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Preliminary communication

MECHANISMS OF NUCLEOPHILIC ATTACK AT COORDINATED CARBON MONOXIDE

I. HYDROXIDE ADDITION TO A CARBON MONOXIDE LIGAND IN $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-DIENYL})]^+$ CATIONS (DIENYL = C_6H_7, C_7H_9)

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Summary

Kinetic studies of aqueous OH^- attack on $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ (IIa) (to yield $[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-}HOC_6H_7)]$ (IIIa) as final product) suggest the involvement of the carboxylic acid species $[Fe(1\text{—}5\text{-}\eta\text{-}C_6H_7)(CO)_2(COOH)]$ (Ia). This complex can be readily isolated as an air-sensitive pale yellow solid admixed with IIIa. Solutions of Ia in n-hexane are stable for at least 1 h at room temperature, but in CH_3NO_2 conversion of Ia to IIIa occurs within 10 min. The related carboxylic acid derivative $[Fe(1\text{—}5\text{-}\eta\text{-}C_7H_9)(CO)_2(COOH)]$ has been similarly prepared and characterised from the reaction of $[Fe(1\text{—}5\text{-}\eta\text{-}C_7H_9)(CO)_3]^+$ with aqueous KOH.

Carboxylic acid complexes of the type $L_nMCOOH^{(m-1)+}$, formed via attack of hydroxide ion on a CO ligand in L_nMCO^{m+} species, have been proposed as crucial intermediates in a wide range of reactions. These include the conversion of metal carbonyls to metal carbonyl anions or hydrides via treatment with base [1], and the homogeneous catalysis by transition metal complexes of the industrially important water gas shift reaction (eq. 1) [2]. However, apart from very recent kinetic studies of the reactions of OH^- with $M(CO)_5$ and $M_3(CO)_{12}$

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (1)$$

(M = Fe, Ru) [3,4], there is no quantitative information on the formation of

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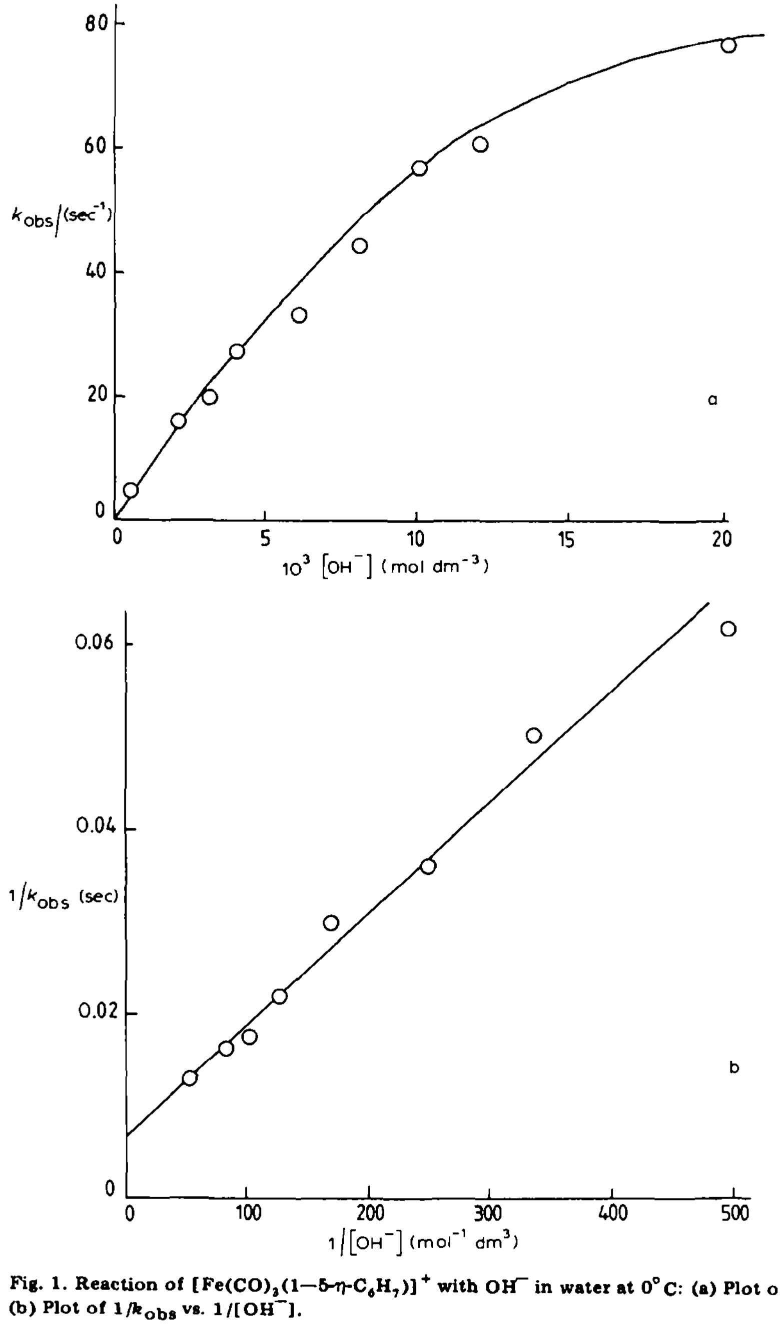


Fig. 1. Reaction of [Fe(CO)$_3$(1—5-η-C$_6$H$_7$)]$^+$ with OH$^-$ in water at 0°C: (a) Plot of k_{obs} vs. [OH$^-$], (b) Plot of $1/k_{obs}$ vs. $1/[OH^-]$.

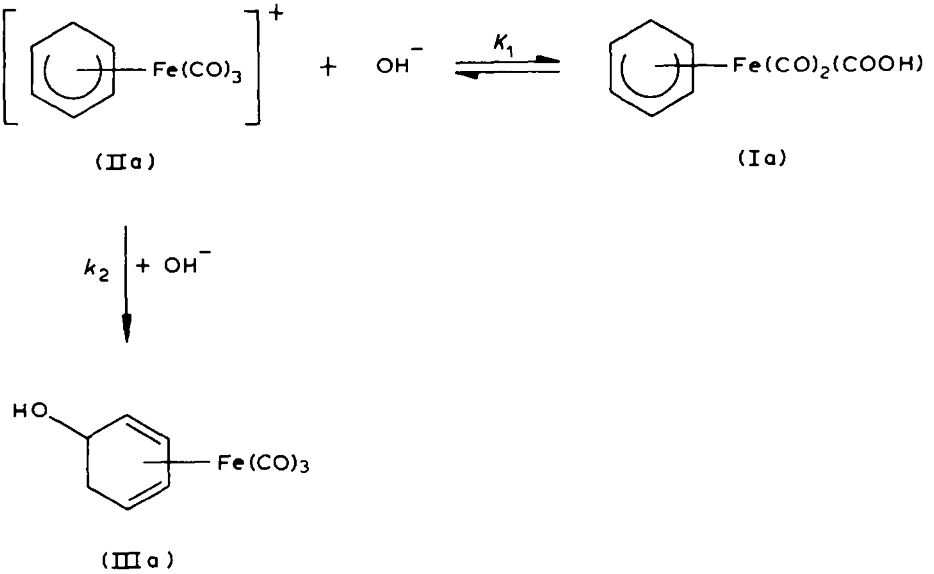
such carboxylic acid complexes. Furthermore, as far as we are aware, there are only four reports of the isolation of MCOOH species, namely [IrCl$_2$(CO)(COOH)L$_2$] (L = PMe$_2$Ph or AsMe$_2$Ph) [5], [PtR(COOH)(diphos)] [6], [Re(η-Cp)(CO)(NO)(COOH)] [7], and the cyclopentadienyl iron complexes [Fe(η-Cp)(CO)(L)(COOH)] (L = CO or PPh$_3$) [8]. We report here the detection kinetically and the subsequent isolation of the moderately stable carboxylic acid complexes

[Fe(1—5-η-dienyl)(CO)$_2$(COOH)] (I) (dienyl = C_6H_7, C_7H_9) from the reaction of the cations [Fe(CO)$_3$(1—5-η-dienyl)]$^+$ (II) with aqueous KOH.

As part of an extensive programme [9] investigating the mechanisms of nucleophilic attack on coordinated π-hydrocarbons, we recently studied the kinetics of aqueous anion (OH^-, N_3^-, CN^-) addition to the cyclohexadienyl ring of [Fe(CO)$_3$(1—5-η-C_6H_7)]$^+$ (IIa) (leading to [Fe(CO)$_3$(1—4-η-XC_6H_7)] products). For the hydroxide reaction at 0°C, a plot of k_{obs} vs. [OH^-] was distinctly curved (Fig. 1a). On the other hand, a plot of $1/k_{obs}$ vs $1/[OH^-]$ was linear with a non-zero intercept (Fig. 1b), confirming a rate expression of the form 2. This kinetic behaviour strongly suggests the transient presence of the carboxylic acid species

$$k_{obs} = \frac{a[OH^-]}{b + c[OH^-]} \qquad (2)$$

[Fe(1—5-η-C_6H_7)(CO)$_2$(COOH)] (Ia), formed either as an intermediate or in a dead-end pre-equilibrium. The latter alternative (i.e. Scheme 1) is favoured, since the hydroxy substituent in the known final ring-addition product [Fe(CO)$_3$(1—4-η-HOC_6H_7)] (IIIa) is considered [10] from ^{1}H NMR and mass spectral evidence to occupy an *exo*-position. The intermediacy of species Ia might be expected to lead to an *endo*-final product.



From the intercept and slope of the plot in Fig. 1b a value of ca. 65 is obtained for K_1. This is the first time that an equilibrium constant has been derived for the formation of a carboxylic acid complex, and its reasonably high value suggested that isolation of Ia and related species may be possible.

This expectation was readily achieved by treating a near-saturated solution of Ia in water with an equimolar aqueous solution of KOH. An immediate pale yellow precipitate was formed, which was rapidly filtered off and sucked dry at the pump. The IR spectrum of this product in n-hexane exhibited three strong ν(CO) bands at 2060, 2040, and 1992 cm^{-1}, as well as a medium intensity peak at 1658 cm^{-1}. The bands at 2060 and 1992 cm^{-1} agree with the reported [10] spectrum of the final ring-substituted product IIIa. The ν(CO) band at 2040 cm^{-1} is consistent with the carboxylic acid complex formulation Ia, the second expected ν(CO) band being masked by the 1992 cm^{-1} band of the final product IIIa. Particularly strong evidence for the presence of Ia in the product mixture is the band at 1658 cm^{-1}, attributable to the COOH group itself. Furthermore the bands assigned to the carboxylic acid species Ia are very similar to those recently reported [11] for the related methoxycarbonyl complex $[Fe(1-5\text{-}\eta\text{-}C_7H_9)(CO)_2(COOMe)]$ in n-hexane (2038, 1991, and 1656 cm^{-1}).

Mixtures of Ia and IIIa darken from pale yellow to brown on exposure to air for a few hours. However, they appear reasonably stable in the solid state under a dinitrogen atmosphere. Also, in n-hexane solution no change in the IR spectrum occurred over 1 hour at room temperature. This behaviour contrasts with the instability of the previously described [7] cyclopentadienyl analogue $[Fe(\eta\text{-}Cp)(CO)_2(COOH)]$, which was reported to rapidly decompose to yield the cyclopentadienyliron dicarbonyl dimer with evolution of H_2 and CO_2.

However, in the more polar solvent CH_3NO_2 (in which Ia exhibits ν(CO) bands at 2030 and ca. 1980 cm^{-1}), the mixture Ia/IIIa converts over 10 min at room temperature to IIIa. This contrasting behaviour in benzene and CH_3NO_2 is consistent with Scheme 1. Dissociation of Ia to regenerate IIa and OH^- ions (which can then react to form the final product IIIa) is hindered in the non-polar benzene solvent. As expected, both Ia and IIIa can be rapidly converted back to the original dienyl cation IIa by the addition of acid (CF_3COOH) in CH_3NO_2.

The analogous carboxylic acid complex $[Fe(1-5\text{-}\eta\text{-dienyl})(CO)_2(COOH)]$ (Ib) (dienyl = 2-$MeOC_6H_6$ or C_7H_9) was similarly isolated (admixed with IIIb) from the reaction of the appropriate cation with aqueous KOH, and identified by its characteristic IR spectrum. Further studies of the formation and rearrangements of these carboxylic acid complexes are in progress as part of a programme investigating the mechanisms of nucleophilic attack at coordinated CO in general.

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