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Abstract

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ISOTOPIC EXCHANGE OF HYDROGEN IN CYCLOPENTADIENYLMANGANESE TRICARBONYL

The recently discovered ([1]) reaction of isotopic hydrogen exchange of ferrocene and its derivatives in acidic media apparently opens up the possibility of establishing a quantitative characteristic of the relative electrophilicity of various metallocene and aromatic systems. In this connection, it was of interest to investigate the reaction of isotopic hydrogen exchange of cyclopentadienylmanganese tricarbonyl ($C_5H_5Mn(CO)_3$) (I) with acids and to compare them with data on the hydrogen exchange of ferrocene and benzene. Until now, only a few reactions of electrophilic substitution of $C_5H_5Mn(CO)_3$ have been known: alkylation ([2a,2]), acylation ([3–6]), and sulfonation ([7]). A reaction of competitive acylation of benzene, cyclopentadienylmanganese tricarbonyl (I), methylcyclopentadienylmanganese tricarbonyl (II), and anisole was also carried out, as a result of which the following series of decreasing reactivity was found: anisole > II > I > benzene.

We investigated the reaction of isotopic hydrogen exchange of $C_5H_5Mn(CO)_3$ with trifluoroacetic acid in benzene under the same conditions in which we had previously studied the hydrogen exchange of ferrocene ([1]). Under these conditions, benzene does not enter into the exchange reaction, whereas ferrocene readily exchanges hydrogen atoms for deuterium ($K^*_{BO} = 1.6 \cdot 10^{-4}$ sec^{-1} at 25°). It turned out that, under the indicated conditions, $C_5H_5Mn(CO)_3$, like benzene, practically did not enter into the hydrogen-exchange reaction.

Table 1

Hydrogen exchange of $C_5H_5Mn(CO)_3$ and benzene in a solution of CH_2Cl_2 with CF_3COOD, in the presence of D_2SO_4

Test substance	A	CF_3COOD	D_2SO_4	CH_2Cl_2	$K^*_{BO} \cdot 10^6$ sec^{-1}
I $C_5H_5Mn(CO)_3$	1	3	0.2	3	4.1
C_6H_6	1	3	0.2	3	3.2
II $C_5H_5Mn(CO)_3$	1	4.8	0.3	2	13.3
C_6H_6	1	4.8	0.3	2	6.0

The hydrogen exchange of $C_5H_5Mn(CO)_3$ was accomplished by increasing the acidity of the medium through the addition of sulfuric acid to it. Under these conditions, however, hydrogen exchange of benzene is also observed simultaneously. To compare the electrophilic activity of $C_5H_5Mn(CO)_3$ and benzene, we studied the kinetics of the hydrogen exchange of these compounds under the conditions indicated below, i.e., in a solution of trifluoroacetic acid with additions of sulfuric acid and methylene chloride as the solvent. The results of the investigations are given in Table 1.

* K_{BO} here and below denotes the rate constant of hydrogen exchange.

It was found that the rate constants of the hydrogen exchange of $C_5H_5Mn(CO)_3$ are 1.3-2 times higher than those of benzene. These results show that the electrophilic activity of $C_5H_5Mn(CO)_3$ only slightly exceeds the electrophilic activity of benzene.

In experiments on the competing hydrogen exchange of $C_5H_5Mn(CO)_3$ and benzene, simultaneously present in the reaction medium, this difference appeared more clearly (Table 2).

Table 2

Competing hydrogen exchange of $C_5H_5Mn(CO)_3$ and benzene, simultaneously present in the reaction medium
(molar ratio of reagents
$C_5H_5Mn(CO)_3 : (C_6H_6) : CF_3COOD : D_2SO_4 : CH_2Cl_2 = 1 : 1 : 3 : 0.2 : 3$)

Duration,* h	Exchange, %	Exchange, %
	$C_5H_5Mn(CO)_3$	C_6H_6
18.0	20.7	4.5
24.0	30.7	6.8
47.5	41.3	7.3
70.3	50.0	10.9

* Experiments were carried out at 25°.

Experimental Part

1. Starting reagents. Cyclopentadienylmanganesetricarbonyl, m.p. 76-77°, obtained by the method of Piper, Cotton, and Wilkinson ([8]), was purified by recrystallization from heptane and by sublimation in vacuum. Deuterated trifluoroacetic acid was obtained by treating trifluoroacetic acid with deuterosulfuric acid and was then distilled on a column with an efficiency of 30 theoretical plates.

2. Hydrogen-exchange experiments. The hydrogen exchange of cyclopentadienylmanganesetricarbonyl was carried out in a medium consisting of methylene chloride, trifluoroacetic acid, and sulfuric acid. In the course of the kinetic studies, the reaction was stopped by pouring separate samples into ice water. The cyclopentadienylmanganesetricarbonyl isolated from the experiment was purified by sublimation. Experiments on the hydrogen exchange of benzene were carried out in an analogous manner. The deuterium content in the substances studied was determined from the excess density of combustion water by the drop method. Since all kinetic experiments were carried out under similar conditions, we shall confine ourselves to describing only a few typical cases.

a) **Hydrogen exchange of cyclopentadienylmanganesetricarbonyl** in a medium of CH_2Cl_2, CF_3COOD, and D_2SO_4 at molar ratios of 1 : 3 : 3 : 0.2, respectively (experimental temperature 25°).

Table 3

Duration, h	E.d.c.w.,* γ/ml calculated	E.d.c.w.,* γ/ml found	$K_{BO} \cdot 10^6$ sec^{-1}	Duration, h	E.d.c.w.,* γ/ml calculated	E.d.c.w.,* γ/ml found	$K_{BO} \cdot 10^6$ sec^{-1}
17-50	28250	6000	3.8	24-00	28250	8815	4.3
22-00	28250	8200	4.4	42-50	28250	11560	3.5

* E.d.c.w. —excess density of combustion water.

b) **Hydrogen exchange of benzene under conditions analogous to experiment (a).**

Table 4

Duration, h	E.d.c.w., γ/ml calculated	E.d.c.w., γ/ml found	$K_{BO} \cdot 10^6$ sec^{-1}	Duration, h	E.d.c.w., γ/ml calculated	E.d.c.w., γ/ml found	$K_{BO} \cdot 10^6$ sec^{-1}
18	24600	5250	3.1	42	24600	9200	3.1
25	24600	6650	3.4	48	24600	9500	3.0

c) **Competitive hydrogen exchange of $C_5H_5Mn(CO)_3$ and benzene** in a solution of CF_3COOD, D_2SO_4, and CH_2Cl_2 (molar ratios = 1 : 1 : 3 : 0.2 : 3, respectively) at 25°

Table 5

Reaction time, h	$C_5H_5Mn(CO)_3$, initial counts/min/mol	$C_5H_5Mn(CO)_3$, found counts/min/mol	Benzene, initial counts/min/mol	Benzene, found counts/min/mol	Exchange, %, $C_5H_5Mn(CO)_3$	Exchange, %, benzene
18.00	16600	3430	16600	750	20.7	4.5
24.00	16600	5100	16600	1130	30.7	6.8
47.50	16600	6860	16600	1220	41.3	7.3
70.25	16600	8120	16600	1810	50.0	10.9

It has been established that cyclopentadienylmanganese tricarbonyl enters into the reaction of hydrogen isotope exchange in an acidic medium. A comparison of the kinetics of hydrogen exchange of cyclopentadienylmanganese tricarbonyl and benzene under identical conditions shows that the rate constant of hydrogen exchange for the former is 1.3–2 times higher than that for benzene.

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