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Preliminary communication

MASS SPECTROMETRY OF TRANSITION-METAL π-COMPLEXES

II*. THE MECHANISM OF KETENE ELIMINATION FROM ($C_6H_5NHCOCH_3$)-$Cr(CO)_3$

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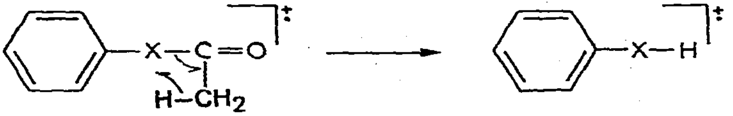
Summary

Studies of the mass spectra of acetanilidetricarbonylchromium and its 2,4- and 2,6-dimethyl analogues indicate that ketene elimination from the ion $[(C_6H_5NHCOCH_3)Cr]^{+\cdot}$ occurs via a six-membered transition state. This contrasts with the four-membered transition state involved in the analogous fragmentation of the molecular ions of the non-complexed organic molecules.

Introduction

Studies of the mass spectra of acetanilide and phenyl acetate indicate that the rearrangement processes in which CH_2CO is eliminated from the molecular ion of both compounds proceed via four-membered transition states (Scheme 1). Evidence for this mechanism comes from an examination of *o*- and 2,6-methyl-



(X = NH or O)

Scheme 1

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substituted analogues of $PhXCOCH_3$ [2, 3] in which introduction of these blocking groups has little effect on the abundance of $[M{-}CH_2CO]^{+\cdot}$ and thus precludes rearrangement operating via a six-membered transition state and involving the *ortho* positions of the ring. The observation of a deuterium isotope effect on the subsequent decomposition of $[M{-}CH_2CO]^{+\cdot}$ (formed from acetanilide) by loss of HCN also supports this mechanism [4]. Thus, although measurements at the threshold indicate that molecules of the type C_6H_5XR (X = NH or O) form molecular ions by loss of a ring π-electron [5], at the higher energies involved in mass spectral fragmentation at least a proportion of the molecular ions of $PhXCOCH_3$ (those which decompose by loss of ketene) appear to have their positive charge located essentially on the hetero atom (X in Scheme 1)*. This approach is further substantiated by examination of the blocking effects on the abundances of $[M{-}C_3H_6]^{+\cdot}$ ions formed by n-butylbenzenes [3]. In this case it appears intuitively unlikely that the positive charge would be localised on the α-carbon atom of the side chain and indeed the rearrangement does occur via a six-membered transition state.

Ionisation potential measurements on $[(arene)Cr(CO)_3]$ complexes are in accord with removal of an electron from an orbital which has principally metal character [7, 8], but these studies do not preclude all other possible sites of charge location in ions of sufficient energy to undergo mass spectral fragmentations. Thus the loss of CH_2CO from the ion $[(C_6H_5NHCOCH_3)Cr]^{+\cdot}$ (I) may possibly occur with transfer of a hydrogen atom to the metal, the nitrogen atom or the ring. In the light of such possibilities we have examined the 70 eV mass spectra of $(C_6H_5NHCOCH_3)Cr(CO)_3$ and its 2,4- and 2,6-dimethyl analogues.

Results and discussion

The molecular ions of all three complexes studied give rise to only successsive decarbonylation, however I shows loss of ketene and $CH_3CO^\cdot$ as well as the expected metal—ligand bond cleavage. Table 1 lists the intensities of ions formed by loss of CH_2CO, $CH_3CO^\cdot$ and L from the ions $LCr^{+\cdot}$ in the mass spectra of $LCr(CO)_3$ (L = acetanilide, 2,4- and 2,6-dimethylacetanilide). The results indicate that ketene elimination is greatly hindered by the introduction of one blocking group in an *ortho* position and does not occur when both *ortho* sites are blocked.

TABLE 1

VARIATION OF Z [a] IN SUBSTITUTED ACETANILIDETRICARBONYLCHROMIUM COMPLEXES

Fragmentation process	Z value [b,c]		
	Acetanilide	2,4-Dimethylacetanilide	2,6-Dimethylacetanilide
$LCr^{+\cdot} \rightarrow LCr{-}CH_2CO^{+\cdot}$	0.066 (1)	0.017 (0.25)	0
$LCr^{+\cdot} \rightarrow LCr{-}CH_3CO^{+}$	0.16 (1)	0.06 (0.32)	0.17 (1.1)
$LCr^{+\cdot} \rightarrow Cr^{+\cdot}$	1.1 (1)	0.5 (0.45)	0.66 (0.6)

[a] $Z = [X^+]/[LCr^{+\cdot}]$ for the fragmentation $LCr^{+\cdot} \rightarrow X^+$. [b] The figures in parentheses are Z/Z_0 ratios where $Z_0 = [X^+]/[LCr^{+\cdot}]$ for the acetanilide complex. [c] Isotopic contributions of $LCr{-}CH_3CO^+$ to the $LCr{-}CH_2CO^{+\cdot}$ peaks have been subtracted.

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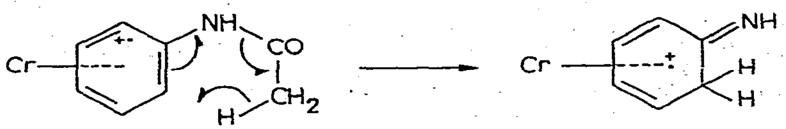
*For a discussion of the concept of charge localisation in relation to mass spectral fragmentation see ref. 6.



Scheme 2

We believe this to indicate a six-membered transition state for this rearrangement in the ions $[LCr]^{+\cdot}$ as shown in Scheme 2. The results shown in Table 1 for loss of $CH_3CO^\cdot$ and L indicate that the non-occurrence of the rearrangement in the 2,6-dimethyl complex is not simply due to the effective intrusion of a low-energy fragmentation process into the decomposition scheme which can compete with the rearrangement, to the exclusion of the latter. The intensities of $L^{+\cdot}$ ions are excluded from the table as we have no evidence from metastables to indicate that these ions arise exclusively from $LCr^{+\cdot}$ and previous energetic studies have shown that they can arise from fragmentation of $[LCr(CO)]^{+\cdot}$ in closely related complexes [8].

It therefore appears that the nitrogen atom is not involved in the rearrangement discussed above and more surprisingly, neither is the metal atom. Further evidence, albeit speculative, for the absence of metal atom involvement is the fact that no CrH^+ ions are observed in the spectra of any of the complexes. Similar ions have been widely reported in rearrangements directly involving metal atoms [9, 10]. The results, however, do not preclude initial hydrogen rearrangement to the metal atom followed by rapid migration to an accessible site on the organic moiety prior to further decomposition. The results are also consistent with a substantial localisation of charge on the aromatic ring in ions formed under high energy conditions and undergoing subsequent fragmentation.

Further work is in progress on these and related complexes and will be reported later.

Experimental

The complexes were prepared by the method of Nicholls and Whiting [11], and were characterised by the usual methods. Mass spectra were recorded on an A.E.1 MS9 operating at 70 eV and 100 μamps trap current.

Acknowledgement

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