✲Photo-activated Metal Carbonyl Complexes as Stereoselective Catalysts for the Homogeneous Hydrogenation of Dienes

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ABSTRACT

Significantly increased activity of $Cr(CO)_6$ was achieved for the stereoselective homogeneous hydrogenation of methyl sorbate and *trans,trans*-conjugated fatty esters at ambient temperature and pressure by exposing the catalyst to UV irradiation (3500Å) in a solvent mixture of cyclohexane-acetonitrile (20:1). In this solvent mixture, methyl sorbate was converted quantitatively at ambient conditions into methyl *cis*-3-hexenoate, and methyl *trans*-9,*trans*-11-octadecadienoate into methyl *cis*-10-octadecenoate (99.9%). These products are expected by 1,4-addition of hydrogen. Under these conditions no hydrogenation of methyl linoleate occurred. Under the same conditions, cycloheptatriene-$Cr(CO)_3$ showed lower activity than $Cr(CO)_6$, and $Mo(CO)_6$ and mesitylene-$Mo(CO)_3$ showed no significant activity toward conjugated substrates. When $Cr(CO)_6$ and $Mo(CO)_6$ were irradiated at 2537Å they caused the geometric isomerization of methyl sorbate without hydrogenation, but had no effect on methyl linoleate. A hydrogenation mechanism is proposed for $Cr(CO)_6$ that involves CH_3CN- and H_2-$Cr(CO)_3$ complexes as intermediates for the stereoselective 1,4-addition of hydrogen to *trans,trans*-conjugated dienes.

INTRODUCTION

Our previous work (1-4) showed that complexes like arene-$M(CO)_3$ and $M(CO)_6$ (M = Cr, Mo and W) are active and selective catalysts for the partial hydrogenation of unsaturated fatty esters. The Cr-complexes exhibit an unusually high stereoselectivity for 1,4-addition of hydrogen to the cisoid configuration of *trans,trans* conjugated dienes giving *cis* monoenes (5,6) without significant formation of saturated compounds. The corresponding Mo-complexes show a lower selectivity, but higher activity than the Cr-complexes (1).

These complexes require activation before they can act as catalysts. Several different mechanisms have been proposed for this activation (7-9), which generally involves dissociation of the complexes forming unsaturated coordinative bonds. The activation mechanism may depend on how it is performed. The complexes can be activated by thermal treatment, by UV-irradiation or by using activating solvents. Thermal activation requires high temperatures (120-180 C) and high pressure (550 psi). Using UV-irradiation and activating solvent, it has been possible to perform hydrogenation at ambient temperature and pressure.

Complexes like naphthalene-$Cr(CO)_3$ are activated by solvents such as THF, acetone, dioxane, acetonitrile and others, making the hydrogenation possible at ambient conditions (10). Similar solvent activation has been obtained with $(CH_3CN)_3$-$Cr(CO)_3$ as catalyst (11). In both cases, the activity was fairly low, but the high selectivity was maintained. UV-irradiation has been used to activate complexes such as $Cr(CO)_6$ (12-17), $RuHCl(PPh_3)_3$ (18), $RhH(CO)(PPh_3)_3$ (19), $RhCl(PPh_3)_3$ (20), $Fe(CO)_5$ (21) and different Ir complexes (22,23). UV-irradiation also has been used for the formation of very unstable and catalytically active complexes in situ, such as $(CH_3CN)_3$-$Cr(CO)_3$ (11).

Generally, no isomerization of either dienes or monoenes occurred during hydrogenation of conjugated dienes with $Cr(CO)_6$ as precatalyst (14,24). Wrighton and Schroeder (14) have shown that $Mo(CO)_6$ and $W(CO)_6$ also are activated by UV-irradiation, but both complexes isomerized monoenes and dienes during the hydrogenation. Solvents influence catalytic activity during UV-irradiation, and benzene, when added in small amounts, was shown to inhibit the reaction (9), whereas acetone enhanced the reaction rate (15). These results indicate that it would be possible to combine the activation effect of solvents and UV-irradiation.

The aim of the present work was to establish the influence of UV-irradiation on the activity and selectivity of Cr and Mo complex catalysts for the hydrogenation of fatty esters with conjugated and methylene-interrupted double bonds.

EXPERIMENTAL

Methyl sorbate, linoleate and conjugated linoleate were prepared as described elsewhere (25,26), purified over activated alumina and stored under N_2 at -27 C. Methyl *trans*-9,*trans*-11-octadecadienoate was derived by dehydration of methyl ricinoleate (27). A concentrate containing 69% *trans*-9,*trans*-11-octadecadienoic acid was purified by repeated crystallization in 95% ethanol at -20 C. After three crystallizations, the acid product reached a purity of 99.4% (by capillary gas chromatography [GC] of the methyl ester). The methyl ester, prepared by refluxing the acid in methanol containing 5% conc. H_2SO_4, was chromatographed on a silicic acid column and eluted with a mixture containing 1 to 20% diethyl ether in hexane. The combined fractions eluted with 5-10% ether in hexane contained 100% methyl *trans*-9,*trans*-11-octadecadienoate (by capillary GC).

The hydrogenations were performed in a solution of the catalyst in one or more solvents. Hydrogen was allowed to bubble through the reaction mixture at ambient temperature and pressure. The UV-apparatus was a Rayonet Photochemical Mini-Reactor (Hamden, Connecticut, Model RMR-500) with four lamps (2537Å and 35 watt or 3500Å and 21 watt). Quartz-glass reactors used were 7 in. × 13 mm I.D. tube. The carbonyl complexes used were purchased from Strem Chemicals, Inc., Newburyport, Massachusetts, and all solvents used were of spectroscopic grade.

A typical experiment with methyl *trans*-9,*trans*-11-octadecadienoate was performed as follows. The catalyst [32 mg $Cr(CO)_6$] was weighed into the reactor and dissolved in the solvent (8 ml cyclohexane, 0.4 ml acetonitrile) and connected to the UV apparatus. The air in the system was removed by carefully blowing argon through the reactor. The argon flow was then replaced with hydrogen with bubbling gentle enough to avoid losses of solvent. The UV-lamps were turned on, and after 20 min of irradiation the substrate (0.28 g) was injected through a septum on the top of the reactor tube. Irradiation at 3500Å was continued throughout the reduction.

Samples withdrawn were analyzed by capillary GC using a Silar 10C column with programming from 70 to 120 C at 2 C/min. Double bond position in the monoene product from methyl *trans*-9,*trans*-11-octadecadienoate was determined by reductive ozonolysis and GC analysis of the aldehyde ester cleavage products (28).

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RESULTS

Hydrogenation of Methyl Sorbate

The pre-irradiation of the catalyst solution prior to the addition of methyl sorbate had a great effect on the hydrogenation activity (Table I). Both with cyclohexane and mixture of cyclohexane and acetonitrile, the pre-irradiation increased activity 2 to 3 times. Comparing rates of hydrogenation (% per hr), acetonitrile produced a 7-fold enhancement without pre-irradiation, and irradiation produced a 5-fold enhancement with cyclohexane and a 3-fold enhancement with acetonitrile. No reaction was observed in the absence of irradiation. Increasing pre-irradiation time to 1 hr did not increase the activity significantly, compared to 20 min pre-irradiation.

The solvent used had a large effect on the activity (Fig. 1). With $Cr(CO)_6$, an inert solvent like cyclohexane gave a much less active catalyst than a mixture of 5 volume % acetonitrile in cyclohexane. Pure acetonitrile gave an inactive catalyst. A similar increase in activity has been reported when acetone was used in pentane under similar conditions (15). Both acetone and acetonitrile are aprotic solvents that have been reported (10) to activate complexes such as naphthalene-$Cr(CO)_3$ at ambient condition without UV-irradiation. GC analysis showed the disappearance of acetonitrile in the reaction mixture during the first hr of hydrogenation. Therefore, solvent activation might be due to ligand exchange by the formation of an acetonitrile complex with the active catalyst, so the effective concentration of this complex is increased. However, the same activating effect by acetonitrile was not observed when cycloheptatriene-$Cr(CO)_3$ was used as catalyst (Fig. 1), thus suggesting a fundamentally different mechanism. This complex has been found (1,4) to be more active than $Cr(CO)_6$ under thermal activated hydrogenation. UV-activation of cycloheptatriene-$Cr(CO)_3$ gave initially a slightly more active complex than UV-activated $Cr(CO)_6$, but the activity leveled off at an earlier stage with the former complex. Significant decomposition of the catalyst was apparent from the green coloration of the final reaction product.

Arene-$Mo(CO)_3$ complexes have been reported (1) to be more active than corresponding chromium complexes. $Mo(CO)_6$ also is activated by UV-irradiation (14). However, in the present work neither $Mo(CO)_6$ nor mesitylene-Mo $(CO)_3$ showed any significant hydrogenation activity under the same conditions as used for the Cr complexes.

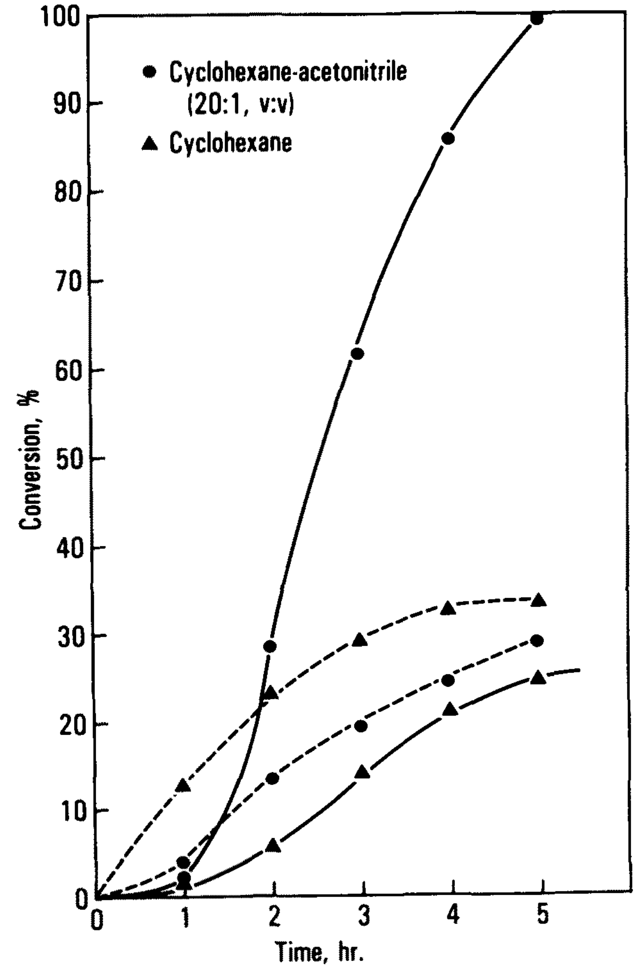


FIG. 1. Effect of solvents on the hydrogenation of methyl sorbate with $Cr(CO)_6$ (——) and with cycloheptatriene-$Cr(CO)_3$ (- - -) photo-activated by UV-irradiation at 3500Å (5 mole % catalyst, ambient temperature and pressure).

Hydrogenation of Methyl *Trans*-9,*Trans*-11-Octadecadienoate

Pure methyl *trans*-9,*trans*-11-octadecadienoate was hydrogenated with 20 mol % $Cr(CO)_6$, cyclohexane:acetonitrile (20:1) at 3500Å. The conversion to monoene was 63% in 9 hr and reached 99.9% in 20 hr (Fig. 2). No stearate was formed. At 5 mol % catalyst concentration the rate of hydrogenation leveled off around 8 hr before complete conversion took place. Capillary GC and analyses by reductive ozonolysis showed that the product methyl *cis*-10-octadecenoate, expected by 1,4-addition of hydrogen, constituted 99% of the monoene formed. The recovered product had no *trans* absorption by infrared analysis (970 cm^{-1}). This hydrogenation procedure is so stereoselective that it can be

TABLE I

Treatment of Catalyst Solution Prior to Addition of Methyl Sorbate[a]

Pre-treatment	Hydrogenation time (hr)	Solvent	Reduced sorbate, %	Rate %/hr
20 min H_2/UV-irradiation[b]	3	Cyclohexane	12	4
	5	Cyclohexane	25	5
None	6	Cyclohexane	5.4	0.9
20 min H_2/UV-irradiation[b]	3	Cyclohexane/ acetonitrile[c]	62	21
	5		100	20
None	3	Cyclohexane/ acetronitrile[c]	21	7

[a] Hydrogenation conditions: ambient temperature and pressure, 0.25 M methyl sorbate, 5 mol % $Cr(CO)_6$.

[b] The catalyst solution was irradiated (λ=3500Å) for 20 min under H_2-atm before sorbate (0.25 M) was added.

[c] Cyclohexane/acetonitrile = 20:1 (v:v).

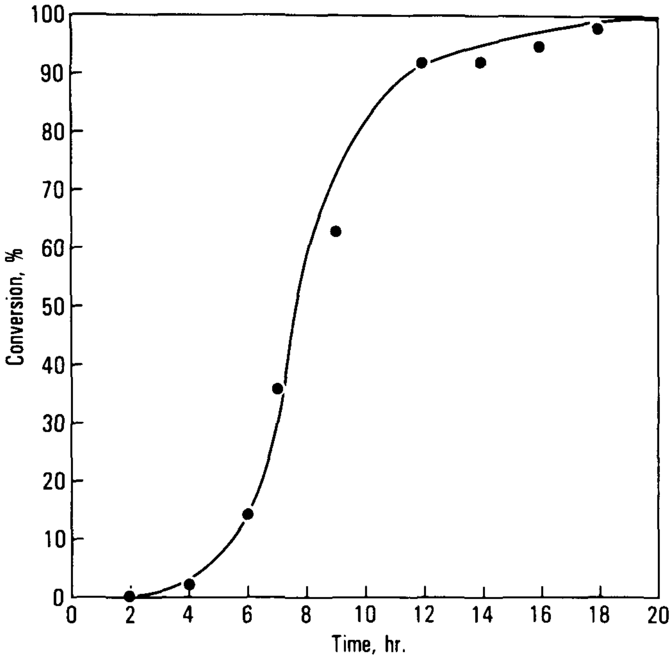


FIG. 2. Hydrogenation of methyl *trans*-9,*trans*-11-octadecadienoate with $Cr(CO)_6$ photoactivated by UV-irradiation at 3500Å (20 mol % catalyst, ambient temperature and pressure; solvent: cyclohexane: acetonitrile 20:1).

TABLE II

Hydrogenation of a Mixture[a] of Conjugated Linoleate, Linoleate and Monoenes with $Cr(CO)_6$ (5 Mol %)[b]

Composition (%)	Time (hr) 0	Time (hr) 3
C-18:0	0	0.3
C-18:1	36.9	40.0
C-18:2	8.0	8.8
C-18:2, CD[c]	53.6	49.8

[a] Prepared by esterification of a commercial sample of conjugated linoleic acid (Pamolyn 380; Hercules Inc., Wilmington, Delaware).

[b] Hydrogenation conditions: ambient temperature and pressure, UV-irradiation at λ = 3500Å, cyclohexane:acetonitrile, 20:1.

[c] Conjugated diene mixture of *cis,trans*-9,11- and 10,12-octadecadienoate.

used preparatively for the quantitative conversion of *trans, trans*-conjugated dienes into the 1,4-addition *cis* monoene product.

Hydrogenation of Methyl Linoleate and Conjugated Linoleate

Hydrogenation of a mixture of conjugated methyl linoleate, linoleate and monoenes was tried under the conditions established above for conjugated substrates. The results (Table II) showed very low activity compared to the simple conjugated esters. Hydrogenation of pure methyl linoleate gave less than 1% conversion after 4 hr reaction under the same conditions as used for methyl sorbate [3500Å, 5 mol % $Cr(CO)_6$, ambient temperature and pressure, cyclohexane: acetonitrile, 20:1]. Therefore, UV-activated $Cr(CO)_6$ is not active for the hydrogenation of methylene interrupted double bonds at ambient conditions.

Geometric Isomerization of Methyl Sorbate

As methyl sorbate was not isomerized by hydrogenation at 3500Å, the effect of irradiation at a lower wavelength was investigated. A change in wavelength to 2537Å resulted in extensive geometric isomerization but no hydrogenation of methyl sorbate with both $Cr(CO)_6$ and $Mo(CO)_6$. Under the same conditions used for hydrogenation with $Cr(CO)_6$ (Table II), at 2537Å methyl sorbate was converted into a mixture of 62.6% *trans,trans (t,t)*, 20.6% *cis,trans (c,t)*, 12.8% *t,c* and 4.0% *c,c*-2,4-hexadienoates, separated and tentatively identified by capillary GC. With $Mo(CO)_6$, the isomerization product consisted of 78.4% *t,t*, 10.8% *c,t*, 9.5% *t,c* and 1.3% *c,c*. With methyl linoleate, irradiation with $Cr(CO)_6$ at 2537Å gave neither hydrogenation nor isomerization. Therefore, catalytic irradiation at 2537Å causes geometric isomerization of a conjugated substrate like methyl sorbate but not positional isomerization of a methylene-interrupted substrate like linoleate.

DISCUSSION

The mechanism for photo-induced activation of Cr carbonyl complexes proposed by Platbrood et al. (9) follows a two step dissociation, forming a tetracarbonyl complex:

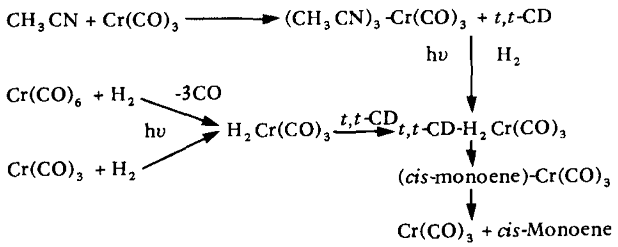
$$Cr(CO)_6 + \text{Diene} \xrightarrow{h\nu} (\text{Diene})\text{-}Cr(CO)_5 \xrightarrow{h\nu} (\text{Diene})\text{-}Cr(CO)_4$$

Fischler et al. (12) have shown that this tetracarbonyl complex is stable and not catalytically active. A further irradiation of this complex gives the tricarbonyl complex which is supposed to be catalytically active:

$$(\text{Diene})\text{-}Cr(CO)_4 \xrightarrow{h\nu} (\text{Diene})\text{-}Cr(CO)_3 \xrightarrow{H_2} (\text{Diene})\text{-}H_2Cr(CO)_3$$

The catalytic activity of the carbonyl complex proceeds in dark after a short initial UV-irradiation (14), which indicates that the action of UV-irradiation in these cases is photocatalytic (13).

On the basis of previous studies (9,12-14) and the present work, a mechanism can be advanced that involves both solvent activation, by formation of a CH_3CN complex intermediate, and dissociation of $Cr(CO)_6$, by irradiation in the presence of hydrogen. The conversion of *trans,trans*-conjugated dienes (*t,t*-CD) into *cis*-monoenes proceeds by 1,4-addition of hydrogen by the formation of the active $H_2Cr(CO)_3$ species.



By this mechanism, acetonitrile in large concentrations would inhibit the formation of the active $H_2Cr(CO)_3$ complex by preferential formation of $(CH_3CN)_3\text{-}Cr(CO)_3$. Under the ambient conditions used in this work, no isomerization of methylene-interrupted dienes was observed. Previous work (29) showed that such double bond isomerization required high temperatures (185-195 C), and conjugation is necessary before hydrogenation takes place with Cr complex catalysts (1-8). Therefore, although $Cr(CO)_6$ is a highly stereoselective catalyst photoactivated in the presence of small amounts of acetonitrile, this catalyst system is unsuitable for the selective hydrogenation of methylene interrupted dienes such as linoleate.

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Detection of Cocoa Butter Equivalents in Chocolate

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ABSTRACT

The fatty acids at the sn-2 position and the sterol composition of cocoa butter and three common cocoa butter equivalents (CBE), namely Coberine, Choclin and Calvetta, were studied comparatively, in order to develop a sensitive method for detecting CBE in chocolate. Differences observed in the composition of saturated fatty acids at position-sn-2 present some interest in detecting CBE in chocolate. Differences found in 4-desmethyl and 4-methylsterol compositions, although quite significant, did not present any practical interest because of the relatively small amounts present in CBE. The 4,4′-dimethylsterol or triterpene alcohol fraction was found to have a potential for determining CBE in chocolate. Thus, the triterpene alcohols of Coberine were further fractionated on argentation thin layer chromatography (TLC) and analyzed by gas liquid chromatography (GLC) and gas chromatography-mass spectrometry (GC-MS). α-Amyrin was found in 48.2% of the triterpene alcohols of Coberine and was absent from cocoa butter. Cycloartenol, the main 4,4′-dimethylsterol of cocoa butter, and α-amyrin were well resolved on an OV-17 glass capillary column.

INTRODUCTION

Cocoa butter equivalents (CBE) are produced from vegetable oils by hydrogenation, fractionation and interesterification and possess chemical and physical properties similar to cocoa butter. The difficulty in determining CBE in cocoa butter is not only their similar composition, but also the natural variation of the composition of cocoa butter itself. Moreover, chocolate fats usually contain, in addition to cocoa butter, milk fat or other permitted fats (e.g. hazelnut oil or other seed oils), the presence of which hinders the determination of the nonpermitted CBE in most European countries. In the United Kingdom, Denmark and Ireland the addition of 5% non-cocoa butter fats, apart from milk fat, is permitted (1).

Among the methods proposed for the determination of CBE or other cocoa butter substitutes in chocolate, the most discussed is the GLC analysis of chocolate fat triglycerides, which are separated according to their carbon number (1,2). However, the sensitivity of the method is 15% in cocoa butter (5% in chocolate), and in the case of milk chocolate additional test procedures must be used to establish the presence of foreign fats, independently of the single triglyceride analysis (3).

The objective of the present study was to develop a sensitive method for the detection of CBE which would be suitable for plain (not containing milk) and milk chocolate. Thus, the triglyceride structure and the sterol composition of cocoa butter and three common CBE's, Coberine, Choclin and Calvetta, were studied comparatively (4).

EXPERIMENTAL

Cocoa butter was extracted from powdered cocoa beans (roasted) deprived of shells and seed buds, in a Soxhlet apparatus with petroleum ether, for 24 hr. The samples of cocoa beans were obtained from chocolate manufacturers in Greece. The samples of prime pressed cocoa butter, Coberine, Choclin and Calvetta were provided by Croklaan b.v., Holland, and the milk powder sample by Ion Co., Greece.

Fatty acid methyl esters were prepared according to AOCS method (5). Determination of fatty acids at position-sn-2 of glycerides was performed according to the modified IUPAC method 2.210 (6). GLC: Tracor 550, stainless steel column EGGS 10% on gas chrom Q 100-120 mesh, 1.8 m x 3 mm i.d.

The fat (100g) in 1000 ml alcoholic 1.0 N potassium hydroxide was refluxed for 1 hr under nitrogen. The mixture was diluted with 2000 ml distilled water and the unsaponifiable matter extracted with three 1000-ml portions of diethyl ether, freshly distilled. The combined extracts were washed five times with 800-ml portions of distilled water, dried over anhydrous sodium sulphate, and the solvent was removed by a rotary evaporator.