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Halide Ion and Radical Reactions of Zinc(II) β-Ketoenolates in the Gas Phase

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Introduction

Applications of mass spectrometric methods to the study of negative ionisation processes involving metal complexes in the gas phase recently have uncovered much useful fundamental chemistry under conditions which are unencumbered by solvation phenomena [1–3]. Both electron attachment and negative ion/molecule processes can be examined under negative chemical ionisation (NCI) conditions [4–9]. Moreover, by the use of this approach, the selectivity of bimolecular encounters between nucleophiles and reactive Lewis acid metal centres can be established by ionic reaction product identifications and distributions and usefully coupled with rationalisations involving electronic and structural features of the precursor metal complexes. Competitive electron attachment processes can also be identified [4]. As part of a programme focused on the electron attachment and ion–molecule chemistry of metal complexes in the gas phase, novel reactions involving radical additions and ligand displacements have now been identified in the chloride ion NCI mass spectra of the zinc(II) complexes Zn(RCOCHCOR′)$_2$, ZnL$_2$, with R,R′ = CH$_3$; tert.-Bu; R = CH$_3$, R′ = CF$_3$; R,R′ = CF$_3$; respectively compounds **I–IV**.

Experimental

The zinc(II) complexes were prepared and recrystallised by established methods [10, 11]. Reagent grade dichlorodifluoromethane (Freon-12, >99%, Pacific Chemical Industries) was the preferred reagent gas whose purity was established from its positive ion mass spectrum. Under negative ionisation conditions 99% of the total ion current was carried by Cl$^-$. AR grade dichloromethane, trichloromethane, tetrachloromethane and chloroethane were alternative sources of Cl$^-$ and were purified by freeze–pump–thaw cycles before their regulated admission to the ion source. Bromotrifluoromethane (Freon-13B1) was used as the reagent gas for the generation of bromide ions which carried in excess of 99% of the total ion current.

TABLE I. Percentage of the Total Ion Current carried by Significant Ions in the Cl$^-$ NCI Mass Spectra of Zn(RCOCHCOR′)$_2$, ZnL$_2$, Complexes; **I–IV**[a,b,c].

Ions	R·····CH$_3$	t-Bu	CH$_3$	CF$_3$
	R′·····CH$_3$	t-Bu	CF$_3$	CF$_3$
	I	II	III	IV
[ZnL$_2$Cl]$^-$ (%ΣI)	55	52	55	27
[ZnL$_2$]$^{-\cdot}$	–	–	6	33
[ZnLCl$_2$]$^-$	27	29	5	0.6
[ZnLCl]$^{-\cdot}$	–	–	1	0.5
[ZnCl$_3$]$^-$	8	12	1	0.1
[L]$^-$	2	0.8	12	17
[L – H$^\cdot$ + X$^\cdot$]$^-$ [d]	4	0.5	10	5
Ligand fragments[e]	0.1	–	4	7
Rearrangement ions[f]	0.1	–	1	5
[Zn$_x$L$_y$Cl$_z$]$^-$ [g]	2	5	0.1	0.1
[ZnL$_2$ + A]$^-$ [h]	1	0.3	5	5
[ZnL$_2$ – H]$^-$	0.4	0.1	–	–
[Cl]$^-$	i	i	i	i

[a] All isotopes of all atoms in the various clusters are included. [b] Ion source temperature 100 °C, primary electron beam energy 50 eV, emission current 500 μA, accelerating voltage 4 kV, repeller 0–IV, reagent gas pressure in ion source ~0.1 Torr. [c] Sample sizes in all cases *ca.* 100 μg. [d] X$^\cdot$ = Cl or L. [e] Predominantly [L – H]$^{-\cdot}$, [RCOCHCO]$^{-\cdot}$ where R = CF$_3$ and/or CH$_3$, and [CF$_3$CO$_2$]$^-$ [19]. [f] [ZnLF$_2$]$^-$, [ZnLF]$^{-\cdot}$ [19] and [ZnL$_2$F]$^-$. [g] x = 2 and 3, y + z = 2x + 1; *e.g.* [Zn$_2$Cl$_5$]$^-$, [Zn$_3$Cl$_7$]$^-$, [Zn$_2$LCl$_4$]$^-$ and [Zn$_3$LCl$_6$]$^-$. [h] A includes (L – H$^\cdot$ + Cl$^\cdot$], L, [L – H], [RCOCHCO] with R = CF$_3$ and/or CH$_3$, and [CF$_3$CO$_2$]. [i] Relative to a normalised %Σ for each complex of 100: **I** = 47, **II** = 35, **III** = 46, **IV** = 38.

Negative chemical ionisation mass spectra were obtained on a VG MM-16F single focusing mass spectrometer fitted with a dual EI/CI source (common also to VG 70–70 series instruments), under conditions described previously [12–14] or specified in Table I. Ion source pressures were monitored routinely by a source housing ionisation gauge which was calibrated regularly against a type 170/315-BHS-10 MKS Baratron capacitance manometer system attached directly to the ionisation chamber [9]. The NCI mass spectra reported in Table I were obtained from 2 s scans over the m/z range 10–770 during the selective ion monitoring of the most intense ion, that is either [ZnL$_2$Cl]$^-$ or [ZnLCl$_2$]$^-$, during the total evaporation and ionisation of metal complex samples into the plasma containing chloride ions [8, 15]. An alternative method used for the emission dependence experiments was to monitor the decrease in Cl$^-$ abundance. Sample sizes were comparable for **I–IV** at *ca.* 3 X 10^{-7} mol, and were

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delivered quantitatively into the ionisation chamber on dished Vespel rods on a solids probe and gave total evaporation times within the source of 50–100 s [8, 16]. Steady CF_2Cl_2 ion source pressures of 0.05–0.1 Torr were typically used which provided Cl^- yields within the ionisation chamber of *ca.* 7 X 10^{10} ions cm^{-3} before the introduction of the metal complexes. By standardisation of these and other ion source parameters as shown in Table I, reproducibility of the mass spectra could be achieved. Computer simulated ion cluster patterns were used to verify unequivocally ion assignments where both zinc and chlorine were present.

Results and Discussion

Table I lists the ionic products identified from the chloride ion NCI mass spectra of **I–IV**. In contrast to the highly specific reaction of chloride ions with zinc(II) dithiophosphato complexes to yield $[M + Cl]^-$ adduct ions [3], additional ions in high abundances have now been observed with the β-ketoenolato complexes, namely the molecular negative ion $[M]^{-\cdot}$ or $[ZnL_2]^{-\cdot}$, as well as $[ZnLCl_2]^-$, $[ZnLCl]^{-\cdot}$, $[ZnCl_3]^-$ and cluster ions in low abundances containing two and three zinc atoms. The adduct ion $[ZnL_2Cl]^-$ also formed by **I–IV** is a product consistent with the known Lewis acid properties of these complexes and the established stability of zinc(II) in a pentacoordinated environment [17, 18].

The tendency of **I–IV** to undergo resonance electron capture is dependent upon the level of fluorination present in the ligand, as evidenced by the increasing ion currents carried by $[M]^{-\cdot}$ for **I–IV**. Whereas **I** and **II** displayed a negligible cross section for resonance electron capture in these and also in separate experiments, fluorination of the ligands of **III** and **IV** would appear to have the effect of lowering the energy of the ligand-based LUMO. Coupled with the fact that electron capture may be up to three orders of magnitude more rapid than diffusion controlled ion–molecule reactions [4], this effect will favour electron capture for compounds such as these where negative ionisation may occur by competing electron capture and ion–molecule reactions. The sharp decrease in the $[ZnL_2Cl]^-:[ZnL_2]^{-\cdot}$ ratio given over the series **I–IV** supports this conclusion. For all compounds total evaporation and ionisation of closely similar sample sizes resulted in the observation of similar total ion currents. Taken together with the percentages of the total ion currents given by the $[ZnL_2Cl]^-$ adduct species, it can be concluded that increasing the level of fluorination in the β-ketoenolate ligands does not contribute markedly to an enhanced cross section for Cl^- capture by the metal Lewis acid centres.

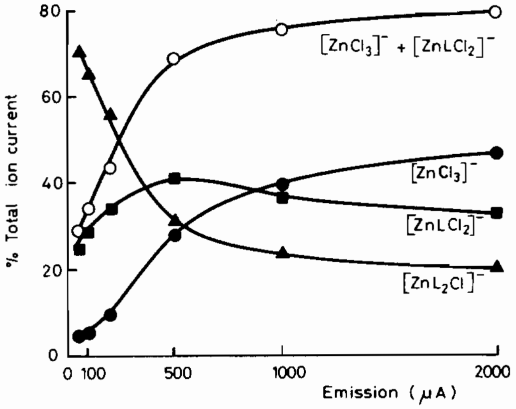
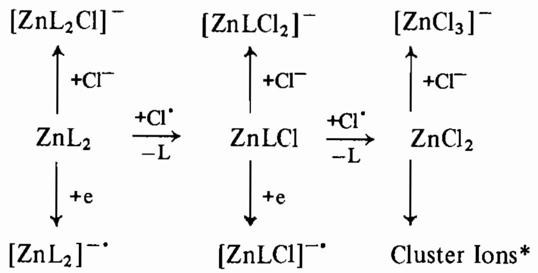


Fig. 1. Emission dependence of the principal ionic products given in the CF_2Cl_2 NCI mass spectrum of $Zn(CH_3COCHCOCH_3)_2$, ZnL_2, **I**.

Particularly noteworthy is the observation of $[ZnLCl_2]^-$, $[ZnLCl]^{-\cdot}$ and $[ZnCl_3]^-$ ions in the spectra of **I–IV**, which are indicative of the partial and complete displacement of the β-ketoenolate ligands from the coordination sphere of the metal. These ions are also formed in similar abundances by the use of CH_2Cl_2, $CHCl_3$ and CCl_4 as alternative sources of Cl^- reagent ions [7]. However, enhanced abundances of $[M]^{-\cdot}$ are observed with CH_2Cl_2 and C_2H_5Cl while negative cluster ions of $CHCl_3$ tend to complicate the Cl^- spectra when this compound is used as the reagent gas. Processes involving ligand displacement in the form of $[L]^-$ leading to the formation of $[ZnLCl_2]^-$ and $[ZnCl_3]^-$ may be discounted because of the relatively low abundances of $[L]^-$ compared with the metal-containing ions, particularly for **I** and **II**. Detection of $[L]^-$ species for **III** and **IV** is consistent with the known ion decomposition reactions of the molecular negative ions derived from these compounds, *viz.*, $[ZnL_2]^{-\cdot} \rightarrow [L]^- + Zn^{I}L$, whereas $[ZnLF_2]^-$ and $[ZnLF]^{-\cdot}$ are known rearrangement ions [19]. However, the formation of $[ZnLCl]^{-\cdot}$, $[ZnLCl_2]^-$ and $[ZnCl_3]^-$ can be rationalised in terms of ligand displacement as $L^\cdot$ prior to ion formation by chlorine radicals which are known to be produced by electron impact upon CF_2Cl_2, particularly in the reaction $CF_2Cl_2 + e \rightarrow CF_2Cl^+ + Cl^\cdot + 2e$ [15]. Under equivalent positive chemical ionisation conditions the principal ions formed from CF_2Cl_2 are found to be CF_2Cl^+ (84% ΣI) and $CFCl_2^+$ (15% ΣI), whereas the CF_2Cl^+: Cl^- ratio has been determined to be 0.7 ± 0.2. Since non-charged species are not subject to loss mechanisms which deplete the ion source population of charged species [20], it can be reasonably assumed that the $Cl^\cdot$ level within the ion source for these experiments approximated to or exceeded that of the chloride ions. Rapid molecule/radical reactions within a Cl plasma prior to negative ionisation have recently become well recognised in cases where the radicals are carbon centered [20–23]. Such reactions are expected to be enhanced when the radical population in the ion source is raised relative to the ion and electron populations by increasing the emission current up to the space-charge controlled limit. This is the case with **I–IV** and it is shown for **I** in Fig. 1 that increasing the electron emission current (and hence the ion source $Cl^{\cdot}$: Cl^- ratio) substantially enhances the ion currents carried by the species $[ZnLCl_2]^-$ and $[ZnCl_3]^-$ compared to that of the chloride ion adduct $[ZnL_2Cl]^-$. Displacement of ligands may occur to such an extent that $[ZnCl_3]^-$ constitutes the most abundant ion in the NCI mass spectrum.

Scheme 1



$*[Zn_2Cl_5]^-$, $[Zn_2LCl_4]^-$, $[Zn_3Cl_7]^-$, $[Zn_3LCl_6]^-$

Scheme 1 illustrates the various competing reactions involving radicals, ions, electrons and molecular species which is compatible with the experimental data. Recognition that the cluster ions observed in decreasing low abundances as $[Zn_2Cl_5]^-$, $[Zn_3Cl_7]^-$, $[Zn_2LCl_4]^-$, $[Zn_3LCl_6]^-$, can be the products of clustering of neutral ZnL_2, ZnLCl and $ZnCl_2$ with the principal negative ions further supports the proposed reaction scheme.

The higher electron affinity of $Cl^{\cdot}$ relative to $L^{\cdot}$ is seen as the principal driving force for these ligand displacement reactions. Substituent fluorination is known to increase markedly the electron affinity of β-ketoenolate radicals [24], and thus the decreased prominence of the ionic products $[ZnLCl_2]^-$ and $[ZnCl_3]^-$ in the spectra of **III** and **IV** is compatible with an enhanced level of electron attachment for these complexes. An important practical consequence of competitive ligand displacement and ionisation processes concerns the considerable variations in the NCI spectra which may be encountered, being dependent on ion source conditions such as reagent gas pressure, sample pressure and temperature, particularly with **I** and **II**. With the former complex, as the sample pressure is raised to the level where $[Cl]^-$ ions are significantly depleted in the ion source, ligand displacement is enhanced to the extent where the ionic product abundances follow the order: $[ZnCl_3]^- > [ZnLCl_2]^- > [ZnL_2Cl]^-$. Similar trends are observed as the temperature is raised, Table II. Conversely, when much reduced amounts of sample are introduced into the ion source (< *ca.* 10^{-8} mol) the NCI mass spectra are dominated by the metal-free ions $[L]^-$ and $[L - H^{\cdot} + Cl^{\cdot}]^-$.

TABLE II. Temperature Influence on the Cl^- NCI Mass Spectrum of $Zn(CH_3COCHCOCH_3)_2$, I.[a]

Ion source temperature (°C)	Relative Ion Abundances[b]		
	$[ZnCl_3]^-$	$[ZnLCl_2]^-$	$[ZnL_2Cl]^-$
100	0.2	0.5	1.0
120	1.0	1.1	1.0
140	2.0	1.8	1.0

[a] All isotopes included; 100 μg sample. [b] At 140 °C $[ZnLCl_2]^- > [ZnL_2Cl]^-$ for all complex/Cl^- ratios within the ion source. At 100 °C the $[ZnL_2Cl]^-$ abundance exceeds that of $[ZnLCl_2]^-$ as the complex/Cl^- ratios are increased. Hence, the observed ion product ratios cannot be attributed to an increased volatilisation rate and a higher sample pressure at increased temperatures but are consistent with temperature dependent bimolecular processes occurring within the ion source.

The use of CF_3Br as a reagent gas for the production of bromide ions leads to the formation of analogous bromine-containing ionic products with **I–IV**. Thus, the species $[ZnL_2Br]^-$, $[ZnLBr_2]^-$ and $[ZnBr_3]^-$ were identified in similar abundances to the corresponding chlorine-containing ions with **I–IV**.

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