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Acid catalysed complexation of arenes with $\text{Cr}(\text{CO})_6$ *

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Abstract

Several acids were tested as potential catalysts for complexation of arenes with $\text{Cr}(\text{CO})_6$ in boiling decalin. Acetic acid was found to be an efficient catalyst for complexation of acyl- and acyloxybenzenes. A mixture of butanone or cyclohexanone and acetic acid, with THF and acetic acid was found to be an efficient catalytic system or complexation of other arenes. The complex $(\eta^2\text{-acenaphthylene})_4\text{Cr}(\text{CO})_2$ was isolated during an attempt on acetic acid catalysed complexation of acenaphthylene with $\text{Cr}(\text{CO})_6$.

Introduction

Several esters were found to be good catalysts for complexation of arenes with $\text{Cr}(\text{CO})_6$ in boiling decalin [1,2]. The catalytic effect could be caused either by the ester itself or by an acid possibly present as an impurity. This hypothesis is supported by the fact that formation of a Cr–H bond has been demonstrated in some H/D exchange reactions on $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ with strong acids [3,4]. The main goal of this paper was to find whether the acids could have such a catalytic effect on complexation of arenes with $\text{Cr}(\text{CO})_6$, and to compare the catalytic effect of acids and other substances.

Results and discussion

During attempts to complex different arenes with $\text{Cr}(\text{CO})_6$ in boiling decalin [5,6] we observed that some complexations went smoothly to equilibrium, and after prolonged heating an autocatalytic decomposition started, demonstrated by green impurities or green colour of the reaction mixture. The equilibrium was reached at low conversion especially with substrates like benzene, naphthalene, acetophenone, benzophenone etc. The complexation of arenes with $\text{Cr}(\text{CO})_6$ using butyl acetate as a catalyst solved most of the problems and the yields of complexes were usually high, but again the conversion of acetophenone, naphthalene and benzoic acid was

* Dedicated to Professor P.L. Pauson.

Table 1

The comparison of uncatalysed and acetic acid catalysed complexation of some arenes with $\text{Cr}(\text{CO})_6$ in boiling decalin^a

No.	Arene	No catalyst (a) yield/time (%/h)	Catalyst/co-catalyst (b/c)	Yield/time (%/h)
1	Acetophenone	48/1.5	AcOH/-	82/2
2	Benzophenone	45/3	AcOH/-	85/2
3	1-Tetralone	23.5/3	AcOH/-	87.5/2.5
4	Phenyl acetate	16.5/3	AcOH/-	60/3.25
5	Phenol (d)	41/14	AcOH/-	70/2.5
6	Benzene	3.5/4	AcOH/-	18/4
7	Benzene		butanone/AcOH	72/3
8	Chlorobenzene	1/7	AcOH/-	8/4
9	Chlorobenzene		Butanone/AcOH	62/4
10	Toluene	34/4.5	AcOH/-	50/4
11	Toluene		butanone/AcOH	86/3
12	Toluene		butanone/AcOH (e)	98.7/4
13	Toluene		cyclohexanone/-	88/2
14	Toluene		cyclohexanone/AcOH	90/2
15	Toluene		butyl acetate/-	85/3.5
16	Toluene		butyl acetate/AcOH	85/3.5
17	Toluene		THF/-	85/7
18	Toluene		THF/AcOH	83/2.75
19	Naphthalene	36/7	AcOH/-	12/3
20	Naphthalene		butanone/AcOH	10/1
21	Acenaphthylene	see text		

^a a, b, c, d, e - see Experimental.

low. It was of interest therefore to test some acids as catalysts of complexation in the hope that the equilibrium could be shifted to higher conversion.

Toluene was chosen as the standard for acid catalysed complexation with $\text{Cr}(\text{CO})_6$, and formic acid, acetic acid, propionic acid and H_3PO_4 were examined as catalysts. The yield of $(\eta^6\text{-toluene})\text{Cr}(\text{CO})_3$ varied from 30% (H_3PO_4) through 35% ($\text{CH}_3\text{CH}_2\text{COOH}$) to 50% (HCOOH , CH_3COOH). The reaction time was 4–7 h. The reaction was complicated by formation of a red solid defined as $\text{Cr}(\text{OCOR})_2$, but no green decomposition product was observed. The smallest amount of the red solid was formed when acetic acid was used as the catalyst and therefore the complexation of some arenes with this catalyst was tested further. The arenes which did not give complexes in boiling decalin [5] as benzaldehyde, benzoic acid, benzonitrile, 5-phenyl-1,3-cyclohexanedione and chalcone also resisted complexation with acetic acid as catalyst.

Acetic acid was found to be a good catalyst in other cases (see Table 1), and a better catalytic effect than with butyl acetate was observed in complexation of ketones (acetophenone, 1-tetralone, benzophenone) as well as in complexation of phenyl acetate and phenol. Yields of complexes as high as 80–87% were obtained in a very short time. The complexation of benzene, toluene and chlorobenzene was not improved so much using acetic acid as the catalyst. The complexation of naphthalene stopped at a very low conversion. In the last four cases a considerable amount of $\text{Cr}(\text{OCOCH}_3)_2$ was separated. The amount of this salt could be mini-

mized by reducing the amount of acetic acid used. The exact yield of the salt could not be given as it decomposed in air. In no case was autocatalytic decomposition of the complex observed. From these observations it can be suggested that the acetic acid might act as a trap for traces of Cr in low oxidation states which could catalyse decomposition.

The attempt to complex acenaphthylene resulted in a reddish compound stable in air, and the analysis proved its structure to be $(\eta^2\text{-acenaphthylene})_4\text{Cr}(\text{CO})_2$.

As acetic acid proved to be a very good catalyst for ketones it was worth making some attempts to complex sluggish arenes with a catalytic system of ketone + acetic acid. Butanone and cyclohexanone were chosen as the catalysts. The results given in Table 1 prove that reaction are faster and complexes were isolated in yields which are comparable to those obtained in experiments using butyl acetate as the catalyst [1]. Naphthalene is again an exception to this rule. Its extraordinary behaviour could be explained by its very fast ligand exchange reactions [7]. The catalytic effect of acetic acid could be stronger on reversal of the ligand exchange reaction of $(\eta^6\text{-naphthalene})\text{Cr}(\text{CO})_3$ than on its formation.

A plausible explanation of the effect of the butanone/acetic acid system could be that the protonation of either Cr or CO makes the Cr-CO bond weaker and therefore easily displaced by the carbonyl group of the ketone. This could be the rate determining step of the complexation. It is interesting that no effect of acetic acid on complexation of toluene was observed when butyl acetate was used as the catalyst. On the other hand an extraordinary acceleration of acetic acid-induced toluene complexation was observed when THF was used as the catalyst. The 83% yield of $(\eta^6\text{-toluene})\text{tricarboxylchromium}$ was isolated after less than 3 h heating. The generalisation of the co-catalytic effect of AcOH to different catalysts has yet to be shown.

Experimental

All the experiments were carried out as described earlier [1,6]. The volume of the reaction mixture was usually 70 ml, and 1 g of $\text{Cr}(\text{CO})_6$ was used per experiment as a rule.

The molar ratios of the components were: (a) arene: $\text{Cr}(\text{CO})_6 = 4:1$; (b) arene: $\text{Cr}(\text{CO})_6$:AcOH = 4:1:0.3 (0.1 ml of AcOH in 70 ml); (c) arene: $\text{Cr}(\text{CO})_6$:catalyst:AcOH = 4:1:4:0.3 again 0.1 ml of AcOH was added into 70 ml of the reaction mixture; (d) the molar ratio was as in c, the product was isolated as the acetyl derivative (quenching with 3 mol excess of AcCl); (e) the molar ratio was as in b, but only 25 μl of the acetic acid was added to the reaction mixture*.

All complexes have been described in the literature and have correct elemental analysis and $^1\text{H-NMR}$ spectra.

$(\eta^2\text{-acenaphthylene})_4\text{Cr}(\text{CO})_2$. M.p. 120°C (dec.). Anal. Found: C, 83.41; H, 4.92. $\text{C}_{51}\text{H}_{32}\text{CrO}_2$ ($M = 716$) calc.: C, 83.79; H, 4.46%. IR (Nujol): 1875, 1957 and 1976 cm^{-1} ($\text{Cr}(\text{CO})_2$); 1364, 1452, 1487 and 1590 cm^{-1} . The ^1H NMR spectrum was not measurable due to some paramagnetic impurity being in the sample.

* The $(\eta^6\text{-phenol})\text{tricarboxylchromium}$ was trapped with acetyl chloride, and $(\eta^6\text{-phenyl acetate})\text{Cr}(\text{CO})_3$ was therefore isolated.

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