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Preliminary communication

ELECTROPHILIC SUBSTITUTION OF 1,3-DIMETHOXYBENZENE BY PENTADIENYLTRICARBONYLIRON CATIONS

TREVOR G. BONNER, KEITH A. HOLDER and PAUL POWELL

Department of Chemistry, Royal Holloway College, University of London, Egham Hill, Egham, Surrey, TW20 0EX (Great Britain)

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Summary

Kinetics of reactions of several open-chain pentadienyltricarbonyliron cations with 1,3-dimethoxybenzene have been studied; the reactions are faster than those of the cyclohexadienyltricarbonyliron cation and a mechanism is proposed.

Kane-Maguire and coworkers have recently shown that the cyclohexadienyltricarbonyliron cation acts as an electrophile towards activated aromatic systems including indole, pyrrole [1] and 1,3-dimethoxybenzene [2]. These reactions show second order kinetics (rate = k_2 [cation] [ArH]) over an appreciable range of concentration of the aromatic compound [3].

We have studied kinetically the attack of several open-chain pentadienyltricarbonyliron cations (I) on 1,3-dimethoxybenzene, and have found not only that the reactions are considerably faster than those of their cyclic analogues, but also that some show different kinetic characteristics. Only compounds Ib and Ic* obey second order kinetics (up to at least sixty times excess of dimethoxybenzene, with the rate of reaction of Ic almost 700 times faster than that of the cyclic Ia. With compounds Id, Ie and If the reactions follow a different rate equation (rate = $k_1 k_2$ [cation] [ArH] /(k_{-1} + k_2 [ArH])) tending towards first order kinetics at high concentration of dimethoxybenzene. This implies the formation of a reactive intermediate, which can either react further to yield the products or can reform the starting material. We suggest that this reaction intermediate is the *trans*-pentadienyltricarbonyliron cation II, postulated by Clinton and Lillya [4] on the basis of the stereochemistry and kinetics of hydrolysis of the dinitrobenzoates of dienoltricarbonyliron complexes. Sorensen and Jablonski [5] obtained evidence for such a *trans* iron from ^{1}H NMR studies at low temperatures.

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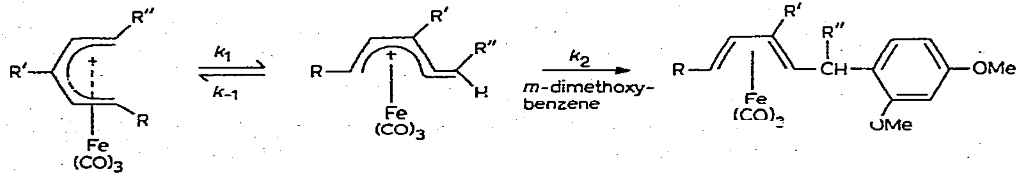
*See Table 1 for substituents.

The mechanism of Scheme 1 is consistent not only with the observed kinetic form, but also with the fact that the cations with open-chain ligands, and which can form *trans* cations, are more reactive towards nucleophiles than those with cyclic ligands, which can exist only in the *cis* form. The difference in the kinetics between compounds Ib, Ic and Id, Ie, If implies that k_1 and k_{-1} do not influence the rate-determining step in the former cases either because k_1 and k_{-1} are much greater, or that k_2 is smaller, than in the latter cases.



(I) (II) (III)

SCHEME 1

The rate constants were measured by following the rate of disappearance of the dienylcarbonyl band at ca. 2110 cm^{-1} in the IR. Linear pseudo-first order plots were obtained up to at least 75% reaction. Some representative results are listed in Table 1.

TABLE 1

RATES OF REACTION OF SUBSTITUTED PENTADIENYLTRICARBONYLIRON(II) TETRAFLUOROBORATES (0.01 M) WITH 1,3-DIMETHOXYBENZENE (DMB) IN NITROMETHANE AT 25 ± 0.1°C.

Compound	Substituents	k_2 ($l\ mol^{-1}\ sec^{-1}$)	k_{obs} (sec^{-1}) 0.1 M DMB	k_{obs} (sec^{-1}) 0.5 M DMB
Ia	cyclohexadienyl [a]	1.5×10^{-6}	—	—
Ib	1,3,5-trimethyl	3.3×10^{-5}	—	—
Ic	1,5-dimethyl	1.0×10^{-3}	—	—
Id	5-methyl	—	4.0×10^{-4}	1.3×10^{-3}
Ie	1-phenyl-5-methyl	—	5.1×10^{-4}	1.4×10^{-3}
If	1-phenyl-2,5-dimethyl	—	5.6×10^{-4}	1.4×10^{-3}

[a] At 20.8°C [3].

Only one product, in which the aromatic ring is substituted in the 4-position, was observed in each reaction. Nucleophilic attack on the cations occurs at a terminal carbon atom. For the unsymmetrically substituted cations Id, Ie, If, this is the carbon which bears a methyl substituent. The rate of reaction increase along the series Ib, Ic, Id with decreasing methyl substitution at the 1 and 3 positions. Compounds Ie and If react at very similar rates, indicating that a methyl substituent at the 2-position has little effect, as might be predicted from a simple picture of the charge distribution in the pentadienyl system.

Further evidence for the intermediacy of *trans* cations in our reactions comes from the ^1H NMR spectra of the products III, which are consistent with the *trans,trans* structure shown. This arises via geometrical inversion at C(5) during nucleophilic attack [6]. Direct attack on the *cis* cation leads to a *cis, trans* configuration in the product [7].

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