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Preliminary communication

KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES.

XVIII*. NUCLEOPHILICITY OF ANIONS TOWARDS THE TRICARBONYL-(η-BENZENE) MANGANESE (I) CATION.

D.J. EVANS, L.A.P. KANE-MAGUIRE**
Chemistry Department, University College Cardiff, P.O. Box 78, Cardiff CF1 1XL, Wales (Great Britain)
and D.A. SWEIGART
Chemistry Department, Brown University, Providence, Rhode Island 02912 (U.S.A.)

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Summary

Kinetic results for the addition of OH^- to $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ (I) in water (eq. 1, X = OH) obey the expression $k_{obs} = k_{OH}[OH^-]$, and give a k_{OH} value of 290 mol^{-1} dm^3 s^{-1} at 20.0°C and ionic strength of 0.25 mol dm^{-3}. The analogous reaction of NaCN with I in water fits the two-term expression $k_{obs} = k_{OH}[OH^-] + k_{CN}[CN^-]$, and leads to a k_{CN} value of 0.8 mol^{-1} dm^3 s^{-1} at 20.0°C and ionic strength of 0.25 mol dm^{-3}. Interestingly, the related reaction (eq. 1, X = N_3) is too rapid to follow by stopped-flow spectrophotometry, indicating the overall rate trend $N_3^- \gg OH^- \gg CN^-$. This unusual nucleophilicity order, unexpected on the basis of both basicity and polarizability, is similar to that previously observed for anion addition to free carbonium ions.

Recent studies have begun to establish a nucleophilicity order for the addition of various neutral nucleophiles (β-diketones [1], activated arenes [2], aromatic heterocycles [3], phosphines and phosphites [4], and amines [5,6]) to coordinated π-hydrocarbons. We now wish to report the first quantitative information concerning the addition of anions to coordinated cyclic π-hydrocarbons, namely for attack by OH^- and CN^- on $[Mn(CO)_3(\eta\text{-}C_6H_6)]PF_6$ (I; eq. 1; X = OH, CN).

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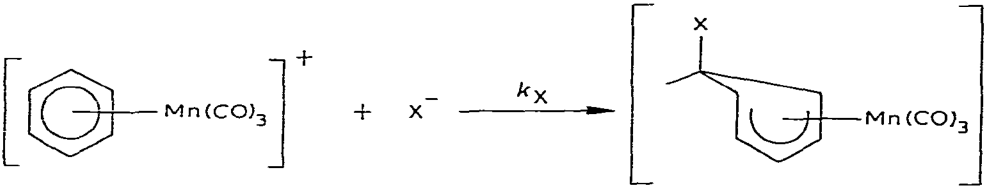
*Part 17, see ref. 6.
**Author to whom correspondence to be addressed.



(1)

(I) (II)

Both reactions are rapid and were followed by monitoring the large decrease in absorbance at 350 nm using a stopped-flow spectrophotometer. Under the kinetic conditions employed ([Mn] = 8×10^{-4} mol dm^{-3}; [OH$^-$] = 2×10^{-3} – 2×10^{-2} mol dm^{-3}; [CN$^-$] = 4.8×10^{-2} – 24.7×10^{-2} mol dm^{-3}) both reactions effectively proceed to completion. Kinetic results for reaction 1 with OH$^-$ in water obey the expression 2, and give a second-order rate constant, k_{OH}, for OH$^-$ addition to the benzene ring of ca. 290 mol^{-1} dm^3 s^{-1} at 20.0°C

$$k_{obs} = k_{OH}[OH^-] \qquad (2)$$

and an ionic strength of 0.25 mol dm^{-3}.

For the analogous reaction of I with NaCN in water the OH$^-$ concentrations were determined in each case using a pH meter. Employing the above k_{OH} value of 290 mol^{-1} dm^3 s^{-1}, k_{obs} was found to fit the expression 3, leading to a k_{CN} value of ca. 0.8 mol^{-1} dm^3 s^{-1} at 20.0°C and an ionic strength of 0.25 mol dm^{-3}. Interestingly, the present kinetic results indicate that, with

$$k_{obs} = k_{OH}[OH^-] + k_{CN}[CN^-] \qquad (3)$$

the cyanide concentrations employed, species (II, X = OH) would be the major product in the reaction with NaCN. However, under preparative conditions the cyano adduct (II, X = CN) is isolated in up to 80% yield [7]. This suggests that reaction (1, X = OH) is slightly reversible and that precipitation of the less soluble cyano adduct under concentrated preparative conditions leads eventually to its quantitative formation.

The rate trend $k_{OH} \gg k_{CN}$ (360/1) observed here for reactions 1 is similar to that previously found by Ritchie [8] for addition of these anions to a variety of free carbonium ions. It is also consistent with the location of significant positive charge on the coordinated benzene ring in I, as has been estimated [9] from INDO/SCF molecular orbital calculations.

A striking feature of Ritchie's results for anion addition to free carbonium ions was the remarkable nucleophilicity of the azide ion, which was generally ca. 10^4 more reactive than cyanide ion [8]. For other types of substrate CN$^-$ is generally more nucleophilic than N_3^-, as one would anticipate on both basicity and polarizability grounds. Since organometallic cations of the type $[M(CO)_3(\pi\text{-hydrocarbon})]^+$ are sometimes regarded as metal-stabilized carbonium ions, we have been interested for some time in determining whether N_3^- also exhibits unusual reactivity towards such coordinated π-hydrocarbons. Reaction 1, X = N_3 has been reported preparatively [10], and our spectroscopic studies show that this process causes an increase in absorbance at 350 nm. However, under the conditions employed ([N_3^-] = 8×10^{-4} – 5×10^{-2} mol dm^{-3}) the reaction was too rapid to follow by stopped-flow spectrophotometry at 20°C. This indicates that k_{N_3} is larger than 10^5 dm^3 mol^{-1} s^{-1}, establishing the overall trend $N_3^- \gg OH^- \gg CN^-$. Interestingly, a similar reactivity order has recently been reported [11] for ferrocenyl-stabilized carbocations.

We are currently exploring whether this unusual nucleophilicity order for anions holds for other π-hydrocarbon metal complexes. Preliminary results with $[Fe(CO)_3(\eta\text{-}C_6H_7)]^+$ suggest that for this cation the more normal order $CN^- \geqslant N_3^-$ is obeyed. It is hoped that different behaviours of this type may shed light onto the source of abnormal azide reactivities.

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