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On the Mechanism of Acidic Hydrogen Isotopic Exchange in Transition Metal σ-benzyl-π-cyclopentadienyldicarbonyl Complexes

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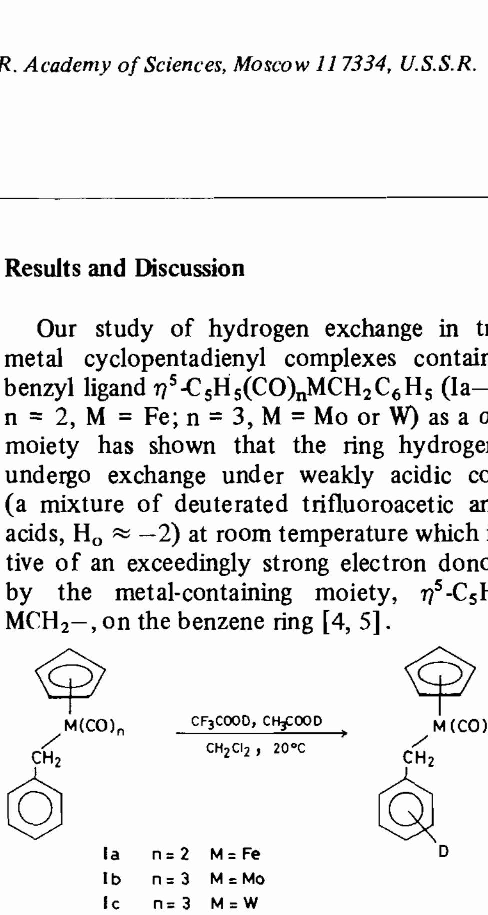
The hydrogen isotopic exchange reaction in Fe, Mo and W σ-benzyl-π-cyclopentadienyl complexes has been discovered and studied. The reaction mechanism has been investigated by means of the stereochemical indication, kinetic isotopic effect etc. *techniques.*

Introduction

Reactivities of transition metal complexes are widely studied by means of the acidic hydrogen isotopic exchange technique which affords quantitative as well as qualitative estimates of a compound's ability to undergo electrophilic substitution. Transition metal complexes containing organic ligands σ-bonded to the metal which occur as intermediates in various catalytic processes (oxosynthesis, polymerization of olefins, *etc.*) attract much attention from chemists. Earlier, a considerable electron donor effect of the η^5-$C_5H_5(CO)_nMCH_2$– group where M is Fe, Mo, or W was deduced from measurements of acidic dissociation constants of η^5-$C_5H_5(CO)_nMCH_2COOH$ [1] and of pK_a's of the conjugated acids of the corresponding pyridine derivatives, η^5-$C_5H_5(CO)_nMCH_2$-C_5H_5N [2]. Anderson *et al.* [3] studied the interaction of η^5-$C_5H_5(CO)_2FeCH_2C_6H_5$ with $^2H_1$ trifluoroacetic acid and measured the ^1H NMR and mass spectra of toluene formed by cleavage of the σ-bond in that reaction. They concluded that the η^5-$C_5H_5(CO)_2FeCH_2$ moiety activated the benzene ring towards electrophilic substitution to a larger extent than the OCH_3 group did. We deemed it important to obtain more complete and accurate data on the electronic effects of the η^5-$C_5H_5(CO)_n$-MCH_2 group on the benzene ring using the hydrogen isotopic exchange technique*. In this work, acidic hydrogen isotopic exchange in transition metal σ-benzyl-π-cyclopentadienyl complexes has been studied and the mechanism of this reaction has been determined.

Results and Discussion

Our study of hydrogen exchange in transition metal cyclopentadienyl complexes containing the benzyl ligand η^5-$C_5H_5(CO)_nMCH_2C_6H_5$ (Ia–c, where n = 2, M = Fe; n = 3, M = Mo or W) as a σ-bonded moiety has shown that the ring hydrogen atoms undergo exchange under weakly acidic conditions (a mixture of deuterated trifluoroacetic and acetic acids, $H_o \approx -2$) at room temperature which is indicative of an exceedingly strong electron donor action by the metal-containing moiety, η^5-$C_5H_5(CO)_n$-MCH_2–, on the benzene ring [4, 5].



Ia n = 2 M = Fe
Ib n = 3 M = Mo
Ic n = 3 M = W

The kinetic measurements have made it possible to estimate the effect quantitatively. The introduction of the η^5-$C_5H_5(CO)_nMCH_2$ substituent has been found to increase the acidic hydrogen exchange rate in the benzene ring by nearly seven orders of magnitude. The unusual electron donor action of the metal-containing group, η^5-$C_5H_5(CO)_nMCH_2$–,

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*Shortly after our paper had been prepared for presentation, a paper by S. N. Anderson, C. J. Cooksey, S. G. Holton and M. D. Johnson, 'Substitution and Cleavage in the Reaction of Some Benzyl(carbonyl)metal complexes with Trifluoroacetic Acid', *J. Am. Chem. Soc., 102,* 2312 (1980), was published. The authors also investigated hydrogen exchange for $C_5H_5(CO)_2FeCH_2C_6H_5$ in CF_3COOD with results consistent with ours. However they paid attention mostly to the mechanism of acydolysis of the M–C bond, while we were interested in the isotopic hydrogen exchange mechanism of the benzene ring.

TABLE I. Acidic Hydrogen Exchange in the Complexes η^5-$C_5H_5(CO)_2FeCH_2C_6H_5$ (Ia), η^5-$C_5H_5(CO)_2FeCH_2C_6H_4$- *ortho*Me (IIa), η^5-$C_5H_5(CO)_2FeCH_2C_6H_4$-*meta*Me (IIb), η^5-$C_5H_5(CO)_2FeCH_2C_6H_4$-*para*Me (IIc)*.

Complex	k 10^6 sec^{-1} **
Ia	4.0
mesitylene	9.0
IIa	18.0
IIb	45.2
IIc	3.5

*Reagent ratio complex: CF_3COOD:CH_3COOD:CH_2Cl_2 of 1:10:10:13. **Values averaged over 3 to 4 experiments.

has prompted us to investigate the nature of the effect in more detail using the complex η^5-C_5H_5-$(CO)_nFeCH_2C_6H_5$ as model compound.

To study the analogous effect of the η^5-C_5H_5-$(CO)_2FeCH_2$– substituent hydrogen exchange kinetics in *ortho-*, *meta-*, and *para-*substituted derivatives of η^5-$C_5H_5(CO)_2FeCH_2C_6H_4Me$ (IIa–c, respectively) have been measured. The reaction with the *para-*substituted species proved to be the slowest and that with the *meta-*substituted derivative the fastest. The kinetic data are given in Table I.

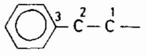
The data suggest that the η^5-$C_5H_5(CO)_2FeCH_2$– group has a predominantly *para-* and *ortho-*orienting action on the benzene ring which is typical of reactions following the electrophilic aromatic substitution mechanism. This conclusion is in agreement with that made by Anderson *et al.* [3] on the basis of ^1H NMR and mass spectrometric measurements of the degree of deuteration of various positions in toluene.

As an extension to the study of electronic effects by the η^5-$C_5H_5(CO)_2FeCH_2$– group on the benzene ring, we have studied acidic hydrogen exchange in the complex η^5-$C_5H_5(CO)_2FeCH_2CH_2C_6H_5$ (III) containing a CH_2– group between the η^5-C_5H_5-$(CO)_2FeCH_2$-substituent and the benzene ring. We find that the introduction of that group preventing conjugation between the substituent and the ring bars exchange completely [6].

The study of the complexes Ia–c by the ^{13}C NMR technique has shown that the benzene ring carbon signals in I are shifted to the higher field from free benzene and toluene which is an evidence in favour of the electron-donor nature of the η^5-$C_5H_5(CO)_n$-MCH_2– group. This effect is most manifest with the ring carbon atom positioned *para-* the substituent. Comparison of the ^{13}C NMR spectra of I and III suggests that in the latter compound, the electronic density of the benzene ring is lowered noticeably compared with I.

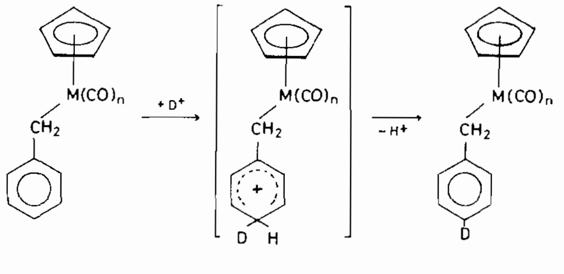
Similar data on the electronic density distribution in the benzene rings of I and III were obtained by Fong *et al.* [7] who compared ^{19}F chemical shifts in the ^{19}F NMR spectra of the complexes η^5-C_5H_5-$(CO)_2FeCH_2C_6H_4F$-*p* and η^5-$C_5H_5(CO)_2FeCH_2$-$CH_2C_6H_4F$-*p*. The combined experimental evidence is in agreement with the acidic hydrogen exchange mechanism similar to the mechanism of electrophilic aromatic substitution which includes the formation of the carbenium ion intermediate (A) stabilized by conjugation between the M–C σ-electrons and the benzene ring π-electronic system [8, 9].

TABLE II. Carbon-13 NMR Spectra of the Complexes η^5-$C_5H_5(CO)_nMCH_2C_6H_5$ (Ia–c) and η^5-$C_5H_5(CO)_2FeCH_2$-$CH_2C_6H_5$ (III).*



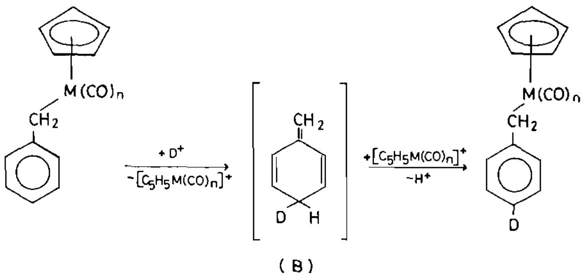
Complex	Chemical shift, ppm					
	1 C	2 C	benzene ring para-	meta, ortho-	3 C	Cp
Ia	4.7		122.8	127.2 127.8	144.0	85.9
Ib	5.1		123.8	127.4 127.9	151.1	94.0
Ic	8.66		123.4	127.0 127.5	151.4	92.4
III	5.5	44.0	125.2	127.6 128.8	146.6	85.2
$CH_3C_6H_5$	21.4		125.4	128.2 129.1	136.8	
C_6H_6			128.2			

*The ^{13}C NMR spectra were recorded on a Bruker HX-90 instrument (operating frequency 22.63 MHz) using TMS as internal reference.

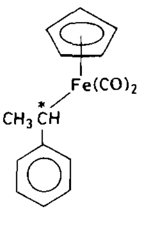


(A)

However, an alternative acidic hydrogen exchange mechanism has been discussed in the literature for organometallic systems ($ClMCH_2C_6H_5$ where M is Hg or Sn) containing a σ-benzyl group [10]. This mechanism involves fragmentation of the organoelement compound affording methylenecyclohexadiene (B) deuterated in the ring, followed by electrophilic addition of the organometallic moiety at the exocyclic double bond.



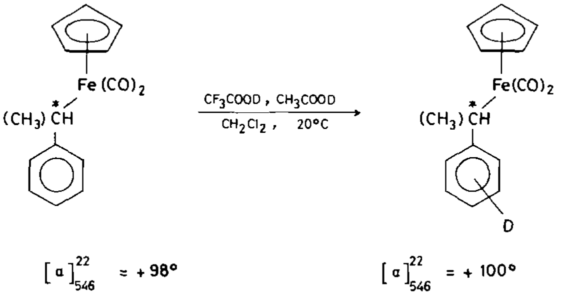
To study the mechanism of acidic hydrogen exchange in transition metal σ-benzyl-π-cyclopentadienylcarbonyl complexes we applied the stereochemical indication technique. Optically active complex IV was synthesized for that purpose



(IV)

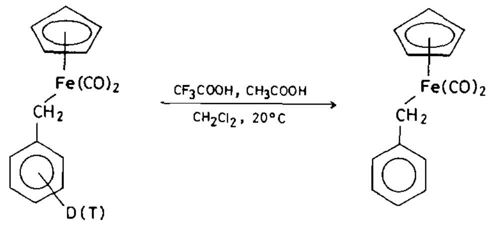
Hydrogen exchange in an optically active complex having a chiral centre at either the metal or the carbon atom σ-bonded to the metal would be expected to occur with retention of optical activity if mechanism (1) governs the process (the C–M bond remains intact) and with the loss of optical activity if mechanism (2) operates (the C–M bond undergoes cleavage).

The acidic hydrogen kinetic measurements for racemic IV have shown that the replacement of a hydrogen atom in Ia with the Me group has practically no effect on the exchange rate ($k = 3.9 \times 10^{-6}$ sec^{-1}). The acidic hydrogen exchange in an optically active IV was run under the conditions indicated above. We found [11] that the specific rotation of the complex isolated from the reaction is the same as that of the initial species which rules out the formation of methylenecyclohexadienes as intermediates in acidic hydrogen exchange in I.



$[\alpha]_{546}^{22} = +98°$ $[\alpha]_{546}^{22} = +100°$

To gain more insight into the mechanism of acidic hydrogen exchange in transition metal σ-benzyl-π-cyclopentadienylcarbonyl complexes we have also measured [12] the kinetic isotopic effect (k_D/k_T) of this reaction for η^5-$C_5H_5(CO)_2FeCH_2C_6H_5$. To do this we have synthesized complex Ia labelled with deuterium and tritium in the benzene ring and measured the hydrogen exchange rate in CF_3COOH–CH_3COOH in CH_2Cl_2 at room temperature.



The k_D/k_T value thus obtained was 1.6.

Acidic hydrogen exchange in the benzene series compounds following the electrophilic aromatic substitution mechanism is characterized by k_D/k_T values in the range 1.4 to 2 depending on the compound reactivity, medium solvation effects *etc.* Thus the exchange in benzene is characterized by k_D/k_T of 2 in 80% sulphuric acid [13], and in durene by k_D/k_T of 1.4 in CF_3COOH [14].

The k_D/k_T value for acidic hydrogen exchange in Ia compares well with the k_D/k_T values characteristic of the benzene series of compounds which is indicative of the similarity of the exchange mechanisms.

The data obtained in this work thus show that acidic hydrogen exchange in the benzene ring of transition metal σ-benzyl-π-cyclopentadienylcarbonyl complexes follows the electrophilic aromatic substitution mechanism involving as intermediate the formation of a carbenium ion stabilized by σ–π conjugation.

Experimental

The complexes η^5-$C_5H_5(CO)_nMCH_2C_6H_5$ (Ia–c) were prepared from the sodium salts of cyclopentadienylmetalcarbonyls and benzyl chloride by the literature procedures [15–17].

The complexes η^5-$C_5H_5(CO)_2FeCH_2C_6H_4Me$ (IIa–c) were obtained by reacting the sodium salts of cyclopentadienylmetalcarbonyls and *ortho-*, *meta-*, and *para-*methylbenzyl chlorides [18]. The complex η^5-$C_5H_5(CO)_2FeCH_2CH_2C_6H_5$ (III) was obtained from the sodium salt of cyclopentadienylirondicarbonyl and β-phenylethyl chloride [19]. The complex η^5-$C_5H_5(CO)_2FeCH(CH_3)C_6H_5$ (IV) was prepared from the sodium salt of cyclopentadienylirondicarbonyl and α-phenylethyl chloride [6].

Hydrogen exchange reactions were studied in a mixture of CF_3COOD and CH_3COOD in CH_2Cl_2 at room temperature under argon. To quench the process, the mixtures were poured into ice-cold water. The products were extracted with benzene and purified by chromatographing on Al_2O_3, followed by low-temperature crystallization from hexane. Deuterium content was measured from excess density of combustion water determined by the drop technique [20].

The complex η^5-$C_5H_5(CO)_2FeCH_2C_6H_5$ labelled with deuterium and tritium in the benzene ring was obtained by D and T exchange using $CF_3COOD(T)$ and CH_3COOD. The rate of acidic hydrogen exchange of the complex with a mixture of unlabelled CH_3COOH and CF_3COOH was measured. Tritium content was determined by the liquid scintillation technique [21]. The k_D/k_T ratios were measured in four experiments. The averaged value was 1.6.

Optically active complex η^5-$C_5H_5(CO)_2FeCH(CH_3)C_6H_5$ (IV) was prepared using the technique described by Wojcicki *et al.* [22]. The specific rotation value was $[\alpha]^{22}_{546}$ +98 °C (hexane). Hydrogen exchange was carried out in a CF_3COOD–CH_3COOD–CH_2Cl_2 mixture containing the complex and the reagents in a 1:10:10:13 ratio. The degree of exchange was 20% of the equilibrium value. Complex IV isolated from the reaction mixture had the specific rotation, $[\alpha]^{22}_{546}$, of +100 °C;. The specific rotation values were measured with a Jouan–Roussel (France) polarimeter. The values cited were averaged over four to five measurements. The [α] values differed within 5° owing to instability of the complex in solution.

Conclusions

The combined data obtained in this work including the kinetic measurements of acidic hydrogen exchange in transition metal σ-benzyl complexes and their derivatives, the stereochemical data, and the kinetic isotopic effect data indicate that acidic hydrogen exchange in the benzene ring of transition metal σ-benzyl-π-cyclopentadienylcarbonyl complexes follows the electrophilic aromatic substitution mechanism involving the intermediate carbenium ion stabilized by σ–π conjugation.

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