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Isotopic Exchange of Hydrogen in Aromatic Complexes of the Transition Metals

V.N.Setkina and D.N.Kursanov

This paper examines and evaluates the data on the isotopic exchange of hydrogen in aromatic complexes of the transition metals. Results of the kinetic investigation of isotopic exchange of a series of metallocenes in acid media are given, and these data are compared with those on hydrogen exchange of benzenoid compounds, permitting the relative reactivity of the sandwich compounds in electrophilic hydrogen exchange to be characterised. The isotopic exchange reactions of hydrogen are used to obtain quantitative data on the influence of electron-donating and electron-withdrawing substituents on the ferrocene system. A deep difference in the nature of the interaction of the substituents with the electron systems of ferrocene and benzene has been established.

The isotopic exchange of hydrogen in alkaline media is used to evaluate the acidic properties of aromatic complexes of the transition metals and as a characteristic of the effect of the nature of the central metal atom on the reactivity of the aromatic ligands.

A combination of hydrogen isotopic exchange and proton magnetic resonance enables the partial rate of exchange of hydrogen atoms at different ligand positions to be determined and hence the quantitative evaluation of their relative reactivity. A levelling of differences in the field of the orientating action of substituents in aromatic ligands π-bonded with the atoms of the transition metals has been established.

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INTRODUCTION

With the discovery of ferrocene[1] the chemistry of the complexes of the transition metals with organic ligands underwent considerable development. It has now become a large branch of organic chemistry containing enormous factual material and of great theoretical and practical interest[2-9].

The present paper considers the results obtained in the investigation of aromatic complexes of the transition metals by the hydrogen isotopic exchange method.

A series of features of the isotopic exchange of hydrogen allows it to be considered as worthy of separate consideration. Reactions which include the replacement of hydrogen by other atoms or groups, are widely distributed in organic chemistry. Hence the isotopic exchange of hydrogen models this extremely typical and important group of reactions of organic substances. Moreover, an important feature of isotopic exchange reactions is that during the isotopic substitution the electronic structure of the molecule does not change and this allows a more general characteristic of the reactivity of a substance to be obtained than on the basis of the replacement of hydrogen by other atoms or groups.

An investigation of the kinetic isotopic effects due to a difference in the zero-point energies of molecules with C–H, C–D, and C–T bonds, frequently permits significant conclusions about reaction mechanism to be drawn, particularly about the nature of the slowest stage.

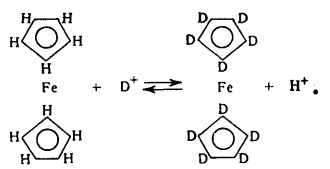
The isotopic exchange of hydrogen is sensitive to the change in the acidity of the medium. Knowledge of this dependence enables the reactivity of substances which differ considerably in their behaviour towards the acidity of the medium to be compared.

A comparison of the methods of proton magnetic resonance and hydrogen exchange allows the partial rates of exchange of various hydrogen atoms in the organic ligands to be determined and hence their relative reactivities to be evaluated quantitatively.

1. ISOTOPIC EXCHANGE OF THE HYDROGEN OF FERROCENE WITH ACIDS

The ability of the hydrogen atoms of aromatic ligands of sandwich compounds to undergo isotopic exchange with acids was first observed with ferrocene[10–12].

Nesmeyanov and coworkers[10] found that all the hydrogen atoms of the cyclopentadiene rings of ferrocene undergo isotopic exchange with acids enriched in deuterium. For example, this reaction occurs with hydrochloric, phosphoric, trichloroacetic, and trifluoroacetic acids enriched in deuterium[10,11]:



Simultaneously with these investigations a reference appeared in the literature[12] to unpublished work by Santer, who observed hydrogen exchange between ferrocene and the complex of boron fluoride and deuterium oxide.

Ferrocene reacts with concentrated deuteriosulphuric acid in a peculiar manner[11]. It was found that in this instance rapid deuterioexchange is accompanied by the oxidation of ferrocene to the ferricinium cation, which, however, is incapable of undergoing isotopic exchange. Both the competing reactions—deuterioexchange and oxidation—take place at different rates, the rate of isotopic exchange the greater, in consequence of which the oxidised form (ferricinium ion) contains a considerable amount of deuterium[11].

Quite recently Pavlik and Šubrt[13] reported that very rapid deuteriation of the cyclopentadienyl rings of ferrocene takes place during its reaction with deuterium chloride in the presence of aluminium chloride.

It was found[14] that the rate of isotopic exchange of the hydrogen of ferrocene depends significantly on the acidity of the medium. There is a linear dependence of the logarithm of the rate constant of the hydrogen exchange $k_{h.e.}$ on a function of the acidity of the medium, that is, Hammett's relation[15]

$$\lg k_{h.e.} + H_0 = \text{const},$$

is observed in the hydrogen exchange of ferrocene with acids.

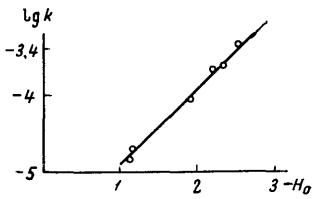


Figure 1. Effect of the acidity of the medium on the rate of isotopic exchange of the hydrogen of ferrocene.

Fig. 1 shows the results[14] which characterise the variation of the hydrogen exchange rate of ferrocene with the acidity of the solutions of trifluoroacetic acid of various concentrations in acetic acid. These results show that for ferrocene, as also for benzene[16], the rate of hydrogen exchange is proportional to the acidity of the medium.

The electrophilic isotopic exchange of hydrogen was used to study the relative reactivity of the compounds of the ferrocene series and other sandwich compounds of the transition metals. Compounds of the benzene series, whose reactivity in reactions with isotopic exchange of hydrogen has been well studied, were used as standards of comparison[17].

A comparison of the kinetic data on the hydrogen isotopic exchange of ferrocene and benzene allowed the relative reactivity of ferrocene to be evaluated. It was found that the relative rate constant for the hydrogen exchange of ferrocene ($k_{rel} = 7.8 \times 10^5$) is almost six orders of magnitude greater than that for benzene[11]. At acidities of the medium differing by six orders of magnitude the rates of hydrogen exchange of benzene and ferrocene are approximately the same.

Later Rosenblum and coworkers[18] compared the rates of acetylation of ferrocene and benzene by a Friedel–Crafts reaction and found that the acetylation of ferrocene ($k_{rel} = 3.3 \times 10^6$) is more rapid by approximately six orders of magnitude.

Hence results on the acetylation of ferrocene and benzene agree well with data on the isotopic exchange of hydrogen and show that in the electrophilic substitutions ferrocene exhibits considerably greater reactivity than benzene.

2. INFLUENCE OF SUBSTITUENTS ON THE ISOTOPIC EXCHANGE OF HYDROGEN OF FERROCENE DERIVATIVES WITH ACIDS

Before the use of the method of isotopic exchange of hydrogen quantitative information on the influence of substituents on electrophilic substitution in the ferrocene series was scarce and related only to alkyl[19], phenyl[20], and acetyl[21] groups. Quantitative data on the effect of substituents of electron-donating and electron-withdrawing character on the ferrocene system were obtained with the aid of the isotopic exchange of hydrogen with acids[22]. With this aim the kinetics of isotopic exchange of hydrogen in acid medium was studied for various monosubstituted and heteroannular disubstituted ferrocenes and the overall rate constants for the isotopic exchange of the hydrogen of these compounds were determined.

If the rate constant for the hydrogen exchange of ferrocene is taken as unity, then the relative rate constants for the exchange of substituted ferrocenes is expressed by $k_{rel} = k_{fc-X}/k_{fc-H}$. Table 1 gives the relative constants for the rate of hydrogen exchange which have been found experimentally.

Table 1. Relative constants k_{rel} of the rate of isotopic exchange of the hydrogen of substituted ferrocenes.

Substituent X	Compound	
	$C_5H_5FeC_5H_4X$	$(C_5H_4X)_2Fe$
—H	1	1
—CH_3	10.7	—
—C_2H_5	10.7	50.8
—OCH_3	6.7	23.3
—C_6H_5	0.6	0.3
—Cl	$2.5 \cdot 10^{-2}$	$7 \cdot 10^{-4}$
—$COOCH_3$	$1 \cdot 10^{-3}$	—

These kinetic results on the influence of substituents on the reactivity of ferrocene derivatives showed[23] that the logarithms of the relative rate constants of the isotopic exchange of hydrogen of the monosubstituted and disubstituted ferrocenes depend linearly on the substituent constants σ_p^0 and that the correlation coefficient r has a high value (r = 0.992) (Fig. 2).

Hence the substituent constants σ_p^0 determined from the dissociation constants of phenylacetic acids are a quantitative characteristic of the influence of the substituent on the rate of hydrogen exchange of the ferrocene system. These substituent constants take into account the conjugation of the substituent with the aromatic system but not the conjugation of the substituent with the reaction centre.

From the linear relation between $\lg k_{rel}$ and σ_p^0 it follows that the relation between the inductive effect and the effect of conjugation of the substituent in the electrophilic hydrogen exchange of ferrocene derivatives is approximately the same as in reactions in the side chain of benzene derivatives, that is, the contribution of the conjugation of the substituent is considerably less for the ferrocene compounds than in electrophilic substitution in the benzene series.

This conclusion follows especially clearly from a comparison of the influence of the CH_3– and CH_3O-groups on the ferrocene and benzene systems.

The methyl group, exhibiting a positive inductive effect and a positive conjugation effect (+I, +C effects), increases the rate of hydrogen exchange in cyclopentadienyl rings of ferrocene to a less extent than in benzene[24]:

$$k_{C_6H_5CH_3}/k_{C_6H_6} \simeq 150;$$

$$k_{fe-CH_3}/k_{fe-H} \simeq 10.$$

The methoxy-group, exhibiting a positive conjugation effect and a negative inductive effect (+C, –I) increases the rate of hydrogen exchange in the benzene system 40 000 times[25] but in the ferrocene system by no more than 7 times, that is, the activating influence of the CH_3O group on the benzene ring and on the ferrocene ring differ by almost four orders of magnitude.

$$k_{C_6H_5OCH_3}/k_{C_6H_6} \simeq 4 \times 10^4;$$

$$k_{fe-OCH_3}/k_{fe-H} \simeq 7.$$

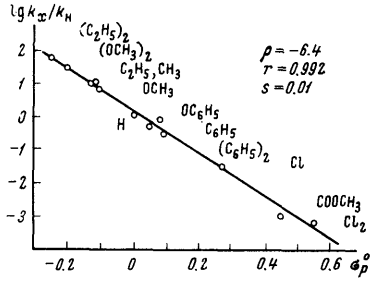


Figure 2. Variation of $\lg k_{rel}$ of hydrogen exchange on σ_p^0.

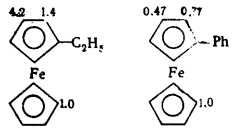
It is significant that the effect of substituents in the ferrocene series on the rate of isotopic exchange of hydrogen seemed identical with the effect of the substituents on the value of the redox potentials of the substituted ferrocenes. A linear relation was found between the logarithms of the equilibrium constants of the redox reactions and σ_p^0 by Nesmeyanov and coworkers[26] for a large number of substituted ferrocenes.

The same type of substituent effect in substitutions (isotopic exchange) and in the oxidation of ferrocene can evidently be explained by the presence in both reactions of a common reaction centre, which it is natural to assume is the iron atom.

3. INFLUENCE OF SUBSTITUENTS ON THE REACTIVITY OF THE 2-, 3-, AND 1′-POSITIONS OF CYCLOPENTADIENYL RINGS OF FERROCENE IN EXCHANGE WITH ACIDS

Quantitative information on substituent effects on the reactivity of the different positions in the cyclopentadienyl rings of monosubstituted ferrocenes is extremely scanty and, as already mentioned, is limited to data characterising the influence of alkyl, phenyl, and acetyl groups[19-21]. From these results it follows that the reaction capability of various positions in cyclopentadienyl rings (2-, 3-, and 1′-positions) is not very different for alkyl- and aryl-substituted ferrocenes. As an example, we give numerical

data on the relative reactivity of the 2-, 3-, and 1'-positions in ethyl- and phenyl-ferrocenes during acetylation[19,20].

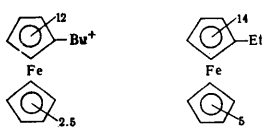


It should be noted that the determination of the reactivity of different positions of the ferrocene substituents in electrophilic substitutions involves great experimental difficulties and in several instances is impossible. For example, the influence of methoxy- and methylthio-groups on the reactivity of the ferrocene system in a Friedel–Crafts acetylation, since methoxy- and methylthio-ferrocenes seemed unstable under these conditions[27].

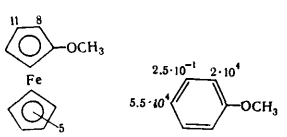
An extremely promising method of studying the reactivity of various positions in the cyclopentadienyl rings of substituted ferrocenes is evidently the method of isotopic exchange of hydrogen in conjunction with the high-resolution proton magnetic resonance (PMR) method.

The proton magnetic resonance spectra of a large number of monosubstituted ferrocenes[28] show that the differences in the chemical shifts of the signals of the protons of the 2-, 3-, and 1'-positions are rather great and consequently the deuterium content in these positions can be determined from the change in the integral intensity of the corresponding PMR signals in the isotopic exchange of hydrogen. Even for alkyl substituents, for which the differences in the chemical shifts of the corresponding protons are relatively small, success was achieved on a spectrometer with working frequency 60 MHz in separating the protons of substituted and unsubstituted rings and hence of evaluating their reactivity[29].

The values determined by this method of partial rate factors for isotopic exchange of the hydrogen of unsubstituted and substituted rings of t-butyl- and ethyl-ferrocenes with deuteriated trifluoroacetic acid have been given by Setkina[30].



The partial rate factors for electrophilic hydrogen exchange with deuteriated trifluoroacetic acid were determined in an analogous manner for the 2-, 3-, and 1'-positions in methoxyferrocene[31]. These values were 8, 11, and 5 for the 2-, 3-, and 1'-positions respectively. It is interesting that the partial rate factors for hydrogen isotopic exchange of the *o*-, *m*-, and *p*-positions of methoxybenzene under analogous conditions are 2×10^4, 2.5×10^{-1}, and 5.5×10^4 respectively[25].



The marked difference in the influence of the methoxy-group on the reactivity of ferrocene and benzene shows the deep difference in the nature of the interaction of this substituent with the electronic systems of both substances†.

4. MECHANISM OF ELECTROPHILIC ISOTOPIC EXCHANGE OF HYDROGEN IN THE FERROCENE SERIES

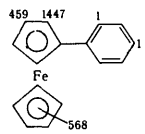
Electrophilic substitutions are characteristic of ferrocene[32]. Such a reaction capability appears clearly also in the isotopic exchange of the hydrogen atoms of ferrocene with acids[10–14]. However, the mechanism of electrophilic substitution in the ferrocene series still cannot be considered established.

In considering the mechanism of electrophilic exchange of the hydrogen of ferrocene it is necessary to settle the following questions: (1) the problem of the position of initial attack of the electrophilic reagent, (2) what are the elementary steps of the process and which of them is rate-determining, and (3) what are the nature and structure of the intermediate species and activated complex.

There is evidence that electrophilic substitution in cyclopentadienyl rings, in particular the isotopic exchange of hydrogen with acids, begins with the addition of the electrophilic reagent to the iron atom.

The formation of an addition product containing an iron–hydrogen bond by the addition of a proton to ferrocene was proved experimentally by Rosenblum and coworkers by the NMR method[12] and also by Pavlik and Šubrt by infrared spectroscopy[13]‡. Having accepted this stage as the initial one, it must be assumed that subsequent stages are the

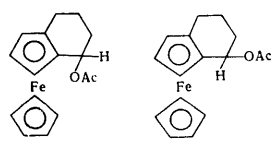
† After the present article had been sent to the press a paper appeared[81] in which values were given for the relative rate constants for the various positions of phenylferrocene in the isotopic exchange of hydrogen with trifluoroacetic acid.



Partial rate factors were determined from the change in the integral intensity of the signals of the corresponding protons in the PMR spectrum. In complete agreement with the data given above[19–21,30,31], the authors[81] concluded that the relative rates of hydrogen exchange in positions 2, 3, and 1' of ferrocene differ very little.

Pauson and coworkers[82–85] came to a similar conclusion after having investigated the aminomethylation of monosubstituted and disubstituted heteroannular derivatives of ferrocene (CH_3-, CH_3O-, and CH_3S-derivatives).

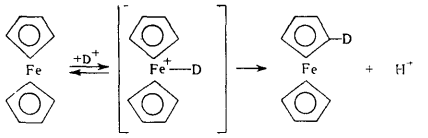
‡ The ability of the iron atom to react with electrophilic reagents agrees with other experimental results. These include, for example, data on the formation of intramolecular hydrogen bonds in ferrocenylcarbinols between the hydrogen of the hydroxyl group and the iron atom[33], between the hydrogen of a protonated carbonyl group and the iron atom in alkylferrocenylketones[34], data on the stabilisation of the carbonium centre in α-ferrocenylcarbonium ions and their conversion into radicals owing to internal single-electron transitions from the iron atom to the α-carbonium centre[35], data on the rates of solvolysis of the *endo*- and *exo*-isomers of the esters of the α-ferrocenylcarbinols A and B[36]:



endo-isomer A *exo*-isomer B

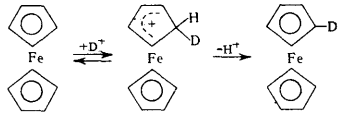
It was found that the rate of solvolysis of isomer B, in which the spatial position of the acetate group does not ensure its interaction with the iron atom (transoidal arrangement of the OAc group), is almost three orders of magnitude greater than the rate of solvolysis of isomer A, but both isomers form only the *exo*-alcohol[37].

migration of the attacking reagent into the cyclopentadienyl ring and the loss of a proton. As a result the final products of the electrophilic substitution are formed. For the isotopic replacement of hydrogen by deuterium in the action of deuterio-acids on ferrocene this final product is deuterioferrocene (scheme 1).



(1)

An alternative mechanism could be one including the immediate addition of a deuteron to the cyclopentadienyl ring (scheme 2) with the formation of a σ-complex similar to that found for aromatic compounds of the benzene series:

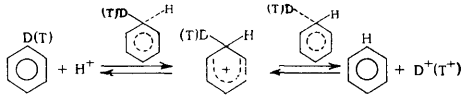


(2)

Recently kinetic isotopic effects (KIE) were used to study the mechanism of this reaction and, in particular, its rate-limiting stage. For this, the kinetics of isotopic exchange at protium of ferrocenes enriched in deuterium and tritium was investigated[38]. The following considerations applied: when the reaction proceeds by a mechanism represented in scheme 1 and its slow stage is the addition of a proton to iron and subsequent stages leading to the final product are fast, then the primary isotopic effect in this reaction should not be observed and the ratio of the rate constants of the exchange of both isotopes should approximate to unity ($k_D/k_T \simeq 1$).

On the other hand, if the reaction proceeds by a mechanism represented by scheme 2, then the kinetic isotopic effect should be observed. Actually, in the isotopic exchange of the hydrogen of benzene aromatic compounds it has been found experimentally by a large number of examples [39-42] that the ratio $k_D/k_T \simeq 2$.

The considerable KIE in the electrophilic isotopic exchange of hydrogen in aromatic compounds of the benzene series is the consequence of the difference in the rate of breaking of the C–H, C–D, and C–T bonds in the intermediate σ-complex in which the hydrogen and deuterium (tritium) atoms occupy equivalent positions (scheme 3).



(3)

However, an investigation of the kinetics of isotopic exchange of ferrocenes containing tritium and deuterium by protium when acids act on them showed that the ratio k_D/k_T here is considerably less and is 1.2 [38]§. This result shows that the isotopic exchange of hydrogen in ferrocene does not proceed by mechanism 2. On the contrary, the above result agrees with mechanism 1.

However, as Hammond stated[43], the low value of the KIE can also be due to the free energies of the transition state and the intermediate compound being similar.

At the present time our information about the nature and structure of the activated complex and intermediate substances in the reaction being considered are insufficient and do not allow us to settle this question theoretically. However, in addition to the above results there are several experimental results which also support mechanism 1.

The possibility that the cyclopentadienyl nucleus exerts a specific influence on the KIE is disproved by the data obtained in studying the KIE of azulene[44]. It was shown that the KIE of azulene in electrophilic isotopic exchange of hydrogen has a normal value.

Furthermore it was found that in the protophilic substitution of hydrogen in the cyclopentadienyl rings of ferrocene in liquid ammonia with potassium amide, in which the nucleophilic reagent directly attacks the hydrogen atoms of the cyclopentadienyl rings and consequently mechanism 1 cannot occur, there is actually a significant KIE $k_D/k_T = 2.3$ (see Ref. 38).

The existence of a linear relation between the logarithm of the rate constant of the isotopic exchange of hydrogen of ferrocene and the acidity function of the medium also agrees with the fact that in the rate-determining stage of the hydrogen exchange a protonated form of ferrocene is involved.

Another fact in support of mechanism 1 is that the effect of the substituents on the redox potentials of the ferrocene–ferricinium system and on the kinetics of isotopic exchange of hydrogen in cyclopentadienyl rings is similar. This is shown by the logarithms of the rate constant of the hydrogen exchange and the logarithms of the ratio of equilibrium constants of the redox reaction of the corresponding substituted ferrocenes being linearly correlated with the same substituent constants σ_p^0.

This suggests that both reactions have the same reaction centre, probably the iron atom. Moreover, since the addition of a proton (deuteron) to the iron atom is the rate-determining stage the presence of non-equilibrium positions in the cyclopentadienyl rings will not be reflected in the kinetics of the reaction.

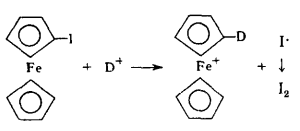
In addition it must be noted that such an explanation of the mechanism of electrophilic isotopic exchange of hydrogen in the ferrocene system encounters certain difficulties. For example, according to X-ray structural analysis the iron atom in the ferrocene compounds is shielded by the cyclopentadienyl rings (distance between the rings 3.32 Å)[45], which should hinder the approach of the attacking reagent towards it.

Quantum-chemical calculations show that the excess of electron density in the ferrocene molecule is concentrated on the cyclopentadienyl rings, and the iron atom has an excess of positive charge and consequently preferential attack of electrophilic reagents on the cyclopentadienyl rings can be expected[46,47].

The explanation of this discrepancy may be that the X-ray structural analysis and the quantum-chemical calculations consider the unexcited ferrocene molecule, present in the ground state and do not take into account the changes which occur to the molecule in the reaction process.

New facts showing the significant part played by the iron atom in the substitution were obtained[48] in studying the reaction of deuteriofluoroacetic acid with iodoferrocene.

It appeared that under these conditions the iodine is replaced by the deuteron of the acid with the simultaneous oxidation of the ferrocene to ferricinium and the detachment of the iodine as atomic iodine (scheme 4):



(4)

§ In a recent paper[86], in which a new point of view about the mechanism of electrophilic substitution in metallocenes was expressed, the value $k_H/k_D = 1.8$ was given for the hydrogen exchange of ferrocene in acid medium. If the ratio $k_H/k_D = (k_D/k_T)^{2.26}$ given by Swain and coworkers[87] is used, then $k_D/k_T = 1.3$ and consequently the values of the KIE given in Refs. 38 and 87 seem similar.

The synchronism of the processes of the replacement of iodine by a deuteron and the oxidation of ferrocene to ferrocinium shows that in the intermediate compound (or transition state) the iron atom plays an active part, with the redistribution of the electrons readily taking place in the system.

5. ISOTOPIC EXCHANGE OF THE HYDROGEN OF METALLOCENES

a. Data on the Relative Nucleophilicity of Some Metallocenes

Over sixty elements are now known to be capable of forming π-cyclopentadienyl compounds[49]. Many metallocenes have been found capable of undergoing electrophilic substitution (compounds of Fe, Mn, Re, Os, Ru, V, Cr, etc.).

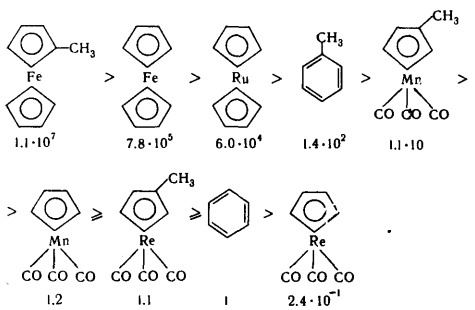
These reactions have been especially widely investigated for ferrocene, whereas other metallocenes have been considerably less studied and for many of them generally nothing is known about substitutions in the cyclopentadienyl ligands.

The failures in attempts to bring about substitution in such metallocenes are not always due to lack of reactivity but are often explained by the instability of the metallocenes under the reaction conditions.

This therefore gives rise to the quite important requirement for a sufficiently general method which will allow the reactivity of the ligands to be characterised both qualitatively and quantitatively. It was shown earlier that the isotopic exchange of hydrogen is extremely suitable for this purpose.

The possibility of changing within wide limits the acidity of the medium, on which the rate of hydrogen exchange depends to a considerable extent, allows systems which differ greatly in reactivity to be compared.

The study of the kinetics of isotopic exchange of hydrogen of certain metallocenes and their methyl derivatives and the comparison of these results with those on the isotopic exchange of benzene compounds led to the following series, in which the rate of hydrogen exchange of benzene is taken as unity and the number characterising the relative rate of hydrogen exchange of the given compound is written under its formula:



It could be expected that in other electrophilic substitutions also these systems will show approximately the same relative reactivity.

Quite recently Fischer and coworkers[50] investigated the reactions of competing Friedel–Crafts acetylation of π-cyclopentadienyl compounds of the transition metals, using the PMR method to determine the composition of the acylation products. On the basis of their results the compounds investigated are arranged in the following order of decreasing reactivity to acetylation:

$$(C_5H_5)_2Fe > CH_3OC_6H_5 > (C_5H_5)_2Ru > C_5H_5Mn(CO)_3 > (C_5H_5)_2Os > C_5H_5Cr(CO)_3NO > C_5H_5V(CO)_4 \approx C_6H_6 > C_5H_5Re(CO)_3.$$

It is essential to note that the Fischer series compiled on the basis of the qualitative data on the competing reactions of acetylation agrees completely with the series constructed on the basis of the kinetic data on the hydrogen exchange rates in acid media.

At the present moment we still do not possess the necessary facts to trace sufficiently broadly the dependence of the reactivity of the ligands on the position of the complex-forming metal in the Periodic System.

However, the results of a study of the kinetics of hydrogen exchange of the π-cyclopentadienyl compounds of the transition metals show that on going from an element of the fourth period (Mn) to an element of the sixth period (Re) in Periodic Group VII the reactivity of the π-cyclopentadienyl ligands in acid media diminishes. A similar picture is observed also for the π-cyclopentadienyl compounds of the Group VIII metals. The cyclopentadienyl derivatives of iron (fourth period) are more reactive than the corresponding ruthenium derivatives (fifth period). More detailed information on the isotopic exchange of hydrogen of some metallocenes is given below.

b. Isotopic Exchange of the Hydrogen of the Metallocenes of the Group VII Transition Metals

π-Cyclopentadienyl compounds are now known for all the transition metals of Group VII—manganese, rhenium, and technetium[51]. The greatest number of papers relate to compounds of manganese, and in particular to cyclopentadienylmanganesetricarbonyl (CMT) and its derivatives.

Electrophilic substitutions are characteristic for the cyclopentadienyl ring π-bonded to the $Mn(CO)_3$ group—alkylation[52], acylation[53], sulphonation[54], phosphorylation[55], mercuration[56], etc.

The reactivity of CMT in electrophilic substitutions was compared with the reactivity of benzene and anisole in competing acylations[57]. It was found that the compounds investigated are arranged in the following series according to their reactivity:

$$CH_3OC_6H_5 > CH_3C_6H_4Mn(CO)_3 > C_5H_5Mn(CO)_3 > C_6H_6.$$

Results which characterise the relative reactivity of CMT quantitatively were obtained in studying the kinetics of isotopic exchange of hydrogen of CMT and benzene with a mixture of deuteriated trifluoroacetic and sulphuric acids in methylene chloride solution[58].

It was found that the rate constant of hydrogen exchange of CMT is 1.3–2 times that for benzene under the same conditions.

Experiments[58] on the competing hydrogen exchange of a mixture of CMT and benzene have been described; they led to the conclusion that there was little difference in the relative reactivity of these substances.

The isotopic exchange of hydrogen with acids was used for studying the influence of alkyl substituents on the reactivity of the CMT system and these results are compared with analogous data for the benzene series (Tables 2 and 3)[59].

It appeared that the influence of electron-donating alkyl groups in CMT is much less than in benzene. The introduction of one methyl group into CMT increases the rate of

isotopic exchange of hydrogen nine times, whereas one methyl group in the benzene ring increases the rate of hydrogen exchange 155 times. Three ethyl groups in the cyclopentadienyl ring of CMT activates the deuterio-exchange less than one methyl group in the benzene ring. The rate constant of the hydrogen exchange of triethylcyclopentadienylmanganese tricarbonyl increases 126 times and the hydrogen exchange of 1,3,5-trimethylbenzene more than 7 orders. It is interesting to note that in the ferrocene series the alkyl groups activate the cyclopentadienyl ring approximately the same as for CMT. Evidently the lesser influence of the alkyl groups in the cyclopentadienyl rings of the metallocenes compared with the compounds of the benzene series has a general character and depends little on the nature of the metal connected with the cyclopentadienyl ring.

Table 2. Isotopic exchange of the hydrogen of derivatives of CMT.

Substance	Relative rate of isotopic exchange of hydrogen
$C_5H_5Mn(CO)_3$	1
$(CH_3)C_5H_4Mn(CO)_3$	9
$(C_2H_5)C_5H_4Mn(CO)_3$	5
$(C_2H_5)_2C_5H_3Mn(CO)_3$	57
$(C_2H_5)_3C_5H_2Mn(CO)_3$	126
$(C_2H_5)_4C_5HMn(CO)_3$	512
$(C_2H_5)_5C_5Mn(CO)_3$	0

Table 3. Isotopic exchange of the hydrogen of alkylbenzenes[60].

Substance	Relative rate of isotopic exchange of hydrogen
Benzene	1
Toluene	155
o-Xylene	850
Mesitylene	$135 \cdot 10^5$

It was shown recently[61] that cyclopentadienylrheniumtricarbonyl (CRT) is capable of electrophilic hydrogen exchange under the same conditions as those under which CMT undergoes this reaction.

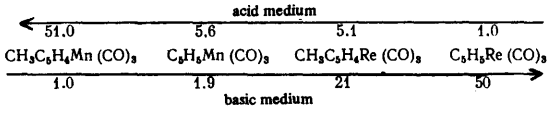
The influence of the nature of the metals of the same group, Re and Mn, was compared by the reactivity of the cyclopentadienyl rings π-bonded with them in reactions of electrophilic isotopic exchange. The rate constants of the hydrogen exchange under the same conditions were 0.7×10^{-6} s^{-1} for CRT and 3.9×10^{-6} s^{-1} for CMT. These results show that in the reaction being considered the nucleophilic reactivity of the manganese compound is greater than that of the rhenium compound and therefore it can be expected that the rhenium compounds will also appear less reactive in other electrophilic substitutions.

On the introduction of a methyl group into the cyclopentadienyl ring of CRT the rate of electrophilic hydrogen exchange increases by approximately 5 times and consequently the activating influence of the methyl group in this system is approximately the same as in other metallocenes.

An interesting feature of the cyclopentadienyl derivatives of manganese and rhenium was their ability to undergo isotopic exchange of hydrogen in basic media (protophilic exchange) under comparatively mild conditions with ethanol in the presence of sodium ethoxide[62]. Under these conditions neither benzene nor ferrocene undergoes isotopic exchange.

An investigation of the kinetics of this reaction showed that the rhenium derivative exchanges hydrogen more rapidly than the manganese compound. The rate constant of the hydrogen exchange is 3×10^{-6} s^{-1} for CMT and 80×10^{-6} s^{-1} for CRT. It was found that exchange in alkali media, unlike electrophilic hydrogen exchange is retarded on the introduction of methyl groups into the cyclopentadienyl rings of CMT and CRT.

Hence the investigation of isotopic hydrogen exchange of cyclopentadienyl derivatives of the transition elements of Group VII showed that on going from Mn (fourth period element) to Re (sixth period element) the reactivity of the π-cyclopentadienyl ligands in electrophilic hydrogen exchange is reduced and that in protophilic is increased. The values of the relative constants of the rate of isotopic exchange are as follows:



The influence of electron-donating and electron-withdrawing substituents in the protophilic isotopic exchange was investigated in the case of monosubstituted derivatives of cyclopentadienylmanganesetricarbonyl. The overall hydrogen exchange rate constants for cyclopentadienyl ligands, which characterises their relative reactivity, are given in Table 4.[63]

Table 4. Total and relative rate constants for the isotopic exchange of hydrogen of substituted CMT compounds.

Substance	$10^4 k_{h.e.}$, s^{-1}	k_{rel}*
$C_5H_5Mn(CO)_3$	3.1	1
$CH_3C_5H_4Mn(CO)_3$	1.6	0.5
$C_2H_5C_5H_4Mn(CO)_3$	1.2	0.4
$HSO_3C_5H_4Mn(CO)_3$	8.0	2.6
$HCOOC_5H_4Mn(CO)_3$	3.4	1.1

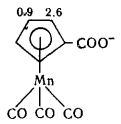
* Rate relative to the rate of exchange of CMT.

From Table 4, the influence of substituents of either donor or acceptor nature appears to be extremely weak in the cyclopentadienylmanganesetricarbonyl system.

The reason for this remarkable feature of the cyclopentadienyl system, π-bonded with a $Mn(CO)_3$ group remains vague and needs further investigation.

Very little is known about the orienting action of the substituents in the cyclopentadienyl nucleus of CMT. The only work in this field is devoted to a study of the orienting action of the carboxyl group in the CMT system in protophilic isotopic exchange[64]. The combined use of the methods of isotopic hydrogen exchange and proton magnetic resonance allowed a difference in the reactivity of the α and β positions of a carboxy-derivative of CMT to be observed. From the change in the integral intensity of the

signals of the α and β protons in the isotopic exchange the partial rate factors for exchange were determined for these positions, which were 2.6 and 0.9 for the α and β sites respectively. The ratio of the factors $f\alpha/f\beta = 2.9$ characterises the difference in reactivity of these sites:



Evidently in protophilic substitution the influence of the electron-withdrawing carboxyl group in the cyclopentadienyl ring π-bonded with the $Mn(CO)_3$ group is due mainly to an inductive effect.

c. Isotopic Exchange of the Hydrogen of Metallocenes of Transition Metals of Group VIII

As already noted, a characteristic reaction for the compounds of the ferrocene series is electrophilic hydrogen exchange, as well as other electrophilic substitutions. However, for the other Group VIII metallocenes—nickelocene and cobalticene, not even one substitution was known.

Unlike ferrocene, cobalticene and nickelocene are unstable in acid media. The rate of oxidation and decomposition of these systems evidently exceeds the rate of the substitution, as a result of which electrophilic hydrogen exchange does not exist for either cobalticene or nickelocene.

However, it was recently found that in protophilic substitution in the presence of bases nickelocene is capable of undergoing isotopic exchange of hydrogen. Thus it appeared that on treating nickelocene with diethylamine containing deuterium at the nitrogen atom, in the presence of lithium diethylamide, isotopic exchange of hydrogen takes place in the cyclopentadienyl rings of nickelocene[65]:

$$(C_5H_5)_2Ni \xrightarrow{Et_2ND,\ Et_2NLi} (C_5D_5)_2Ni\ ,$$

The rate of the hydrogen isotopic exchange of nickelocene depends on the concentration of lithium diethylamide and for example, at a lithium diethylamide concentration of 0.09 N in diethylamine solution (Et_2ND) at 25°C the rate constant of the isotopic exchange is $\sim 6 \times 10^{-5}$ s^{-1}. It is interesting to note that under these conditions neither ferrocene nor cobalticene undergoes hydrogen exchange.

Protophilic isotopic exchange of hydrogen in ferrocene has been brought about only under much more drastic conditions—in liquid ammonia in the presence of potassium amide[38].

The rate constant of the replacement of deuterium in deuterioferrocene by protium in a 0.02 N solution of potassium amide in liquid ammonia at 13°C is 9×10^{-4} s^{-1}. Under the same conditions the rate constant of the exchange of deuterium in benzene is 3×10^{-5} s^{-1}. From these results it follows that in ferrocene and benzene the hydrogen atoms exhibit considerably less acidity than in nickelocene.

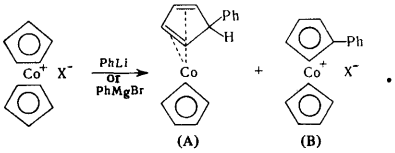
Although the hydrogen isotopic exchange of nickelocene in the presence of bases is so far the only example of substitution in this system, it can be expected that nickelocene is capable of undergoing substitution with catalysis by bases and that these reactions should proceed more readily than in ferrocene and benzene.

The replacement of hydrogen in the presence of bases could also be carried out with the isoelectronic analogue of ferrocene—the cobalticinium ion. It was found that in the reaction of cobalticinium hydroxide with deuteriomethanol in the presence of sodium methoxide cobalticinium hexachloroplatinate, isolated by treatment of the reaction products with hydrogen hexachloroplatinate, contains deuterium in the cyclopentadienyl rings[66].

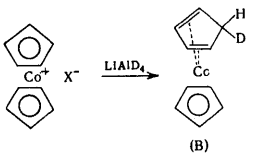
The kinetics of hydrogen isotopic exchange of cobalticinium methoxide with a 10% solution of sodium methoxide in deuteriomethanol (CH_3OD) was studied at 50°C and the rate constant of this reaction is 6.4×10^{-5} s^{-1}:

$$(C_5H_5)_2Co^+X^- \xrightarrow{CH_3OD,\ CH_3ONa} (C_5D_5)_2Co^+X^-\ .$$

An indication of the possibility of substitutions in the cyclopentadienyl rings of the cobalticinium ion was obtained earlier[67], since it was noted that with phenyl-lithium or with phenylmagnesium bromide cobalticinium salts form, as well as addition products (A), a certain proportion of phenyl-containing substitution product (B):



However, in other studies it appeared that compounds of the cobalticinium ion with nucleophilic reagents form only addition products analogous to compound A, and lithium tetradeuterioaluminate, for example, reacts with cobalticinium to form cobaltcyclopentadienylmonodeuteriocyclopentadienide (compound B) and does not form substitution products[68]:



Clearly the available information is insufficient for judging the reactivity of the cyclopentadienyl ligands in the metallocenes of nickel and cobalt, but the above examples of the replacement of hydrogen in these systems provide a basis for assuming that they are capable of undergoing other base-catalysed substitutions.

6. ISOTOPIC EXCHANGE OF HYDROGEN IN THE AROMATIC RINGS OF ARENECHROMIUM TRICARBONYLS

The simplest representative of the arenechromiumtricarbonyls—benzenechromiumtricarbonyl—was obtained by Fischer and Öfele in 1957.[69] A considerable number of representatives of this type of compound have now been listed but their reactions, and especially substitutions in the aromatic ring, have been little studied.

It has been found that electrophilic substitution in arenechromiumtricarbonyl complexes, and particularly Friedel–Crafts acetylation, takes place with much more difficulty than in the corresponding aromatic compounds[70]. However, nucleophilic substitutions take place more readily in these systems than in arenes. For example, the chlorine in chlorobenzenechromiumtricarbonyl is smoothly replaced by the methoxy-group with sodium methoxide in methanol[71]. Quantum-chemical calculations of Brown predict greater ease of nucleophilic replacement in arenechromiumtricarbonyls than in arenes, which agrees with the experimental facts.

One of the cardinal problems of the chemistry of arene complexes of transition metals is the question of how the blocking of the π-electrons of the aromatic ring by the atoms of the transition metals affects the properties of the aromatic system. In particular, it is important to find how the reactivity of an aromatic system π-bonded with a transition metal atom changes and how the electronic effects of the substituents in such systems are passed on.

It is evident that a comparison of the properties of the compounds of the series of benzene and π-arene complexes with the chromiumtricarbonyl group can give valuable information in this respect. Such a type of investigation was made, in particular, by Fischer and coworkers[70]. The Friedel–Crafts acylation of toluenechromiumtricarbonyl and toluene was compared. It was found that the content of the *o*-, *m*-, and *p*-isomers in the acylation products is quite different for toluene and its complex with chromiumtricarbonyl group. Whereas for toluene the proportions of the *o*-, *m*-, and *p*-acetyl substituents were 1.2, 2.0, and 96.8%, for toluenechromiumtricarbonyl they are 43, 17, and 40% respectively.

The much smaller difference in reactivity of the *o*-, *m*-, and *p*-positions of alkyl-substituted arenechromiumtricarbonyls in comparison with the corresponding alkylarenes in the acylation was also noted by Jackson and Jennings[73]. Fritz and Kreiter[74] came to the same conclusion on the basis of studies of the PMR spectra of disubstituted arenechromiumtricarbonyls.

Interesting possibilities for the quantitative study of the transmission of the influence of the substituent in the benzene ring π-bonded with a transition metal atom were presented after it had been observed that the hydrogen atoms in benzenechromiumtricarbonyl are capable of undergoing isotopic exchange with deuterioalcohols or deuterioamines in the presence of bases[75].

It was found that at 100°C in a 10% solution of sodium ethoxide in deuterioethanol the rate constant for isotopic exchange of the hydrogen of benzenechromiumtricarbonyl is $\sim 1.0 \times 10^{-5}$ s^{-1}. It is interesting that benzene itself under such conditions does not undergo isotopic exchange of hydrogen.



Quantitative characterisation of the effect of substituents on the reactivity of the *o*-, *m*-, and *p*-positions of the monosubstituted benzene ring π-bonded with the $Cr(CO)_3$ group were obtained by the combined use of isotopic exchange of hydrogen and proton resonance methods[76,77]. It appeared that in an aromatic ring π-bonded with the $Cr(CO)_3$ group the influence of the substituent in protophilic hydrogen exchange is extremely weak and the difference in the reactivity of the *o*-, *m*-, and *p*-positions of the ring is also very low. Table 5 shows the partial rate factors for isotopic exchange at the various positions of the aromatic ring in toluenechromiumtricarbonyl[76] and anisolechromiumtricarbonyl[77].

For comparison Table 5 also gives partial rate factors for the non-equilibrium positions in toluene and anisole found by Shatenshtein and coworkers[78] in a study of the isotopic exchange of hydrogen of these compounds in liquid ammonia in the presence of potassium amide. These results show that the influence of the methyl, and particularly the methoxyl, group in arenechromiumtricarbonyls is considerably weaker than in the corresponding arene.

Whereas the partial rate factors in anisolechromiumtricarbonyl differ by only a factor of 3, this difference is much greater for anisole.

An investigation of the isotopic exchange of hydrogen of arenechromiumtricarbonyls containing electron-donating (Me_2N–, CH_3–) and electron-withdrawing (CH_3COO–) substituents (Table 6) gave remarkable results: the overall rate constants of hydrogen exchange of arenechromiumtricarbonyls containing substituents with opposite electronic effects do not differ much[77]. Consequently, the influence of different substituents in protophilic hydrogen exchanges in arenechromiumtricarbonyls complexes is weak.

Table 5. Factors of the partial rate of isotopic exchange of the hydrogen of arenechromiumtricarbonyls and arenes.

Compound	Factors of the partial rate of hydrogen exchange			Reaction conditions	Reference
	f_o	f_m	f_p		
$CH_3C_6H_5Cr(CO)_3$	0.3	1.1	1.1	EtOD + 10%	76
$CH_3OC_6H_5Cr(CO)_3$	4.8	1.6	2.5	EtONa 100°	77
$CH_3C_6H_5$	0.2	0.4	0.4	$ND_3 + KND_2$	78
$CH_3OC_6H_5$	500	1	0.5	13°	78

It is interesting to remember that the weak influence of substituents on the reactivity of the cyclopentadienyl rings bound to the $Mn(CO)_3$ group was also noted in studying the reactions of protophilic isotopic exchange in the cyclopentadienylmanganesetricarbonyl system. Despite the fact that quantitative data characterising the reactivity of the arene complexes of chromium are even fewer, nevertheless hydrogen isotopic exchange studies on this system suggest that the electronic effect of the substituents in the benzene ring is much more pronounced than in the system where the benzene ring is π-bound with the $Cr(CO)_3$ group.

Table 6. Total rate constants of isotopic exchange of the hydrogen of arenechromiumtricarbonyls[76,77].

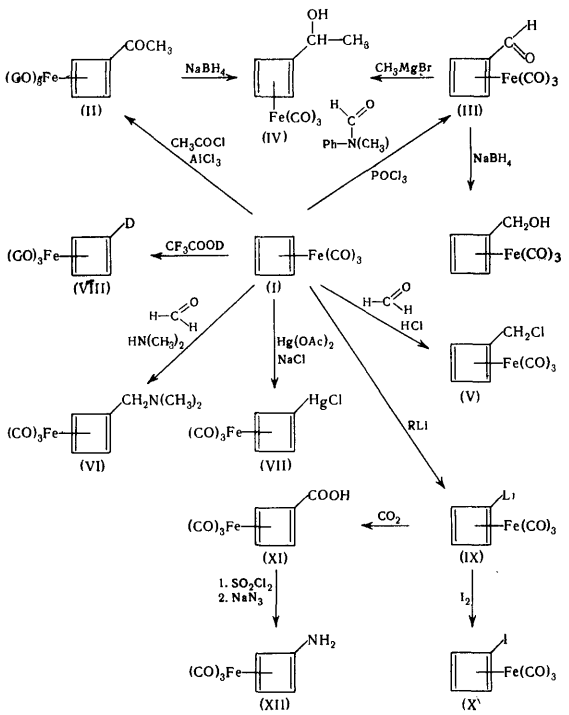
Substance	$10^5 k_{h.e.}$, s^{-1}
$C_6H_5Cr(CO)_3$	1.1
$(CH_3)C_6H_5Cr(CO)_3$	1.4
$(CH_3)_2N{-}C_6H_5Cr(CO)_3$	0.3
$CH_3OC_6H_5Cr(CO)_3$	2.8
$CH_3OCOC_6H_5Cr(CO)_3$	0.8

It is extremely probable that the levelling of the differences in the strength of the orientating action of the substituents in π-bonded aromatic ligands is a common phenomenon.

7. ISOTOPIC EXCHANGE OF HYDROGEN IN CYCLOBUTADIENEIRONTRICARBONYL

In 1965 Pettit and coworkers[79] obtained the first stable complex of cyclobutadiene with irontricarbonyl. It was found that this new complex exhibits aromatic properties and readily undergoes electrophilic substitution[80].

The authors were able to effect most of the usual electrophilic substitutions—acetylation, aminomethylation, chloromethylation, mercuration, etc. (see the scheme, I–XII).



The isotopic exchange of hydrogen with deuterium-enriched trifluoroacetic acid was also studied and it was found that even after a few minutes, in addition to the monodeuterio-derivative, more extensively deuteriated derivatives of cyclobutadieneirontricarbonyl are also formed (see the scheme, VIII).

These investigations led the authors to conclude that the reactivity of cyclobutadieneirontricarbonyl in electrophilic substitutions is very similar to the reactivity of ferrocene, both systems being considerably more reactive than benzene.

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Institute of Organoelemental Compounds, Academy of Sciences of the USSR, Moscow