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KINETIC STUDIES AND MECHANISM OF TRIIRON DODECACARBONYL REACTIONS

I. NUCLEOPHILIC SUBSTITUTION IN TRIIRON DODECACARBONYL BY TRIPHENYLPHOSPHINE IN BENZENE

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Summary

The kinetics of the reaction of triiron dodecacarbonyl with triphenylphosphine has been studied at various temperatures and different concentrations. It is a first order reaction with respect to $Fe_3(CO)_{12}$. $P(C_6H_5)_3$ reacts with $Fe_3(CO)_{12}$ according to the expression $K_{obsd} = K_1[Fe_3(CO)_{12}] + K_2[P(C_6H_5)_3]/[Fe_3(CO)_{12}]$. Up to a certain ratio of $P(C_6H_5)_3$ to $Fe_3(CO)_{12}$ (approx. 10/1), after which K_{obsd} deviates from the above expression. K_{obsd} also depends upon the concentrations of both the reactants. An induction period is always observed which decreases with increase in temperature. Thermodynamic parameters for the reaction have also been calculated.

Introduction

$Fe_3(CO)_{12}$ is used for synthesizing a number of different types of substituted iron carbonyls by using a variety of ligands [1—6]. $P(C_6H_5)_3$ reacts with $Fe_3(CO)_{12}$ to produce mono- and di-substituted iron complexes, namely $Fe(CO)_4L$ and $Fe(CO)_3L_2$ ($L = P(C_6H_5)_3$) [7], and formation of $Fe_3(CO)_{11}P(C_6H_5)_3$ (I) in the course of the reaction has also been reported [8]. I reacts further with $P(C_6H_5)_3$ to give $Fe(CO)_4L$ and $Fe(CO)_3L_2$. In the presence of carbon monoxide, formation of $Fe(CO)_5$ in the reaction has also been reported [9]. The amount of the two products formed depends upon the ratio of the initial concentrations of the two reactants, and with an increase in amount of $P(C_6H_5)_3$ the amount of disubstituted product formed increases. But the kinetics of the above reaction have not been studied so far. Kinetic studies may help in suggesting a mechanism for the reaction and may also give a relationship between structure and reactivity towards various ligands.

Materials

$Fe_3(CO)_{12}$

This was prepared from iron pentacarbonyl by Hieber's method [10] and was purified by Soxhlet extractor.

$P(C_5H_5)_3$

Commercial $P(C_6H_5)_3$ was purified by recrystallizing it from ethanol/water mixture (90% ethanol).

Benzene

This was purified and dried by standard methods before use.

Experimental

The reaction was studied by varying different parameters: *(i)* Initial concentration of $Fe_3(CO)_{12}$ (9.91×10^{-4} *M*—1.65×10^{-3} *M*); *(ii)* Molar ratio of two reactants ($Fe_3(CO)_{12}$: $P(C_6H_5)_3$) (app. 1 : 7—1 : 14); *(iii)* Temperature (30, 34.5, 37.4°C).

The solutions of the two reactants in stoppered flasks were thermostatted in an oil bath, the temperature of which was kept constants within a limit of ±0.05°C. All the experiments were performed in the presence of air, and the reaction was followed using a visible spectrophotometer (VSU-2P). The rate of disappearance of triiron dodecacarbonyl was measured by noting the optical density of the reaction mixture at 530 nm, the wavelength at which only $Fe_3(CO)_{12}$ absorbs, and the products are optically clear after known intervals of time. The reactions were followed up to about 75%.

Results

The presence of the two main products was detected by recording an IR spectrum of the reaction mixture, but no iron pentacarbonyl was detected

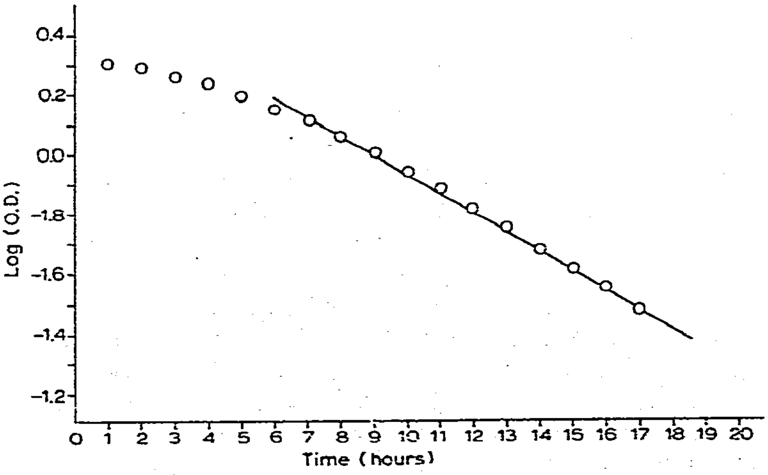

Fig. 1. Reaction of $Fe_3(CO)_{12}$ with $P(C_6H_5)_3$ in benzene at 30°C.

TABLE 1

RATE OF REACTION OF $Fe_3(CO)_{12}$ WITH $P(C_6H_5)_3$ AT 37.4°C IN BENZENE

$Fe_3(CO)_{12}$ concentration (mole $l^{-1} \times 10^3$)	$P(C_6H_5)_3$ concentration (mole $l^{-1} \times 10^3$)	K_{obsd} ($min^{-1} \times 10^3$)
1.321	8.906	5.067
1.321	12.722	5.604
1.321	17.812	5.630
9.91×10^{-1}	12.722	4.836
1.651	12.722	6.141

[a] $K_{obsd} = K_1[Fe_3(CO)_{12}] + K_2[P(C_6H_5)_3]/[Fe_3(CO)_{12}]$. $K_1 = 2.877$ $mole^{-1}$ min^{-1}. $K_2 = 1.879 \times 10^{-4}$ min^{-1}.

TABLE 2

RATE OF REACTION OF $Fe_3(CO)_{12}$ WITH $P(C_6H_5)_3$ AT 30 and 34.5°C IN BENZENE

$Fe_3(CO)_{12}$ concentration (mole $l^{-1} \times 10^3$)	$P(C_6H_5)_3$ concentration (mole $l^{-1} \times 10^3$)	K_{obsd} ($min^{-1} \times 10^3$)	
		30°C	34.5°C
1.321	8.906	1.96	3.685
1.321	12.722	2.42	4.376
1.321	17.812	1.99	3.840

TABLE 3

THERMODYNAMIC PARAMETERS FOR THE REACTION OF $Fe_3(CO)_{12}$ WITH $P(C_6H_5)_3$ IN BENZENE AT 30°C

ΔE (Kcal/$mole^{-1}$)	ΔH (Kcal/$mole^{-1}$)	ΔG (Kcal/$mole^{-1}$)	ΔS (Cal $degree^{-1}$ $mole^{-1}$)	A (sec^{-1})
22.540	21.940	21.375	0.875	1.037×10^{12}

TABLE 4

INDUCTION PERIODS FOR THE REACTION IN BENZENE AT VARIOUS TEMPERATURES

Temperature (°C)	Aproximate induction period (h)
30	7
34.5	4
37.4	2.5

from this. The two products were further confirmed by elemental analysis after their isolation.

The specific rate for the disappearance of $Fe_3(CO)_{12}$ was evaluated from the curve obtained by plotting the log of optical density of the reaction mixture vs. time (Fig. 1). The kinetic data obtained at different temperatures and varying concentrations are tabulated in Tables 1 and 2.

From the kinetic data at various temperatures, Arrhenius plots (log K vs. $1/T$) were drawn for the reaction (Fig. 2). From the Arrhenius plot various thermodynamic parameters were calculated which are tabulated in Table 3.

An induction period was always observed and only after this induction period did the reaction follow first order kinetics (Fig. 1). The induction period decreases with increase in temperature, and its values for this reaction, for benzene and at different temperatures, are given in Table 4.

Discussion

With time the dark green colour of the reaction mixture, which is due only to $Fe_3(CO)_{12}$, gradually disappears. The reaction is monitored in terms of $Fe_3(CO)_{12}$: a solution of $Fe_3(CO)_{12}$ in benzene obeys Lambert Beer's law at 530 nm, so the optical density of the reaction mixture is a measure of the concentration of $Fe_3(CO)_{12}$ in the reaction mixture. The rate of decomposition of $Fe_3(CO)_{12}$ in benzene at 37.4°C is very small, and is negligible compared to the rate of the reaction. As Fig. 1 turns out to be a straight line, this proves that the reaction is of first order with respect to $Fe_3(CO)_{12}$. The slope of the curve gives the specific rate.

As the amounts of the two products formed depend upon the initial concentrations of the two reactants, the reaction must occur in more than one step, modes of which will be dependent upon the initial concentrations or molar ratios of the two reactants.

The observed values of K for the disappearance of $Fe_3(CO)_{12}$ varies according to the expression $K_{obsd} = K_1[Fe_3(CO)_{12}] + K_2[P(C_6H_5)_3]/[Fe_3(CO)_{12}]$ up to a certain ratio which is approximately 10/1. After this ratio K_{obsd} deviates from the above expression. This proves that the reaction can occur by two dif-

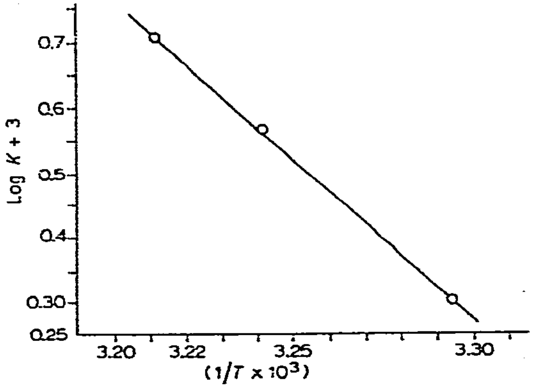

Fig. 2. Arrhenius plot for the reaction of $Fe_3(CO)_{12}$ with $P(C_6H_5)_3$ in benzene.

ferent mechanisms, the change from one to another taking place at a concentration ratio of about 10/1. Values of K_1 and K_2 are calculated at 37.4°C (Table 1). K_1 and K_2 are both temperature dependent and decrease with a decrease in temperature, thus decreasing the overall value of K_{obsd}.

As Fig. 2 is a straight line, the reaction obeys the Arrhenius equation. The activation energy for the reaction is 22.540 kcal per mole and the entropy change is negligible, as is generally the case for reactions in solution.

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