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THE CATALYTIC ACTIVITY OF TRICARBONYLCHROMIUM COMPLEXES OF PHENANTHRENE, NAPHTHALENE AND ANTHRACENE IN THE HYDROGENATION OF DIENES

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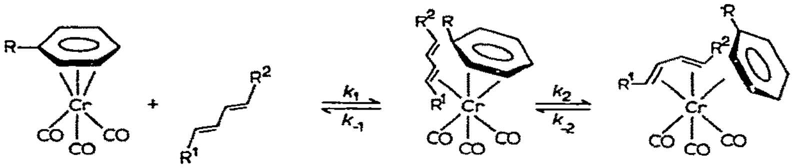
INTRODUCTION

In previous kinetic studies [1] of the hydrogenation of dienes with arenechromium tricarbonyls as catalysts we discussed the effect of arene substituents on the catalytic activity. Electron-withdrawing groups in the benzene moiety accelerated the reaction rate and, most importantly, caused significant shortening of the induction period generally observed in the hydrogenation reaction. For example, with toluenechromium tricarbonyl under rather drastic reaction conditions (150°C and 700 p.s.i. H_2 pressure) there was an approximate induction time of 240 min (out of 420 min total reaction time) whereas with the tricarbonylchromium complex of methyl benzoate under identical reaction conditions the induction time was only 45 min (out of 120 min total reaction time). These results, among others, were interpreted as providing experimental support for our proposed mechanism, which envisaged, for the induction period, substitution of the diene substrate on the tricarbonylchromium moiety through displacement (in part or in toto) of the arene ligand



However, we could not invoke the same type of inductive electronic effect to explain the surprising, at the time, catalytic activity of phenanthrenechromium tricarbonyl which caused full hydrogenation of the diene substrate in less than 20 min, the time required to bring the autoclave to the temperature and pressure reaction conditions mentioned above.

In this communication we wish to present additional data obtained with phenanthrenechromium tricarbonyl as catalyst in the hydrogenation of dienes, and report on the extension of this reaction to the use of naphthalene and anthracene complexes for mild reaction conditions. A possible explanation for the special catalytic activity of this type of fused ring aromatic complex is proposed.

EXPERIMENTAL SECTION

Apparatus and procedure

The special Paar-type hydrogenation bomb designed and built for this work is shown schematically in Fig. 1. The major features of this apparatus include provisions for the maintenance of constant hydrogen pressure and automatic recording of hydrogen consumption in the reaction. As hydrogen is being used up in the reaction vessel, molecular hydrogen is supplied automatically from the gas container, through a reducing regulator. The change in hydrogen pressure in the gas container is translated by a transducer into a voltage fall on a Goerz linear and/or logarithmic recorder. The continuous and automatic recording of the course of reaction eliminates the need for removal of aliquot

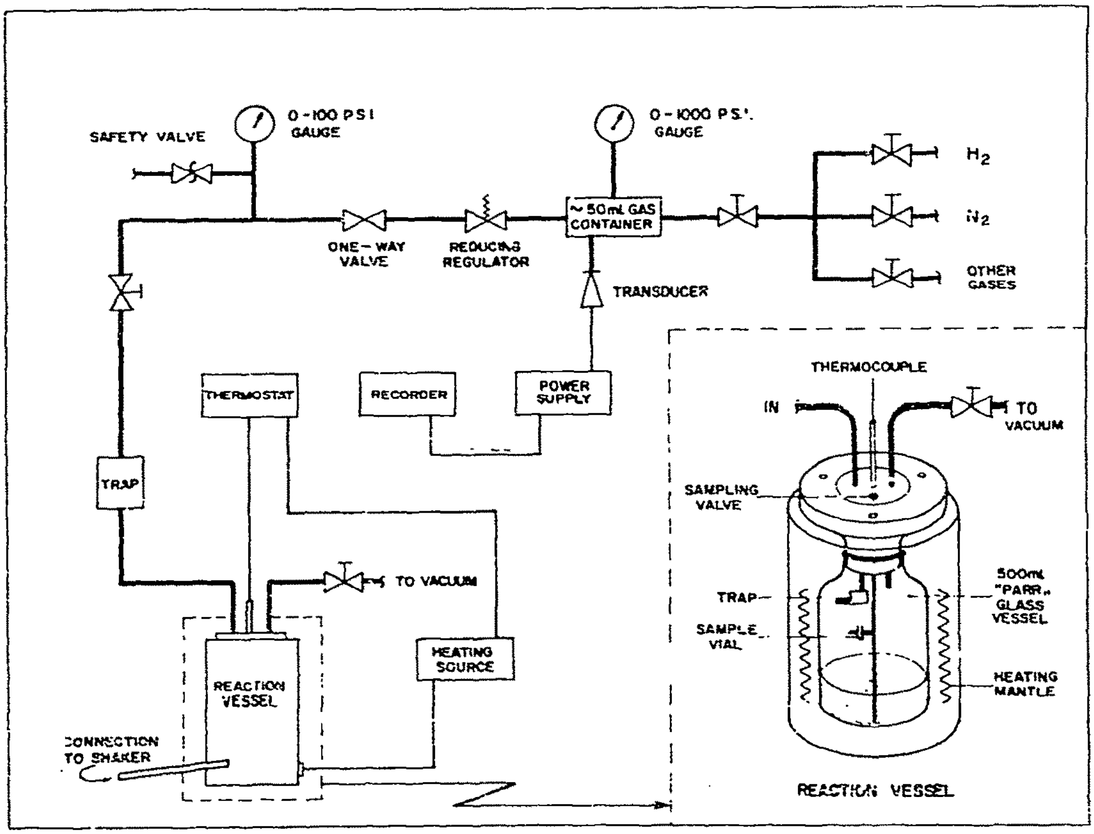


Fig. 1. Schema of hydrogenation apparatus.

samples and their analysis in order to monitor the degree of hydrogenation. (A GLC product analysis of the reaction mixture at various stages of hydrogenation showed a good agreement (± 5%) between the recorded number of moles of hydrogen uptake and number of moles of hydrogenated substrate.)

The reaction vessel is charged with a mixture of diene substrate and solvent and the catalyst is placed in a special sample vial suspended above the liquid phase. The system is evacuated, filled with hydrogen and heated to the required temperature before operation begins. A Eurotherm LP 48/P1D/R2 thermostat maintains constant temperature with an accuracy better than ± 0.5°. Upon attainment of the desired reaction conditions, commencement of the shaking operation causes the catalyst-containing vial to fall into the solvent—diene mixture and marks the start of the reaction.

Materials

The tricarbonylchromium complexes of phenanthrene, naphthalene and anthracene were prepared by refluxing, under nitrogen, a solution of the arene in peroxide-free di-*n*-butyl ether in a 3-necked flask fitted with a cold finger and a modified soxhlet condenser (in which the chromium hexacarbonyl is placed). These arrangements provide a mode for washing back into the reaction mixture most of the metal hexacarbonyl which tends to sublime during the reaction. Purification of the phenanthrene complex was by chromatography on basic alumina [1]. This procedure yielded in addition to phenanthrenechromium tricarbonyl the new compound bis-(tricarbonylchromium)phenanthrene as orange, air- and light-stable crystals, m.p. 165°C (dec.).

Analysis

For $C_{20}H_{10}Cr_2O_6$:

	C (%)	H (%)	Cr (%)
Calc.	53.40	2.24	23.10
Found	53.16	2.38	23.94
			(by atomic absorption)

The naphthalene and anthracene complexes were purified by recrystallization from benzene/petroleum ether as described in the literature [2, 3]. Hydrogen (Air Products, U.S.A.), nitrogen and acetylene (Oxygen Stores Ltd., Israel) and carbon monoxide (Merck, U.S.A.) were used without further treatment. Decalin (Fluka, pract.) containing about 1% tetralin, was treated with oleum followed by distillation (75—81°/20 mmHg) and filtration through active basic alumina. Acetone (Merck, Darmstadt) was used without further purification. Tetrahydrofuran was distilled over calcium hydride and passed through a column of active alumina (basic) immediately prior to use. Methyl sorbate and dimethyl muconate, prepared by acidic esterification of the corre-

TABLE 4

Hydrogenation of dienes catalyzed by naphthalenechromium tricarbonyl under mild conditions [a]

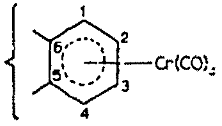
Diene substrate (S)	[S] (mole l^{-1})	10^3 [M] (mole l^{-1})	Induction time (min)	10^4 k_{obs} (sec^{-1})
Methyl sorbate	0.600	2.5	6.1	33.0
(*trans,trans*)	0.300	2.5	4.0	57.7
	0.100	2.5	3.5	60.8
	0.300	5.0	2.3	105.0
	0.100	5.0	2.1	96.3
2,4-hexadiene (*trans,trans*)	0.100	5.0	2.7	52.5
1,4-Cyclohexadiene	0.100	5.0	6.8	7.5
Dimethyl muconate (*trans,trans*)	0.100	5.0	~ 5	~ 1.9
1,4-Diphenyl-1,3-butadiene	0.100	5.0	~20	~ 1.9
(*trans,trans*)	0.100	10.0	6.2	3.8

[a] Reaction conditions; H_2 pressure, 59 ± 2 psi.; temp. 40.5 ± 1°C; solvent, acetone.

anthracene, which had already been discussed by O.S. Mills with regard to the two sets of Cr—C(arene) bond lengths [7]. As can be seen from the pertinent data reproduced in Table 5, a qualitative prediction based on our hypothesis would indicate these two complexes to be at least as active hydrogenation catalysts as the phenanthrene compound and possibly even more so. These expectations were fulfilled as indicated by the hydrogenation results summarized in Tables 3 and 4. The use of naphthalenechromium tricarbonyl, as well as the anthracene complex, enabled us to develop mild hydrogenation conditions. Furthermore, the use of coordinating solvents such as tetrahydrofuran or acetone, expected to facilitate the initial ligand substitution step with either the naphthalene or the anthracene complex, resulted in facile hydrogenation even at room temperature and atmospheric hydrogen pressure. Additionally, we observed that solutions of either naphthalenechromium tricarbonyl or anthracenechromium tricarbonyl in tetrahydrofuran, acetone and other similar solvents, upon standing at room temperature under nitrogen, exhibited extensive changes in the IR carbonyl stretching bands. Preliminary experiments indicated that these changes in the carbonyl bands might have some connection with the ability of such a solution to catalyze the hydrogenation of diene substrate. This observation opened up the possibility of studying the chemical changes occurring during the induction period which hopefully might help elucidate the nature of the active catalytic species. The results of this study which has recently been completed [8] will form the subject of a separate communication. We shall also discuss elsewhere practical organic laboratory applications of the regioselective and stereospecific hydrogenation of a variety

TABLE 5

	Chromium carbon distances (Å)						Mean values for selected pairs			
	1	2	3	4	5	6	1,4	2,3	5,6	(5,6)-(1,4)
Naphthalene	2.214	2.213	2.191	2.186	2.306	2.337	2.200	2.202	2.321	+0.120
Anthracene	2.219	2.217	2.221	2.215	2.340	2.324	2.217	2.219	2.332	+0.115
Phenanthrene	2.212	2.210	2.206	2.208	2.289	2.289	2.210	2.208	2.289	+0.080
Benzene	2.230	2.218	2.216	(2.216)	(2.218)	(2.230)	2.223	2.217	2.224	



Average values: Cr—C(1,4) 2.208
Cr—C(5,6) 2.314

of diene substrates as well as the mechanistic implications of the kinetic results reported herein [9].

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