Yes Vec	22 22 23	$D(Cu^+ - 1-C_4H_3), D(Cu^+ - CH_2CO) > 22$ $D(Cu^+ - CH COCHCH 1 > 33$
n-C ₃ H ₇ COC ₂ H ₅ ^b	CH ¹ CH ₁ CHC(CH ₃)CHCH ₂ ^b C ₃ H ₆ C ₁ H ₆	H,O CH,CHCO ^b C,H,CHO	Yes No No	$\begin{array}{c} 24\\19\\26\end{array}$	$D(\mathrm{Cu}^+ - \mathrm{CH}_3^+\mathrm{CHC}(\mathrm{CH}_3)\mathrm{CHCH}_1) > 24$
CH3COCH2C(CH3)3	C ₁ H [*] CH ₂ C(CH ₃)CHC(CH ₃) ² CH ₂ C(CH ₃) ₂	C,H,COCH, H,O CH,COCH,	Yes No Yes	$22 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\ 20 \\$	$D(Cu^+ - C_2H_4), D(Cu^+ - C_2H_5COCH_3) > 22$ $D(Cu^+ - CH_2C(CH_3)_1), D(Cu^+ - CH_3COCH_3) > 26$
<i>n</i> -C ₄ H ₅ COC ₂ H ₅ ^b	C(CH ₃)4 CH ₃ CH ₂ CHC(CH ₃)CHCH ₂ ^b C ₄ H ₁₀ C,H ₅	сн,со сн,снсо ^ь с,ң,сно	No No No	$\begin{array}{c} 22\\34\\19\\26\end{array}$	$D(Cu^+ - CH_3CH_2CHC(CH_3)CHCH_2) > 34$
	C,H,	C,H,COC,H,	Yes	22	$D(\mathrm{Cu}^+ - \mathrm{C}, \mathrm{H}_{\star}), D(\mathrm{Cu}^+ - \mathrm{C}, \mathrm{H}_{\mathrm{s}}\mathrm{COC}, \mathrm{H}_{\mathrm{s}}) > 22$

hui Ke with Matal Ic Ç î 1 f D Å 1 Ż Table IV.

Table V.	Comparison of the Neutral	Fragment Los	s from Ion-N	Iolecule React	tions Involving C	u ⁺ and from
Collision 1	Induced Dissociation of the	Analogous Pro	tonated Con	npounds		

compounds	Cu+ reac	tion	CID (pr	otonated comp	ound) ^a
$CH_{3}CO_{2}C(CH_{3})CH_{2}$	CH ₃ CO ₂ H	CH_2CCH_2	CH ₃ COCH ₃		CH ₂ CO
CH ₃ CO ₂ C ₃ H ₇ CH ₃ CO ₂ C ₆ H ₅ C ₃ H ₇ CO ₂ CH ₃	C,H, CH,CO CH,CH,CHCO	CH ₃ CO ₂ H C ₆ H ₄ OH CH ₃ OH	C,H, C,H,OH CH,OH CH	CH,	C ₃ H ₇ OH CH ₂ CO C ₃ H ₈
$C_3H_7CO_2C_2H_5$	C,H,CO,H	C ₂ H ₄	$C_2 H_4$ C H OH	C ₂ II ₅ OH	C,H, C,H,CO,H
$C_2H_5COC_3H_7$	C,H ₁₀ C,H COCH	H ₂ O C.H.	C_3H_6	C ₃ H ₈ H.O	C_2H_6
cyclopentanone	No Reaction	- 24	$ \begin{array}{c} $	2-	$ \begin{array}{c} \overset{\circ}{\mathrm{C}_{2}}\overset{\circ}{\mathrm{H}_{6}}\\ \mathrm{CH}_{4}\end{array} $
^a Ref. 31 and 32.					

Finally, an important future consideration will be the comparison of our results to those obtained from cationization of organic molecules with metals using secondary ion mass spectrometry or SIMS (33, 34). Cationization is a relatively new ionization method whereby metal ions are attached to organic molecules under the influence of a bombarding primary ion beam and the mass spectrum of the ejected secondary ions (the SIMS spectrum) is recorded. Cationization appears to hold great promise for the analysis of nonvolatile and thermally labile compounds. Studies in a number of laboratories are under way to understand the mechanism of this form of ionization in order to provide a greater quantitation of the technique. The metal ions generated by the primary beam are thought to attach to the organic species in the gas phase near the surface. Some of the adduct ions are sufficiently energized to fragment. Although no direct comparisons may be cited here except to say that attachment and dissociation are observed in both techniques, it is evident that the study of gas phase metal ion chemistry will aid in elucidating the cationization process.

CONCLUSION

We have shown that Cu⁺ displays definite patterns of reactivity for different classes of oxygenated organic compounds. An understanding of the mechanisms of these reactions provides the basis for predicting the chemistry of new compounds and, hence, their Cu⁺ CI mass spectra. Dissociative attachment reactions of Cu⁺ with esters occur in which the ester is cleaved either to alcohols and ketenes or to carboxylic acids and alkenes. The reaction pathway is strongly influenced by the thermodynamics of the dissociation channels of the free ester. Ketones are split into either H₂O and dienes or alkenes and smaller ketones with the thermodynamics of the free ketone playing a less obvious role than for the esters. Anion abstraction and direct attachment were also observed to compete with dissociative attachment for esters and ketones in a predictable fashion. Limits on metal bond strengths were obtained from the reactions observed.

Of particular significance is the comparison of the differences in reactivity of Cu⁺, Ti⁺, and Li⁺ which provides an indication at this early stage of the flexibility and selectivity afforded by metal reagent ions. Ti⁺, for example, could be utilized to identify the presence of ketones having fewer than five carbons while Cu⁺ and Li⁺ could provide complementary structural and molecular weight information and also could be useful for identification of longer chained ketones.

Although these studies are performed using ion cyclotron resonance spectrometry, one can predict the mass spectrum which will be obtained on a conventional instrument by knowing the rate constants determined above and the pressure and ion lifetime of the particular source being utilized. At low source pressures, for example, Cu⁺ bound to fragment neutrals will be observed useful for differentiation among structures, while at higher pressures Cu⁺ bound to one or more molecules of the parent compound will be observed providing molecular weight information. Chemical ionization mass spectra are in general greatly dependent on source conditions. The ratio of sample to reagent gas, for example, is often not precisely known, limiting reproducibility. An unusual feature of laser ionization CI is that no reagent gas is required. The sample pressure in the source may, therefore, be more precisely known. In addition the absence of reagent gas is especially attractive for chemical ionization studies using ion cyclotron resonance spectrometry (35) because the mass resolution varies inversely with pressure.

In summary, the present work begins to lay the foundation for the understanding and evaluation of a new class of CI reagent ions utilizing a new combination of techniques. The spectrum of metal ions and their chemistry, attainable by laser ionization, promises to provide an unprecedented "tunability" for chemical ionization analysis together with important fundamental information about organometallic chemistry.

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Determination of Individual Organic Compounds in Shale Oil

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Several techniques have been investigated for quantitating individual organic compounds in shale oil. Acid-base extraction and high performance liquid chromatography were emphasized as independent methods of shale oil fractionation. Gas chromatography, gas chromatography-mass spectrometry, and high performance liquid chromatography were used for individual compound quantitation utilizing external and/or internal standards or standard addition techniques. The following compounds were measured in the shale oil: pyrene, fluoranthene, benzo[e]pyrene, benzo[a]pyrene, phenol, ocresol, acridine, and 2,4,6-trimethylpyridine. Comparable results were obtained by the various methods for extraction and quantitation.

Increasing energy demand in the United States and reliance on foreign sources of petroleum have resulted in a national program designed to develop new sources of energy. The conversion of coal to gaseous or liquid fuels and the utilization of oil shale and tar sands are some of the energy sources that appear promising. In terms of energy, it is estimated that domestic coal and oil shale reserves are 8000×10^{15} and 400 $\times 10^{15}$ Btu, respectively, while petroleum reserves are only 200×10^{15} Btu (1). However, a serious and still largely unknown complication of developing these alternate fuels is their potentially deleterious effect on man and the environment. To evaluate this effect properly, it will be necessary to analyze the feedstock, process streams, plant effluents, and final product for their trace element and organic compound content. The accurate quantitative analysis of individual organic compounds will become increasingly important as mutagenicity testing on chromatographic fractions generated from various fuels and effluents expands. These tests should eventually allow scientists to relate health effects to known amounts of specific compounds.

One method for assuring the accuracy of the necessary quantitative analyses is the use of suitable quality assurance standards or Standard Reference Materials (SRMs). The certification of such trace organic SRMs is contingent upon

the development of the analytical expertise to quantitate individual compounds in complex matrices such as shale oil, liquified coal, or petroleum. In the past, many of the analytical techniques that have been used for the evaluation of synthetic oils have been taken from petroleum technology (2-5). These analyses generally have involved an initial separation of the mixture into compound classes by solvent extraction techniques or by use of ion-exchange resins followed by various methods of further characterization. The procedures that have been used for further characterization were usually designed for the determination of physical and chemical properties of distillate fractions which are important to product characteristics but are not designed for individual compound identification and quantitation.

Recently several methods for the analysis of specific organic compounds in samples of petroleum, shale oil, and synthetic coal liquids have been reported. Jackson et al. (6) characterized hydrocarbon types in shale oil distillates by use of a hydroboration-acid adsorption technique; McKay and coworkers (7) utilized a chromatographic-infrared technique to characterize nitrogen bases in high boiling petroleum distillates. Uden et al. (8) have characterized the acidic and basic fractions of shale oil by gas chromatography-Fourier transform infrared spectrometry. Popl et al. (9) have used frontal elution on silica gel followed by adsorption chromatography on alumina and gel permeation chromatography to characterize polynuclear aromatic hydrocarbons (PAH) in white petroleum products. Suatoni and Swab (10) developed a "back-flush" high performance liquid chromatographic (HPLC) technique for the determination of total saturated and aromatic hydrocarbons from crude oils and synthetic crudes derived from coal. Several workers (e.g., 11) have recently applied mass spectrometry to class-specific analyses of coal liquids. Dark and McFadden (12) employed HPLC and liquid chromatography-mass spectrometry for the characterization of coal liquefaction products, and Clark et al. (13) have used both solvent extraction and chromatographic techniques for the isolation of alkanes and PAHs from shale oil. However, none of these methods was developed for the accurate quantitative analysis of individual compounds.