The Reaction of Halogens with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and Related Compounds

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Summary The reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with iodine in chloroform solution has been shown to proceed *via* a rapidly formed ionic intermediate $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2I\}X$ ($X^- = I_3^-$ or I^-) which slowly decomposes to the final product, $(\pi\text{-}C_5H_5)Fe(CO)_2I$.

Although the reactions of halogens with transition-metal carbonyls provides useful synthetic routes to the carbonyl halides, there have been few investigations into the mechanisms involved.[1-3] Noack has suggested that the reactions of pentacarbonyliron with halogens proceed *via* species such as $[Fe(CO)_5Br]Br$ and $BrCO{\cdot}Fe(CO)_4Br$,[1] whilst kinetic studies of the halogenation of $M_2(CO)_{10}$ (M = Mn and Re) have been interpreted on the basis of either radical or CO bridged intermediates of the type $M(CO)_5$ or $(CO)_4M{\cdot}CO{\cdot}M(CO)_5$.[2-4] We have studied the reactions of the binuclear carbonyl complexes, $[(\pi\text{-dienyl})\,Fe(CO)_2]_2$ (dienyl = C_5H_5, $CH_3{\cdot}C_5H_4$, and C_9H_7) with halogens, and have obtained evidence for a reaction pathway related to that suggested by Noack.

When solutions of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and iodine in chloroform at 0° are mixed, there is a rapid colour change to give a gold-brown solution, the i.r. spectrum of which at this stage shows that neither the dimer nor $(\pi\text{-}C_5H_5)Fe(CO)_2I$ are present. The solution contains a species which gives rise to three absorption bands in the C–O stretching region at 2062, 2044, and 2011 cm.$^{-1}$, and on cooling to $-20°$ for 2 hr., it deposits well-formed dark needles of $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2I\}I_3$.

The tetrafluoroborate salt of this cation has been isolated previously by Fischer and Moser.[4]

Therefore, we suggest that $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and iodine reacts rapidly in chloroform solution to give the I^- or I_3^- salt of the $\{[(\pi\text{-}C_5H_5)Fe(CO)_2]_2I\}^+$ cation, and that this slowly decomposes to the covalent iodo-complex, $(\pi\text{-}C_5H_5)Fe(CO)_2I$. Spectroscopic evidence has been obtained for similar intermediates of the type $\{[(\pi\text{-dienyl})Fe(CO)_2]_2I\}^+$ (dienyl = $CH_3{\cdot}C_5H_4$ and C_9H_7) in related reactions, but their salts are much less stable than the compound isolated.

When these reactions are carried out in an inert solvent such as n-hexane, there is no evidence for the formation of ionic intermediates. I.r. spectra of the reaction mixtures show only absorption bands due to the starting material and the final product.

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