For a given set of $K,T$ data pairs, one pair is set as $K_0,T_0$ and the remaining values of $K,T$ are used in a regression of eq 6 to find a value of $\Delta H°$ at $T_0$ and $\Delta C_p°$. Another pair of $K,T$ values are selected as the new $K_0,T_0$, and the process is repeated until values of $\Delta H°$ and $\Delta C_p°$ have been obtained for each temperature. The LASL nonlinear, least-squares program was also used with eq 6 to find "best fit" values of $\Delta H°$ and $\Delta C_p°$ as opposed to the linear form of eq 6 offered by Blandamer. Table VII summarizes the values of $\Delta H°$ and $\Delta C_p°$ obtained for CoTSPC dimerization in water over the temperature range 25–75 °C. These results suggest that $\Delta C_p°$ is finite and constant over the temperature range considered. To confirm this further, the values of $\Delta H°$ in Table VII were fit to a linear equation with resulting values of

$$\Delta H° = -16.20 \pm 0.32 \text{ kcal/mol} + [113 \pm 6 \text{ cal/(mol K)}](T) \quad (7)$$

where $T$ is temperature (°C). Thus, the dimerization of CoTSPC possesses a positive heat capacity of 0.1 kcal/(mol K) over the temperature range 25–75 °C.

A number of factors have been proposed to account for forces contributing to dimerization of dye molecules such as van der Waals forces, charge–charge interactions, hydrophobic interactions, or the role of the water. The presence of a positive heat capacity rules out hydrophobic interaction as a major contributor, since hydrophobic interactions display a negative heat capacity as discussed recently by Evans and Lumry[46] with regard to critical micelle formation.

Another piece of evidence to support our contention that hydrophobic bonding does not contribute to dimerization is the rapid dissolution of CoTSPC in water as opposed to alcohol, which is characteristic of an electrolyte as opposed to a hydrophobic solute. The crucial aspect of dimerization of CoTSPC appears to be electrostatic interactions from the charged sulfonate groups, so that CoTSPC can be considered as a typical polyelectrolyte in solution.

Evans and Lumry also point out that it is dangerous to use $\Delta H°$ and $\Delta S°$ values near room temperature to intrepret the thermodynamics of association, since the unique structure of water imposes contributions to $\Delta H°$ and $\Delta S°$ that compensate. Evans suggests that one use hydrazine in place of water as a solvent or examine $\Delta H°$ and $\Delta S°$ at high temperatures where the unique water structure disappears. Using values of $\Delta H°$ and $\Delta S°$ at 75 °C (Table VII), one sees that CoTSPC dimerization has a positive entropy. In the view of the fact that formation of a dimer should produce a negative entropy, a sizable contribution to entropy may come from release of water molecules on dimer formation. This is further substantiated by a recent article by Ohling[47] who measured the pressure dependence of dimerization of methylene blue and pyronine G dyes. He found that the volume change on dimerization was negative, which he attributed to release of water on dimer formation. Thus, we agree with Abel et al.[34] that water participates in dimer formation, but we find that water is released into the bulk solvent when the dimer forms as opposed to their contention that water is incorporated into the dimer.

**Registry No.** CoTSPC, 14586-48-2.

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(46) Ramadan, M. S.; Evans, D. F.; Lumry, R. *J. Phys. Chem.* **1983**, *87*, 4538–4543.

(47) Ohling, W. *Ber. Bunsen-Ges Phys. Chem.* **1984**, *88*, 109–115.

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# Copper(I) Complexes of Olefins Produced by Olefin Chemical Ionization of Copper(II) β-Diketonates

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Olefins serve as effective chemical ionization reagents for copper(II) complexes of β-diketones. Reactions induced by the proton transfer from ions in the high-pressure olefins include fragmentation of the complex, reduction of the copper(II) to copper(I), and subsequent reaction of the copper(I) species with the reagent olefin. This reaction sequence is most pronounced when the ligand is hexafluoroacetylacetonate, but is observed for trifluoroacetylacetonates and acetylacetonates as well. In addition, condensation reactions of the metal complexes occur to form cluster ions. Comparable reactions are noted between reagent ions and metal complexes. When cluster ions contain Cu(I), these ions are seen to react with neutral reagent molecules to form olefin complexes comparable to those observed for fragment ions.

## Introduction

There has been continued interest in the olefin complexes of Cu(I). Among other properties, they have been implicated as intermediates in the copper-catalyzed photoreactions of many olefins.[1] Considerable attention has been paid to the role of Cu(I) in the photoisomerization of norbornadiene to quadracyclane because of the potential usefulness of these systems for storage of solar energy.[2]

More generally there has been growing interest in the use of metal atoms as potential chemical ionization agents. Metal ions generated by a laser focused on a copper foil have induced reactions in organic molecules.[3] Mass spectrometric investigations of the electron-impact-induced reactions in the vapor phase of volatile neutral copper(II) complexes have been interpreted as exhibiting intramolecular redox steps that yield a variety of Cu(I) species including Cu(I) as a free metal ion.[4] The latter method of generating Cu(I) ions may be more gentle than the former.

The combination of the interest in Cu(I) as a catalyst in photoreactions of olefins and the possibility of directly demonstrating the reactions of the Cu(I) oxidation state and comparing those reactions to reactions of Cu(II) complexes has motivated us to investigate the olefin chemical ionization (CI) of several Cu(II) β-diketonates.

## Experimental Section

A Varian-MAT 112 mass spectrometer equipped with a CI source was used to obtain mass spectra. The typical charge-transfer agent, isobutane, was replaced by various unsaturated hydrocarbons. The unsaturated hydrocarbons used included ethene, propene, allene, propyne, methylpropene (isobutene), 1-butene, *cis*-2-butene, and 1,3-butadiene. These gases were obtained commercially (instrument grade or better) and were used without further purification. Typical pressures in the source were estimated by measuring the ratio of $CH_5^+$ intensity to total ion intensity in the mass spectra of methane, following the work of Field,

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(1) See ref 2 in: Salomon, R. G.; Salomon, M. F. *J. Am. Chem. Soc.* **1976**, *98*, 7456.

(2) Maruyama, K.; Terada, K.; Yamamoto, Y. *J. Org. Chem.* **1981**, *46*, 5294 and references therein.

(3) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1650.

(4) For a review see: Joshi, K. C.; Pathak, V. N. *Coord. Chem. Rev.* **1977**, *22*, 37.

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**Table I.** Major Peaks Found in the High-Pressure Mass Spectra of the Various Unsaturated Reagent Gases

| reagent | *m/z* (% rel intens) |
|---|---|
| ethene | 69 (100), 41 (28) |
| propene | 97 (100), 39 (57), 57 (49), 85 (49), 55 (32), 69 (32), 67 (20), 43 (19), 56 (15) |
| allene | 39 (100), 79 (72), 131 (40), 119 (37), 91 (20), 81 (11) |
| propyne | 39 (100), 79 (76), 131 (54), 81 (28), 119 (26), 91 (17), 53 (14), 155 (14), 95 (11), 116 (11) |
| isobutene | 57 (100), 69 (20) |
| 1-butene | 69 (100), 57 (88), 71 (60), 83 (42), 56 (40), 39 (38), 125 (21), 70 (16), 67 (15), 84 (15) |
| *cis*-2-butene | 56 (100), 69 (74), 57 (48), 39 (20), 71 (18), 55 (17), 83 (15), 125 (11) |
| 1,3-butadiene | 39 (100), 67 (71), 109 (62), 53 (49), 93 (44), 80 (36), 121 (34), 145 (21), 79 (17), 81 (11), 134 (10) |

**Table II.** Assignment of Empirical Formulas to Peaks Found in Table I

| *m/z* | assignt | *m/z* | assignt |
|---|---|---|---|
| 39 | $C_3H_3^+$ | 84 | $C_6H_{12}^{+\cdot}$ |
| 41 | $C_3H_5^+$ | 85 | $C_6H_{13}^+$ |
| 43 | $C_3H_7^+$ | 91 | $C_7H_7^+$ |
| 53 | $C_4H_5^+$ | 93 | $C_7H_9^+$ |
| 55 | $C_4H_7^+$ | 95 | $C_7H_{11}^+$ |
| 56 | $C_4H_8^{+\cdot}$ | 97 | $C_7H_{13}^+$ |
| 57 | $C_4H_9^+$ | 109 | $C_8H_{13}^+$ |
| 67 | $C_5H_7^+$ | 116 | $C_9H_8^{+\cdot}$ |
| 69 | $C_5H_9^+$ | 119 | $C_9H_{11}^+$ |
| 70 | $C_5H_{10}^{+\cdot}$ | 121 | $C_9H_{13}^+$ |
| 71 | $C_5H_{11}^+$ | 125 | $C_9H_{17}^+$ |
| 79 | $C_6H_7^+$ | 131 | $C_{10}H_{11}^+$ |
| 80 | $C_6H_8^{+\cdot}$ | 134 | $C_{10}H_{14}^{+\cdot}$ |
| 81 | $C_6H_9^+$ | 145 | $C_{11}H_{13}^+$ |
| 83 | $C_6H_{11}^+$ | | |

Franklin, and Munson.[5] In this fashion a given ion gauge reading was taken to be proportional to the actual source pressure. Since the ion gauge was located about 10 cm from the source, the calibrated pressure exceeded the gauge reading by about 3 orders of magnitude. No attempt was made to calibrate the ion gauge response to the various hydrocarbon gases. Thus, to the degree that the ion gauge readings are not proportional to source pressures and to the degree that the gauge has a different inherent response to different hydrocarbons, the pressure we estimate may be expected to be in error. On the basis of a cross-correlation with published ion–molecule reactions for alkylsilanes,[6] we feel the possible error in the pressure estimate is well under 1 order of magnitude. For each run the ion gauge pressure reading was brought to $1.5 \times 10^{-4}$ torr (0.02 Pa) with the reagent gas. This corresponds to a nominal source pressure of 0.17 torr (23 Pa). The copper complexes were introduced through a solid inlet. The solid inlet probe temperature was ramped over approximately a 100 °C temperature range to effectively vary sample pressure. Based on ion gauge readings for this temperature range for complexes admitted to the mass spectrometer in the absence of reagent gas, the ratio of sample to reagent gas never exceeded 0.005, but actual ratios were not determined for each experiment. Nominal source temperature at the end of each run was 200 °C.

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) [$Cu(hfa)_2$], bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II) [$Cu(tfa)_2$], and bis(2,4-pentanedionato)copper(II) [$Cu(acac)_2$] were prepared by the method of Bertrand and Kaplan.[7] Purity was checked prior to use on a Varian-MAT CH-5 double-focusing mass spectrometer.

## Results

Table I lists the major peaks found in the spectra for the various reagent gases. Table II lists the assignment of these peaks to corresponding empirical formulas. These eight compounds show only five different base peaks at these pressures. Ethene and 1-butene share *m/z* 69 as the base peak. Allene, propyne, and 1,3-butadiene share *m/z* 39 as the base peak. Propene, isobutene, and *cis*-2-butene have *m/z* 97, 57, and 56 as their base peaks, respectively. Each molecule has as either the most intense or the second most intense peak in its mass spectrum an ion that might be envisoned as a protonated alkene or alkyne.

Table III lists peaks characteristic of the olefin chemical ionization spectra of the three complexes. Peaks normally found in the EI spectra of these compounds have been omitted with the exception of the molecular ion. In practice, several mass spectra were obtained in each run, each corresponding to a slightly higher sample pressure. Figure 1 displays the effects of increasing sample pressure, as indicated by increasing temperature of the solid probe, for selected ions of the three complexes in 1-butene. Effects are similar in other gases. $Cu(acac)_2$ and $Cu(tfa)_2$ show an increase in the percent relative intensity of ions with *m/z* greater than the molecular ion and an associated decrease in $ML_2^+$ and $ML_2H^+$ with increasing sample pressure. $Cu(hfa)_2$ does not exhibit the this tendency to the same degree. Fragmentation so predominates the spectrum of $Cu(hfa)_2$ that few molecular ions and protonated molecules survive to undergo condensation reactions.

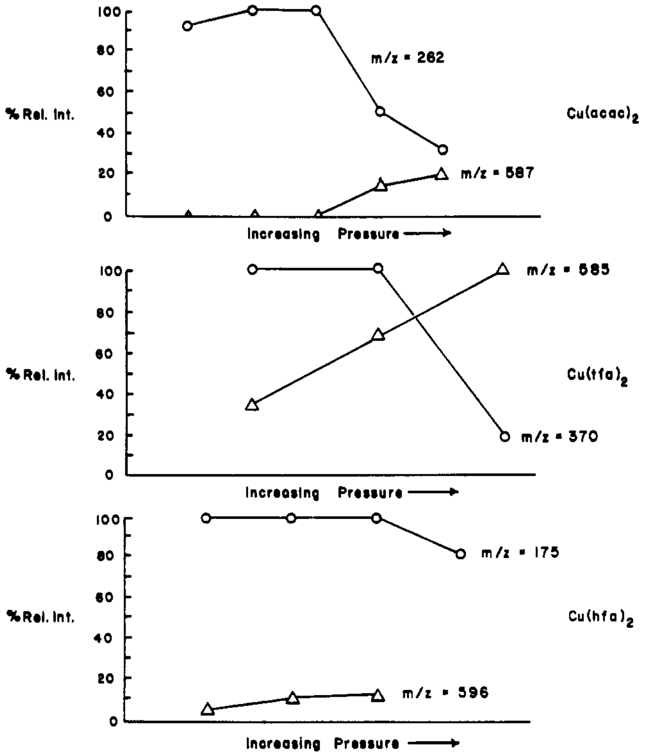

**Figure 1.** Selected ions in the mass spectra of copper complexes in 1-butene as a function of solid probe temperature. Since vapor pressure of the complexes increases with temperature, the variation is presented as a function of pressure, *F*(*P*).

Spectra selected for display in Table III represent those in which significant contributions to polymer ions are found with little or no change observed in the ratio of $MH^+/M^+$ from spectra obtained at lower sample pressures. Each row in the table consists of the *m/z* value of the lighter of the two copper isotope peaks, an assignment of empirical composition of the ion, and the relative intensity of that ion based on the largest metal-containing peak in the spectrum for that system set equal to 100.

When $Cu(hfa)_2$ is the sample, each reagent gas generates a mass spectrum in which the base peak or a peak of very similar intensity is a simple adduct of a Cu(I) and the reagent gas. For ethene and isobutene, this ion is $Cu^IR^+$, and for 1-butene, *cis*-2-butene, propene, propyne, allene, and 1,3-butadiene, this ion is $Cu^IR_2^+$. R in each case represents a molecule of the reagent gas.

When $Cu(tfa)_2$ is the sample, all reagent gases generate a mass spectrum in which the base peak is $Cu(tfa)_2H^+$, i.e. the protonated

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[5] Field, F. H.; Franklin, J. L.; Munson, M. S. B. *J. Am. Chem. Soc.* **1963**, *85*, 3575.

[6] Mayer, T. M.; Lampe, F. W. *J. Phys. Chem.* **1974**, *78*, 2422.

[7] Bertrand, J. A.; Kaplan, R. *Inorg. Chem.* **1966**, *5*, 489.

**Table III.** Selected Results of Olefin CI of Copper(II) β-Diketonates

| | | ligand (L) | | | | | |
|---|---|---|---|---|---|---|---|
| | | hfa | | tfa | | acac | |
| reagent (R) | ion type | *m/z* | RI[a] | *m/z* | RI | *m/z* | RI |
| ethene | $CuR^+$ | 91 | 98.6 | 91 | 14.5 | 91 | 1.6 |
| | $CuC_3H_5^+$ | 104 | 13.9 | 104 | 4.8 | | |
| | $CuR_2^+$ | 119 | 35.9 | 119 | 1.9 | 119 | 0.7 |
| | $Cu(L-CF_3)R^+$ | 229 | 75.2 | 175 | 18.6 | | |
| | $Cu(L-CH_3)R^+$ | | | | | 175 | 3.5 |
| | $Cu(L-CH_3)R_2^+$ | | | | | 203 | 16.7 |
| | $Cu(L-H)R^+$ | 297 | 29.4 | 243 | 6.4 | | |
| | $CuLR^+$ | 298 | 14.0 | | | | |
| | $CuL_2^+$ | 477 | 84.8 | 369 | 91.8 | 261 | 100 |
| | $CuL_2H^+$ | 478 | 66.8 | 370 | 100 | 262 | 62.5 |
| | $CuL_2C_3H_5^+$ | 518 | 20.9 | 410 | 34.9 | 302 | 12.7 |
| | $Cu_2L_2^+$ | 540 | 28.9 | 432 | 11.0 | 324 | 2.7 |
| | $Cu_2L_2R^+$ | 568 | 12.0 | | | | |
| | $Cu_2L_3^+$ | 747 | 27.5 | 585 | 29.5 | 423 | 9.7 |
| 1-butene | $CuR^+$ | 119 | 18.4 | 119 | 16.2 | 119 | 10.1 |
| | $CuR_2^+$ | 175 | 100 | 175 | 9.3 | 175 | 4.7 |
| | $CuC_2H_4R^+$ | | | 147 | 11.2 | | |
| | $Cu(L-CF_3)R^+$ | 257 | 11.0 | 203 | 19.4 | | |
| | $Cu(L-H)R^+$ | 325 | 4.7 | 271 | 16.3 | | |
| | $CuLR^+$ | 326 | 5.3 | | | | |
| | $Cu(L-H)R_2^+$ | 381 | 2.6 | | | | |
| | $CuL_2^+$ | 477 | 1.3 | 369 | 45.2 | 261 | 100 |
| | $CuL_2H^+$ | 478 | 2.0 | 370 | 100 | 262 | 95.8 |
| | $CuL_2C_3H_3^+$ | 516 | 21.8 | | | | |
| | $CuL_2C_3H_5^+$ | | | 410 | 7.3 | 302 | 4.1 |
| | $Cu_2L_2$ | 540 | 6.2 | 432 | 5.6 | | |
| | $Cu_2L_2R^+$ | 596 | 10.9 | 488 | 6.4 | | |
| | $Cu_2L_3^+$ | 747 | 16.4 | 585 | 32.6 | 423 | 11.9 |
| *cis*-2-butene | $CuR^+$ | 119 | 41.9 | 119 | 10.0 | 119 | 7.6 |
| | $CuR_2^+$ | 175 | 100 | 175 | 15.6 | 175 | 4.7 |
| | $Cu(L-CF_3)R^+$ | 257 | 8.6 | 203 | 18.2 | | |
| | $Cu(L-H)R^+$ | | | 271 | 27.7 | | |
| | $CuLR^+$ | 326 | 21.0 | 272 | 11.9 | | |
| | $CuL_2^+$ | | | 369 | 43.3 | 261 | 100 |
| | $CuL_2H^+$ | 478 | 1.4 | 370 | 100 | 262 | 84.8 |
| | $CuL_2C_3H_3^+$ | 516 | 3.6 | | | | |
| | $CuL_2C_3H_5^+$ | | | 410 | 5.5 | | |
| | $CuL_2HR^+$ | | | | | 316 | 8.9 |
| | $Cu_2L_2^+$ | 540 | 1.3 | 432 | 5.0 | 324 | 4.8 |
| | $Cu_2L_2R^+$ | 596 | 1.4 | 488 | 15.2 | 380 | 5.1 |
| | $Cu_2L_3^+$ | 747 | 3.4 | 585 | 73.4 | 423 | 79.8 |
| isobutene | $CuR^+$ | 119 | 100 | 119 | 3.2 | 119 | 17.2 |
| | $CuR_2^+$ | 175 | 22.1 | 175 | 8.9 | 175 | 2.9 |
| | $Cu(L-CF_3)R^+$ | 257 | 15.9 | 203 | 6.5 | | |
| | $Cu(L-H)R^+$ | | | 271 | 24.7 | | |
| | $CuLR^+$ | 326 | 26.9 | 272 | 37.3 | | |
| | $CuL_2^+$ | | | 369 | 7.3 | 261 | 100 |
| | $CuL_2H^+$ | 478 | 7.0 | 370 | 100 | 262 | 61.5 |
| | $CuL_2C_3H_5^+$ | 518 | 2.3 | 410 | 2.4 | | |
| | $CuL_2RH^+$ | | | | | 316 | 3.3 |
| | $Cu_2L_2^+$ | 540 | 5.7 | 432 | 0.1 | 324 | 6.0 |
| | $Cu_2L_2R^+$ | 596 | 1.7 | 488 | 1.1 | | |
| | $Cu_2L_3^+$ | 747 | 2.7 | 585 | 23. | 423 | 11.8 |
| propene | $CuR^+$ | 105 | 18.0 | 105 | 12.4 | 105 | 10.0 |
| | $CuR_2^+$ | 147 | 100 | 147 | 15.4 | 147 | 10.0 |
| | $Cu(L-CF_3)R^+$ | 243 | 12.1 | 189 | 17.3 | | |
| | $Cu(L-CH_3)R^+$ | | | | | 189 | 11.1 |
| | $Cu(L-H)R^+$ | 311 | 15.0 | 257 | 19.1 | 203 | 11.6 |
| | $CuLR^+$ | 312 | 12.2 | | | | |
| | $Cu(L-H)R_2^+$ | 353 | 4.7 | | | | |
| | $CuL_2^+$ | 477 | 1.4 | 369 | 31.8 | 261 | 87.3 |
| | $CuL_2H^+$ | 478 | 4.1 | 370 | 100 | 262 | 100 |
| | $CuL_2C_3H_3^+$ | 516 | 6.5 | | | | |
| | $CuL_2C_3H_5^+$ | | | 410 | 8.9 | 302 | 7.2 |
| | $Cu_2L_2^+$ | 540 | 3.8 | 432 | 3.8 | 324 | 6.8 |
| | $Cu_2L_2R^+$ | 582 | 5.0 | 474 | 6.5 | 366 | 6.2 |
| | $Cu_2L_3^+$ | 747 | 10.9 | 585 | 33.7 | 423 | 98.9 |
| propyne | $CuR^+$ | 103 | 79.0 | 103 | 45.1 | 103 | 51.4 |
| | $CuR_2^+$ | 143 | 100 | 143 | 44.7 | 143 | 11.6 |
| | $Cu(L-CF_3)R^+$ | 241 | 3.3 | 187 | 55.4 | | |
| | $Cu(L-CH_3)R^+$ | | | | | 187 | 17.4 |
| | $Cu(L-H)R^+$ | 309 | 2.6 | 255 | 16.7 | | |
| | $CuLR^+$ | 310 | 8.3 | 256 | 16.8 | 202 | 12.1 |
| | $Cu(L-H)R_2^+$ | 349 | 1.9 | | | | |
| | $CuL_2^+$ | | | 369 | 63.6 | 261 | 74.5 |
| | $CuL_2H^+$ | | | 370 | 100 | 262 | 100 |
| | $CuL_2C_3H_3^+$ | 516 | 1.0 | | | 300 | 8.2 |
| | $Cu_2L_2^+$ | | | 432 | 13.0 | 324 | 0.8 |
| | $Cu_2L_2R^+$ | | | 472 | 33.7 | 364 | 8.2 |
| | $Cu_2L_3^+$ | | | 585 | 59.6 | 423 | 12.5 |
| allene | $CuR_2^+$ | 143 | 100 | 143 | 13.7 | 143 | 4.8 |
| | $Cu(L-CF_3)R^+$ | 241 | 21.5 | 187 | 28.6 | | |
| | $Cu(L-CH_3)R^+$ | | | | | 187 | 10.8 |
| | $Cu(L-H)R^+$ | 309 | 16.3 | 255 | 12.2 | | |
| | $CuLR^+$ | 310 | 10.7 | | | 202 | 8.8 |
| | $Cu(L-H)R_2^+$ | 349 | 8.7 | | | | |
| | $CuL_2^+$ | | | 369 | 61.4 | 261 | 75.8 |
| | $CuL_2H^+$ | 478 | 4.9 | 370 | 100 | 262 | 100 |
| | $CuL_2C_3H_3^+$ | 516 | 9.2 | | | 300 | 9.5 |
| | $Cu_2L_2^+$ | 540 | 4.3 | 432 | 2.5 | | |
| | $Cu_2L_2R^+$ | 580 | 10.9 | 472 | 1.1 | 364 | 5.8 |
| | $Cu_2L_3^+$ | 747 | 12.8 | 585 | 7.9 | 423 | 51.8 |
| 1,3-butadiene | $CuR^+$ | 117 | 96.0 | 117 | 22.4 | 117 | 37.7 |
| | $CuR_2^+$ | 171 | 100 | 171 | 16.5 | 171 | 8.3 |
| | $Cu(L-CF_3)R^+$ | 255 | 15.5 | 201 | 40.0 | | |
| | $Cu(L-CH_3)R^+$ | | | | | 201 | 16.1 |
| | $Cu(L-H)R^+$ | | | 269 | 46.5 | | |
| | $CuLR^+$ | 324 | 30.1 | | | | |
| | $CuL_2^+$ | | | 369 | 28.8 | 261 | 91.7 |
| | $CuL_2H^+$ | | | 370 | 100 | 262 | 100 |
| | $CuL_2C_3H_3^+$ | | | | | 300 | 16.5 |

[a] RI = percent relative intensity.

molecule. The protonated molecule is similarly important when $Cu(acac)_2$ is the sample. It is found as the base peak when propene, propyne, and allene are the reagent gases, and it is found as an intense ion in the other reagent gases. When the reagent is ethene, 1-butene, *cis*-2-butene, or isobutene, however, the base peak in $Cu(acac)_2$ mass spectra is the molecular ion, $Cu(acac)_2^{+\cdot}$. In general, self-reaction peaks for a given sample appear related to the prominence of the molecular ion or the protonated molecule. For example, the ion $Cu_2L_3^+$ is always more important when L is tfa or acac than when L is hfa.

Other ions that appear in all samples for all reagent gases may be represented as $Cu^I(L-X)R^+$ where L = hfa, tfa, or acac, X = $CF_3\cdot$, $CH_3\cdot$, or $H\cdot$, and R = any of the eight reagent gases used in this investigation. For $Cu(hfa)_2$ in propene, propyne, and allene, the ion $Cu^I(L-H)R_2^+$ is also observed.

The condensate ion, $Cu^{II}Cu^IL_2R^+$, an association complex of a metal-containing ion with a reagent gas, is observed for all three copper chelates in at least five different reagent gases. In contrast, a condensate between a reagent ion and a copper chelate molecule, $CuL_2C_3H_6^+$, is observed for those reagent gases that have an important contribution of $C_3H_3^+$ to their mass spectrum. A comparable ion, $CuL_2C_3H_5^+$, is also observed for at least one copper chelate in all of the monoolefins except isobutene.

The only ion that occurs in all reagent gases for at least one copper chelate and may be identified as a Cu(II) complex with neutral reagent molecule is $Cu^{II}LR^+$. This ion is observed in all reagent gases for $Cu(hfa)_2$, in *cis*-2-butene, isobutene, and propyne for $Cu(tfa)_2$, and in propyne and allene for $Cu(acac)_2$.

While not reported in Table III, a small peak is observed at *m/z* 500 in the mass spectra obtained for $Cu(hfa)_2$ in all of the reagent gases except 1,3-butadiene. This peak is assigned to the fragment formed by the loss of the equivalent of two $CF_3$ and $Cu^IH_2CO_2$ from $Cu_2(hfa)_3^+$. A comparable process in the mass spectrum of $Cu(hfa)_2$ has not been reported.[8] However, exam-

**Table IV.** Ionization Potentials (eV) for Reagent and Sample Gases and Appearance Potentials for the Lowest Energy Dissociation Process[a]

| molecule | IP | AP(M–R)$^+$ | molecule | IP |
|---|---|---|---|---|
| Cu(acac)$_2$ | 8.31 | 10.9 | $CH_3CCH$ | 10.36 |
| Cu(tfa)$_2$ | 9.05 | 11.5 | $CH_2CHCH_2CH_3$ | 9.58 |
| Cu(hfa)$_2$ | 9.86 | 11.6 | *cis*-$CH_3CHCHCH_3$ | 9.13 |
| $C_2H_4$ | 10.50 | | $CH_2C(CH_3)_2$ | 9.23 |
| $C_3H_6$ | 9.73 | | $CH_2CHCHCH_2$ | 9.07 |
| $CH_2CCH_2$ | 10.19 | | | |

[a] Data for the copper complexes is from ref 10. Data for the hydrocarbons is from: Kiser, R. W. "Introduction to Mass Spectrometry and Its Applications"; Prentice-Hall: Englewood Cliffs, NJ, 1965.

ination of the EI spectrum of Cu(hfa)$_2$ shows the presence of the analogous ion formed from Cu(hfa)$_2^+$ at *m/z* 230 with a relative intensity of 47.7. This important peak was doubtlessly omitted from previous discussions because it is not accompanied by a second copper isotope peak at *m/z* 232 as would be characteristic of an ion containing copper, which, of course, this ion does not.

## Discussion

The results displayed in the previous section lead readily to several conclusions. The mechanism leading to ionization and dissociation of $CuL_2$ is more exoenergic for hfa complexes than for either the tfa or acac complexes. At least some of the copper initially in the formal oxidation state of +2 is reduced as a result of the ionization-induced dissociation to a formal oxidation state of +1. Once Cu(I) is formed it reacts readily with a variety of alkenes and alkynes to form association complexes. It is unlikely, under the conditions of these experiments, to form complexes that have more than two ligands associated with a given copper ion. Reduced copper ions are observable in binuclear as well as mononuclear complexes, and Cu(I) in binuclear complexes also exhibits a tendency to form olefin complexes.

While chemiionization systems such as those discussed here are complex and hypotheses concerning mechanisms of ionization are necessarily speculative, it is instructive to examine the limitations on possible participants in those mechanisms due to the associated energetics.

Table IV provides a list of the ionization potentials of the copper complexes and the reagent gases used in this study. This table also lists the appearance potentials of the lowest energy dissociation process for each of the complexes. Since in no case is the predominate ion in the reagent gas a molecular ion, one may assume that the molecular ionization potential of the reagent molecule serves as an upper limit to the energy available to the sample via charge transfer. If this assumption is accepted, it becomes immediately obvious from Table IV that dissociation of the molecular ion is energetically forbidden if that ion is formed by charge transfer.

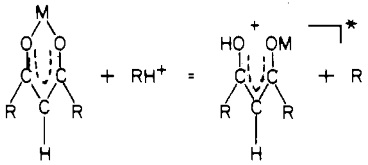
Another mechanism by which dissociation might be initiated has been suggested by Hunt and Sethi.[9] They estimate that 10% of the electrons in a CI source may have energies of 6 eV or more and that, under the condition of low proton-transfer rates, these electrons may serve to ionize sample at a large enough rate to contribute molecular ions to the mass spectrum. While molecular ions are present to a significant degree in the olefin CI mass spectra of Cu(acac)$_2$, the reported ionization potential for this molecule is 8.3 eV. The energy required for even the lowest energy route to dissociation is 10.9 eV.[10] Further, the ratio of $M^+/MH^+$ appears independent of sample pressure until that pressure rises far enough to generate a significant population of metal chelate cluster ions. At this point the ratio tends to increase. Direct EI may begin to contribute to the $M^{+\cdot}$ intensity at higher pressures of sample, while at lower sample pressures charge transfer is a more likely source. Almost certainly there would be too few electrons with energies high enough to contribute ion intensity to the observed dissociation patterns.

Because there is too little energy to induce dissociation if the molecular ion is formed by charge exchange and because the probability is very low that dissociation may be induced by direct electron impact, a mechanism for ionization of $CuL_2$ that must figure prominently for all three sample complexes and all reagent gases is that represented by eq 1. In eq 1 the first formula

$$RH^+ + CuL_2 = R + CuL_2H^+ \qquad (1)$$

represents any of the protonated alkynes that figure so prominently in the mass spectra of the reagents used as displayed in Table I. Direct evidence for the formation of $CuL_2H^+$ for all experiments except Cu(hfa)$_2$ in propyne and 1,3-butadiene is given in Table III. In the two cases where Cu(hfa)$_2$H$^+$ is not observed, it seems reasonable that it is absent by reason of its rapid dissociation rather than failure to form by means of eq 1.

We imagine dissociation of $CuL_2H^+$ to be induced by the protonation of the unsaturated ketonate ligand:



If such a model has validity, then crude comparisons of this step with measurement of the proton affinity of olefinic carbonyl compounds may be made.[11] Values typical of the few measurements made on β-carbonyl compounds range from 190 to 200 kcal/mol.[11a] Proton affinities for the various possible R (alkane, alkene, alkyne) range from 125 to 195 kcal/mol.[11b] Thus, while it is not possible to assign a particular precursor species from the numerous possibilities present in the high-pressure reagent gases, it is apparent that from that range of species proton transfer to $CuL_2$ with sufficient exothermicity to induce dissociation is a real possibility. We recognize that β-carbonyl compounds may not be strictly analogous to metal β-diketonates but propose this illustration to suggest that our observation of rather extensive dissociation of the copper chelates via olefin chemical ionization is reasonable.

The variation in importance of the protonated molecule among the three copper chelates is likely related to the relative stability of the chelate structure as a function of fluorine substitution on the ligand. The increased difficulty of preparing the chelates as the degree of fluorination increases is well-known, and we infer from this that the metal chelate is more stable relative to the metal ion and diketone for Cu(acac)$_2$ than for Cu(hfa)$_2$. On the basis of limited evidence,[11b] the proton affinity of fluorinated compounds appears to be greater than that of comparable nonfluorinated species. One might interpret the considerably more extensive dissociation of the hfa complex as reflecting the greater energy release associated with proton transfer. Certainly this would not be the case if ionization were induced by electron impact or charge transfer, as the higher appearance potential for dissociation in the hfa complex should inhibit dissociation at lower energies.

In numerous instances, the mass spectra of metal complexes have been rationalized in terms of ligand-to-metal electron transfer, i.e. formal reduction of the metal occurring as a result of the dissociation process. Such conclusions are typically based on the observation that radical ions tend to eliminate odd-electron fragments while even-electron ions tend to eliminate even-electron fragments. Accumulated evidence based on this assumption has lead to a formal assignment of net oxidation number to those fragments commonly associated with metal β-diketonate mass spectra.[4] The oxidation numbers necessary for this discussion are as follows: L, −1; L–X, 0 [X = $CF_3\cdot$, $CH_3\cdot$, H·]; H, +1; R, 0 [R = any of the eight reagent gases]. From these assignments, it is possible to determine the appropriate oxidation number for the

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copper in each of the ions listed in Table III. Each ion listed in Table III with $m/z$ less than that of $\mathrm{M^{+\cdot}}$, the molecular ion, with the exception of $\mathrm{Cu^{II}LR^+}$ would have the copper assigned an oxidation state of +1. If one accepts the oxidation states assigned to ligand moieties as reasonable, then it must be concluded that reduction of the copper from the original Cu(II) to Cu(I) is an important process in the olefin CI-induced reactions of $\mathrm{Cu^{II}L_2}$.

Extending the argument to include those ions with $m/z$ greater than $\mathrm{M^{+\cdot}}$, two fragments of ion cluster species may be identified as having resulted from an internal redox reaction: $\mathrm{Cu^{I}Cu^{II}L_2{}^+}$ and $\mathrm{Cu^{I}Cu^{II}L_2R^+}$.

It is of interest that the observed ratio of ion intensities for Cu(II) to Cu(I) species associated with reagent gas never exceeds 0.85 and is zero in 11 of the 24 examples in Table III. This is consistent with the previous observation that Cu(II) olefin adducts are considerably more labile than those of Cu(I).[12] Salomon and Kochi have observed copper(I) olefin complexes in solution-phase chemistry,[13] and that observation has been supported by Schwendiman and Kutal.[14]

The analogy between macroscopic reaction systems and the microreactor that is the source of a mass spectrometer is continued by noting from Table III the overwhelming predominance of ions in which the ratio of ligand to copper does not exceed a value of 2.

There are basically three types of ions found in the olefin CI mass spectra of these complexes with $m/z$ greater than that of the molecular ion or protonated molecule. These are simple cluster ions formed by $\mathrm{CuL_2{}^+}$ and $\mathrm{CuL_2}$ to give $\mathrm{Cu_2L_4{}^+}$ and their dissociation fragments, ions formed by the condensation of a prominent hydrocarbon fragment from the reagent gas with $\mathrm{CuL_2}$ to give $\mathrm{CuL_2R^+}$, and ions formed by the condensation of an ion cluster with a neutral reagent olefin. Peaks of the first type have not been noted in previous CI studies but have been observed by Schildcrout in high-pressure mass spectra of $\mathrm{Cu(hfa)_2}$.[15] Schildcrout also observed a peak corresponding to $\mathrm{Cu_3(hfa)_4{}^+}$, but the mass of this ion is beyond the range used in this study. The presence of these peaks in the high-pressure mass spectra of the neat complexes is attributed to ion–molecule reactions between the molecular ion and the parent molecule. Presumably, the high pressure of isobutene in the CI source allows a similar process to occur in this system. Even though the absolute concentration of the metal complex is relatively low, its residence time in the high-pressure source is long enough to allow the condensation reaction to occur.

At least two methods have been reported recently for producing metal ions that then are allowed to react with organic additives. The methods used were the generation of $\mathrm{Cr^+}$, $\mathrm{Fe^+}$, $\mathrm{Co^+}$, and $\mathrm{Ni^+}$ from the appropriate neutral metal carbonyl by EI[16] and the laser generation of metal ions via impact of the beam on the appropriate metal foil. Freiser and others have reported the generation and reactions of $\mathrm{Cu^+}$, $\mathrm{Ni^+}$, and $\mathrm{Fe^+}$ ions, using this method and ICR or FT-MS.[17] Our method appears complementary to these techniques.

**Registry No.** $\mathrm{[Cu(hfa)_2]}$, 14781-45-4; $\mathrm{[Cu(tfa)_2]}$, 14324-82-4; $\mathrm{[Cu(acac)_2]}$, 13395-16-9; Cu, 7440-50-8; ethene, 74-85-1; propene, 115-07-1; allene, 463-49-0; propyne, 74-99-7; 2-methylpropene, 115-11-7; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; 1,3-butadiene, 106-99-0.

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# Polyether Derivatives of Zirconium Phosphate

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γ-Zirconium phosphate, $\mathrm{Zr(HPO_4)_2{\cdot}2H_2O}$, with a 12.2-Å interlayer spacing is known to react with ethylene glycol solutions to form glycol esters of the zirconium phosphate. It has now been shown that the α polymorph with a smaller interlayer distance (7.6 Å) also behaves similarly. With highly crystalline samples of α-zirconium phosphate, reaction takes place only at the surface. However, if the interlayer distance is first increased so that ethylene oxide can diffuse into the interior, complete reaction ensues. Less crystalline samples were found to react directly with ethylene oxide, either as a gas or as a solution. Attempts to form long polyether chains by direct reaction were unsuccessful. However, by the preparation of first polyether phosphates and then the reaction of these compounds with Zr(IV) species, polyether analogues of α-zirconium phosphate were prepared. These derivatives incorporate electrolytes and form novel colloidal dispersions.

## Introduction

Zirconium bis(monohydrogen orthophosphate) hydrate, $\mathrm{Zr(HPO_4)_2{\cdot}H_2O}$, is a crystalline, insoluble ion exchanger with a layered structure.[2] It has an interlayer spacing of 7.6 Å with zeolite-like cages between the layers. The free space leading into the cages is only large enough to allow a sphere of about 2.6 Å to pass unobstructed.[3] A second form of zirconium phosphate, with an interlayer spacing of 12.2 Å, is also known.[4] It has the composition $\mathrm{Zr(HPO_4)_2{\cdot}2H_2O}$, and while its structure is unknown, the layers are certainly different than those of the monohydrate. It will be referred to as γ-ZrP whereas the monohydrate is termed α-ZrP. Titration of α-ZrP with NaOH yields a half-exchanged phase, $\mathrm{ZrNaH(PO_4)_2{\cdot}5H_2O}$. On removal of the $\mathrm{Na^+}$ with acid the original α-ZrP is not obtained. Rather, a higher hydrate with interlayer spacing of 10.4 Å, termed θ-ZrP, is formed.[3]

Several years ago, Yamanaka reported that γ-ZrP reacts with ethylene oxide to form derivatives of the type $\mathrm{Zr(HPO_4)_{2-\mathit{x}}(O_3POCH_2CH_2OH)_{\mathit{x}}{\cdot}H_2O}$.[5] The interlayer spacing for the compound with $x = 2$ is 18.4 Å. Propylene oxide was also found to react similarly, but only half the phosphate groups were esterified.[6] In addition, these complexes were found to undergo ester interchange on refluxing with other organic phosphates and/or phosphoric acid.[7,8] Yamanaka was unable to obtain

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