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GAS PHASE OXIDATIVE-ADDITION REACTIONS OF ALKYL RADICALS AT COMPLEXED COBALT(II) CENTRES

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Summary

Negative chemical ionisation mass spectrometry is used as a probe to identify reactions between hydrocarbon radicals and complexed cobalt(II) centres in the gas phase. Methane NCI mass spectra of a series of cobalt(II) complexes containing O_4, O_2N_2 and N_4 donor atom sets are characterised by adduct ions of the form $[M + C_nH_{2n+1}]^-$ at m/z values above the molecular ion, $[M]^-$. Formation of such ionic species has been rationalised in terms of a one-electron oxidative-addition mechanism involving attack by hydrocarbon plasma-derived alkyl radicals at the metal centre prior to electron capture: $Co^{II}L_n + R^{\cdot} \rightarrow RCo^{III}L_n \xrightarrow{+e^-} [RCo^{II}L_n]^-$. The competing resonance electron attachment reaction: $Co^{II}L_n + e^- \rightarrow [Co^{I}L_n]^-$ also occurs within the ion source.

Introduction

Recently we showed that the complex *N,N'*-ethylenebis(acetylacetoniminato)-cobalt(II) is highly reactive in the gas phase towards hydrocarbon radicals and displays considerable potential as a radical trap [1]. In addition, the technique of negative chemical ionisation (NCI) mass spectrometry has been demonstrated to be a useful probe for identifying processes arising from oxidative-addition of alkyl radicals, derived from hydrocarbon plasmas, to a metal centre prior to electron capture ionisation [1]. Moreover, by the use of NCI methods, we have identified rapid ligand displacement reactions by halogen radicals from a series of zinc(II) β-ketoenolate complexes in the gas phase [2].

The principal gas phase chemical ionisation (CI) reactions encountered in mass spectrometer ion sources are rapid. Ion-molecule reactions such as proton transfer

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may occur at the diffusion controlled limit of 10^{-9} cm^3 s^{-1} [3] and the rate for resonance electron capture may exceed 10^{-7} cm^3 s^{-1} [4], whereas neutral–neutral reactions are much slower with maximum rates of the order of 10^{-11} cm^3 s^{-1} [5]. These latter reactions traditionally have been expected not to have a dominant role in the bimolecular processes occurring within a high pressure ion source. However, the ion source radical concentration under CI conditions may be one to two orders of magnitude greater than the concentrations of the ionising species, and the reaction of these radicals with certain organic substrate molecules may be sufficiently rapid to cause substantial chemical transformation prior to ionisation [6,7]. Such a combination of molecule–radical and electron capture ionisation processes may give rise to prominent ions in a mass spectrum at m/z values above the molecular ion [1,6–9]. This may seriously complicate interpretation of the spectrum [2], particularly with regard to molecular weight determination [8,9]. However, molecule–radical reactions have been utilised profitably to elucidate alkyl radical [10] and organic ion structures [11].

We now report details of an extended study of alkyl radical induced oxidative-addition reactions of a series of cobalt(II) complexes containing O_4, N_2O_2 and N_4 donor atom sets.

Experimental

The cobalt complexes examined in this study are listed in Table 1, along with their donor atom sets and references for preparation. Complexes I–VII were prepared and purified under argon by procedures based on the published methods. The preparation cited for II was highly suitable for I and IV also. I, II and IV were purified by vacuum sublimation at 140–160°C. Compounds VIII and IX were purchased from Strem Chemicals. Inc., Newburyport, MA, U.S.A. The purity of the metal complexes was established by C, H and N elemental analysis and by electron ionisation mass spectrometry. Although the cobalt(II) dioxime complexes, bis(dimethylglyoximato)cobalt(II), bis(diphenylglyoximato)cobalt(II) and bis(cyclohexylglyoximato)cobalt(II), were prepared for use in this study [18], their thermal

TABLE 1

NAMES, DONOR ATOM SETS AND PREPARATIVE REFERENCES OF THE COBALT(II) COMPLEXES INVESTIGATED [a]

	Complex	Donor atom set	Reference
I	Bis(acetylacetonato)cobalt(II)	O_4	[12,13]
II	Bis(dipivaloylmethanato)cobalt(II)	O_4	[13]
III	Bis(dibenzoylmethanato)cobalt(II)	O_4	[14]
IV	*N,N'*-Ethylenebis(acetylacetoniminato)cobalt(II)	N_2O_2	[13,15]
V	Bis(8-hydroxyquinolinato)cobalt(II)	N_2O_2	[16]
VI	[Bis(salicylidene)ethylenediamine]cobalt(II)	N_2O_2	[17]
VII	[Bis(*o*-aminobenzylidene)ethylenediamine]cobalt(II)	N_4	[17]
VIII	(*meso*-Tetraphenylporphinato)cobalt(II)	N_4	–
IX	(Phthalocyaninato)cobalt(II)	N_4	–

[a] CAS registry numbers: I, [14024-48-7]; II, [13986-53-3]; III, [14405-50-6]; IV, [15744-72-6]; V, [13978-88-6]; VI, [14167-18-1]; VII, [21177-97-9]; VIII, [14172-90-8]; IX, [3317-67-7].

TABLE 2

RELATIVE INTENSITIES OF THE ALKYL ADDUCT IONS OBSERVED IN THE METHANE NCI MASS SPECTRA OF COMPLEXES I–IX [a]

Ion	Complex								
	I	II	III	IV	V	VI	VII	VIII	IX
$[M]^-$	100	100	100	100	100	100	100	100	100
$[M+CH_3]^-$	350	31	2	800	6	0.5	0.3	2	2
$[M+C_2H_5]^-$	9	5	0.8	150	2	0.2	0.1	1	1
$[M+C_3H_7]^-$	1	0.2	–	14	0.7	–	–	–	–
$[M+C_4H_9]^-$	1	0.3	–	2	0.2	–	–	–	–
$[M+C_5H_{11}]^-$	2	–	–	0.4	–	–	–	–	–
Temperature (°C)	110	90	190	100	260	220	170	250	360

[a] Ion source methane pressure, 0.1 Torr; filament emission current, 1000 μA; Primary electron energy, 50 eV; Accelerating voltage, 4 kV; Repeller voltage, 0 to −1 V.

instability within the mass spectrometer ion source prevented reproducible data being obtained from their spectra.

NCI mass spectra were obtained on a VG MM-16F single focusing mass spectrometer under conditions described previously [19–21] or specified in Table 2. Accelerating voltage (V) scans at constant magnetic induction (B) and electric field strength (E), and ion source temperature variation studies, were performed with an AEI MS-902 double focusing mass spectrometer equipped with a heatable solid insertion probe.

Results and discussion

The methane NCI mass spectra of the cobalt(II) complexes are characterised by the presence of alkyl adduct ions above the molecular ion. Table 2 lists the abundances of the adduct ions relative to $[M]^-$ for each compound, along with the ion source temperatures that were required for sample vaporisation. In the case of complex IV alkyl addition is so facile that the adduct ions completely dominate the mass spectrum [1]. Similarly, the methyl adduct of I is the most prominent ion in its mass spectrum.

Verification of the ion assignments was achieved by substituting methane-d_4 for methane as the electron energy moderating gas [22], whereupon the empirical formula of the adducts changed from $[M + C_nH_{2n+1}]^-$ to $[M + C_nD_{2n+1}]^-$. In this way it was also confirmed that the reagent gas is the major source of alkyl radicals [6,7]. Alkyl groups could be detected up to $n = 5$ for complexes I and IV.

Each of the adduct ions increases in intensity relative to $[M]^-$ as the filament emission current is increased, as shown for the $[M+CH_3]^-$ ions in Fig. 1. This indicates that the adduct ions derive from radical reactions since it has been shown that the ratio of radicals to charged species within a typical CI plasma increases as the primary electron current ionising the plasma is increased [6,7]. Hence, the probability of a sample molecule encountering a radical before it encounters an ionising particle such as a thermal electron also increases with increasing emission. Variation of the ion source repeller voltage and hence the ion residence times within

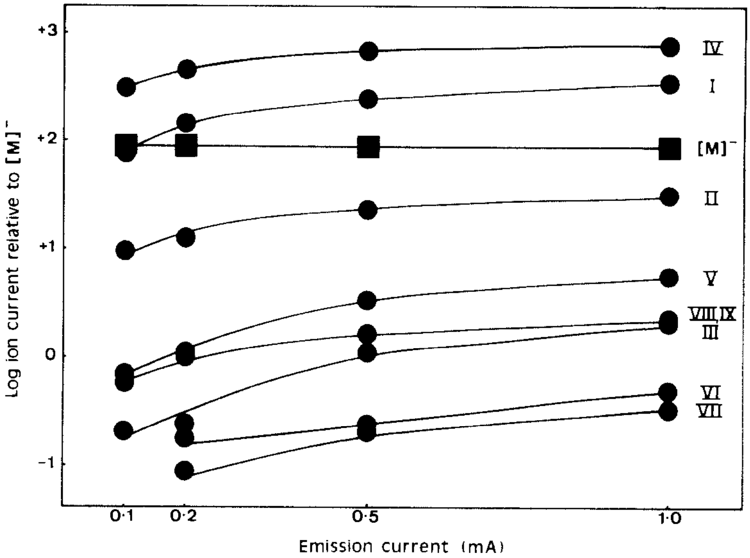

Fig. 1. The effect of electron emission current on the abundance of the $[M+CH_3]^-$ adduct ions relative to $[M]^- = 100$.

the source [8,23] does not markedly affect the ion relative abundances, which indicates that the adduct ions are unlikely to arise from ion-radical reactions between $[M]^-$ and R$^\cdot$. Molecule-radical encounters prior to ionisation are thus indicated.

Replacement of cobalt(II) by nickel(II) and copper(II) in analogues of I–IX markedly decreases the relative ion abundances of the adduct species, although analysis of relevant rate equations suggests that such a decrease may be due in part to an increased rate of electron capture by the nickel and copper complexes [1,45]. This points to the involvement of the transition metal centre in the radical trapping process with the highest detected abundances of adduct negative ions being given by the more readily oxidised cobalt(II) complexes.

The available evidence is consistent with the existence of the two competing reaction pathways, (1) and (2).

$$Co^{II}L_n + e^- \rightarrow [Co^{I}L_n]^- \tag{1}$$

$$Co^{II}L_n + R^\cdot \rightarrow RCo^{III}L_n \xrightarrow{+e^-} [RCo^{II}L_n]^- \tag{2}$$

Ionisation occurs in each pathway by resonance capture of a low energy electron into the lowest unoccupied molecular orbital, which is envisaged to be metal based [25,26]. Radical capture is proposed to occur by a one-electron oxidative-addition process [27] at the metal centre.

Oxidative-addition of alkyl radicals to cobalt(II) complexes is a well known reaction in solution [27–31], where it occurs with only a small activation energy barrier at rates that are diffusion controlled [29,32]. Such reactions are best known for square-planar cobalt complexes which have been extensively investigated as chemical models for vitamin B_{12} [28,33]. The degree of alkyl radical addition to I and II, which are tetrahedral in structure, at least in the solid state and solution [34], suggests that square planar coordination geometry around the metal is not essential for oxidative-addition. Steric hindrance arising from the bulky tertiary butyl groups of II may be responsible for the diminished abundances of adduct negative ions detected for II compared with I.

To a certain extent the results of this study of gaseous reactions are consistent with solution phase studies in that IV appears to have a higher affinity for alkyl radicals than VI. Electrochemical studies have shown that IV is more readily oxidised than a range of other square-planar cobalt(II) complexes including VI [35], and that the organometallic cobalt(III) derivatives of IV are less readily reduced than the corresponding derivatives of VI [36]. Moreover, these differences are enhanced in non-donor solvents [35,37] and presumably, therefore, in the absence of solvent. This infers that the electron density on the metal is higher for IV [38], enabling it to be more readily oxidised to form organometallic derivatives that are less prone to homolytic cleavage of the cobalt-carbon bond. Notwithstanding these correlations between gas phase and solution phase chemistry, it is unlikely that electronic effects alone are sufficient to account quantitatively for the difference in reactivity between IV and VI or to explain the absence of any clearly defined trends in reactivity as the donor atom set is systematically varied.

A noteworthy feature of the results is the distinct correlation that is apparent between the abundances of alkyl adduct negative ions detected and the temperature at which the complexes were vaporised into the ion source. Oxidative-addition reactions occur most readily with the complexes I, II and IV which are volatile at 100°C. The remaining compounds, for which radical addition is markedly less facile, are only volatile above 160°C. Significantly, cobalt–carbon bonds are relatively weak, with dissociation energies in the range 84–139 kJ mol^{-1} [29,39–41], and are prone to thermally induced homolytic cleavage [42–44]. The alkyl adducts of VI may be converted quantitatively to VI in the solid state by heating under vacuum at 200°C [43], which is less than the ion source temperature used in this study. Our results may thus be rationalised in terms of the dynamic equilibrium, (3):

$$Co^{II}L_n + R^{\cdot} \rightleftharpoons RCo^{III}L_n \qquad (3)$$

Although the position of the equilibrium may lie sufficiently far to the right for alkyl adducts to exist in the ion source at 100°C, the thermal instability of the cobalt–carbon bond dictates that the equilibrium should move rapidly to the left as the temperature is increased. Support for this rationalisation was obtained with VI on the MS-902 instrument equipped with a heatable solid insertion probe. By heating the probe to an indicated temperature of 330–350°C it was possible to maintain the ion current at a constant level while the ion source temperature was varied over a small range. In this way it was possible to minimise interference from concentration effects within the ion source. The relative abundance of the $[M + CH_3]^-$ adduct ion was found to increase from 0.6% of $[M]^-$ at an indicated temperature of 200°C to 5% at 170°C. It seems likely that the thermolytic instability of cobalt–carbon bonds is a dominant factor influencing the degree of alkylation and hence the abundances of the negative adduct ions detected in this investigation.

At the temperatures conducive to cobalt–carbon bond formation the adduct ions are apparently stable as evidenced by their minimal degree of fragmentation in the first field-free region of the MS-902 instrument as shown by V scans at constant magnetic induction (B) and electric field strength (E). The alkane elimination reaction (4) was detected for compounds I and IV: $[M-\mathrm{H}]^- = 13\%$ of $[M]^-$ for I and 9% for IV. No other significant ion decomposition pathways were detected.

$$[M+\mathrm{R}]^- \rightarrow [M-\mathrm{H}]^- + \mathrm{RH} \qquad (4)$$

Although the ion source conditions commonly utilised for positive and negative chemical ionisation are essentially identical, differing only in that the polarity of the applied instrumental voltages is reversed, the positive CI mode is a less informative technique for investigating molecule-radical processes such as those described here. Ionisation to form positive ions may occur by a number of mechanisms including charge exchange and the ion-molecule alkylation reaction, $M + [\mathrm{R}]^+ \rightarrow [M+\mathrm{R}]^+$. Consequently, under positive chemical ionisation conditions it is necessary to differentiate between competing alkylation processes in order to define the molecule-radical chemistry giving rise to the mass spectra. In this regard, negative chemical ionisation has proved to be the more useful probe for gas phase molecule-radical reactions where the products of bimolecular neutral encounters may be identified as their negative ions.

In addition to the adduct ions so far described here, other adduct ions have also been identified in the methane NCI mass spectra of complexes I–IX, including ions of the form $[M + \mathrm{C}_n\mathrm{H}_{2n}]^-$. For some complexes, these additional ions are more prominent than the alkyl adduct ions and are attributed to processes involving radical attack at the complexed ligands [45].

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