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THE PHOTO-INDUCED DEGRADATIONS OF TETRANEOPENTYLCHROMIUM AND TRIMESITYLCHROMIUM TETRAHYDROFURANATE: SOME APPLICATIONS TO CATALYSIS

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Summary

Photo-induced reactions of tetraneopentylchromium (I) and trimesitylchromium tetrahydrofuranate (II) have been investigated. Both I and II upon photolysis in solution function as active catalysts for the polymerization of vinyl monomers such as styrene, methyl acrylate, methyl methacrylate, and vinyl acetate, and also for the polymerization of ethylene under very mild conditions. Irradiation of I in tetrahydrofuran in the presence of carbon monoxide leads to the production of $Cr(CO)_6$ and $Cr(CO)_5(THF)$, demonstrating that low valent chromium species are formed under these conditions.

Introduction

Following our initial report [1] that carbon—transition metal σ-bonds of the Group IVB metals are photochemically very labile and can be cleaved under photolysis conditions to produce intermediates of high chemical reactivity, considerable interest in this aspect of organometallic photochemistry has been generated in our laboratory and elsewhere [2—13]. By such a photolytic process, the metal is reduced to a lower, highly reactive oxidation state, and the organic intermediates so produced can undergo a variety of reactions. In light of these results it was of interest to see whether the photolysis of β-elimination-stabilized alkyl and aryl derivatives of the transition metals [14,15] could under suitable photolytic conditions also lead to reactive species which might serve as useful synthetic intermediates as well as active polymerization catalysts. Experiments of this type have proved successful, and the results are described below.

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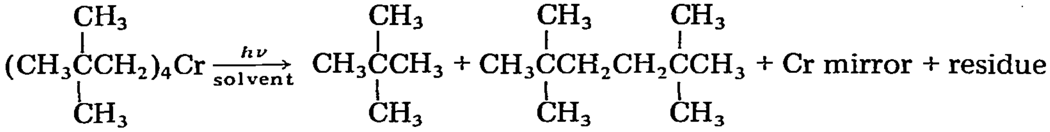
Results and discussion

Photolysis by means of a sunlamp of deep violet solutions (ca. 1 mg/ml) of tetraneopentylchromium (I) [16,17] in hydrocarbon solvents such as hexane, benzene, or toluene over a period of several days led to the formation of an amber solution which contained neopentane and 2,2,5,5-tetramethylhexane as evidenced by GLC and GLC/MS analyses.



$$(CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2)_4Cr \xrightarrow[\text{solvent}]{h\nu} CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_3 + CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_3 + \text{Cr mirror} + \text{residue}$$

A chromium mirror was also produced, as well as a black, pyrophoric solid which was found to contain carbon, hydrogen, and chromium in proportions which varied from one run to another.

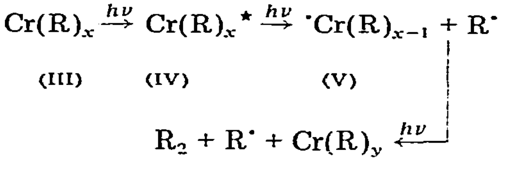
Attempts to trap possible intermediate low valent chromium species as η-arenechromium complexes by photolysis of I in various aromatic solvents or in THF in the presence of mesitylene or halobenzenes have so far been unsuccessful. However, irradiation of I in the presence of carbon monoxide at atmospheric pressure led to the rapid formation of $Cr(CO)_6$ and $Cr(CO)_5(THF)$. These products were identified by IR analysis [18] of the reaction mixture and by conversion of the latter complex into $Cr(CO)_5(PPh_3)$ on the addition (in the dark) of PPh_3.

Polymerization of vinyl monomers

In the absence of light, I is catalytically inactive towards vinyl monomers. Upon exposure to light, however, solutions of I become very active vinyl monomer polymerization catalysts. Although II [19] is a very weak vinyl polymerization catalyst in the dark, exposure of its solutions to light gives a much more active polymerization catalyst. $Cr(CO)_6$, tetramesitylchromium [20], and triphenylchromiumtris(tetrahydrofuran) [21], on the other hand, are catalytically inactive towards vinyl monomers in the dark or upon photolysis with white light.

Table 1 summarizes the results of several polymerizations of methyl methacrylate, using a variety of organochromium compounds as catalysts or catalyst precursors, and under a wide variety of conditions. The results of tacticity determinations on several poly(methyl methacrylate) polymers are summarized in Table 2. It is important to note that the tacticity of polymers produced using I or II as photo-induced catalysts can be controlled by varying the temperature of the polymerization.

The combined results in Tables 1 and 2 indicate that the polymerizations of vinyl monomers using photo-activated σ-bonded organochromium compounds are free radical in nature. Photolysis of a complex such as III gives an activated complex (IV) which could then undergo homolytic cleavage to form



$$\underset{(III)}{Cr(R)_x} \xrightarrow{h\nu} \underset{(IV)}{Cr(R)_x^{*}} \xrightarrow{h\nu} \underset{(V)}{{}^{\cdot}Cr(R)_{x-1}} + R^{\cdot}$$

$$R_2 + R^{\cdot} + Cr(R)_y \xleftarrow{h\nu}$$

TABLE 1

POLYMERIZATION OF METHYL METHACRYLATE WITH σ-BONDED ORGANOCHROMIUM COMPOUNDS

Catalyst [a]	Quantity of catalyst (mmol)	Solvent	Light source	Temperature (°C)	Length of photolysis (h)	Quantity of polymer (g)	Polymer (g)/catalyst (mmol)
$Cr(neo)_4$	0.3	bulk	dark	25	12	—	—
$Cr(neo)_4$	0.3	bulk	*b*	25	1/4 [e]	4.0	13.3
$Cr(neo)_4$	0.3	bulk	*b*	25	2	14.5	48.3
$Cr(neo)_4$	0.47	toluene	*d*	−78	8.5	0.22	0.47
$Cr(mes)_3(THF)$	0.5	toluene	dark	25	2	0.3	0.6
$Cr(mes)_3(THF)$	0.54	toluene	dark	100	2	0.9	1.7
$Cr(mes)_3(THF)$	0.2	toluene	*c*	25	2	0.6	3.0
$Cr(mes)_3(THF)$	0.15	toluene	*c*	100	2	1.06	7.1
$Cr(mes)_3(THF)$	0.26	bulk	*b*	25	3	3.3	12.3
$Cr(CO)_6$	0.92	bulk	*b*	25	2	—	—

[a] neo = neopentyl; mes = mesityl. [b] 275 W sun lamp. [c] 125 W low pressure Hg lamp. [d] 450 W medium pressure Hg lamp. [e] Reaction mixture allowed to stand in the dark 30 min before quenching.

TABLE 2

TACTICITY OF POLY(METHYL METHACRYLATE) OBTAINED WITH σ-BONDED ORGANOCHROMIUM COMPOUNDS UNDER PHOTOLYSIS CONDITIONS

Catalyst	Temperature (°C)	Solvent	Tacticity (%)		
			iso	syndio	hetero
$Cr(neo)_4$	25	bulk	—	65	35
$Cr(neo)_4$	−78	toluene	—	76	24
$Cr(neo)_4$	100	toluene	1	45	54
$Cr(mes)_3(THF)$	25	bulk	—	65	35
$Cr(mes)_3(THF)$	25	THF	1	62	37
$Cr(mes)_3(THF)$	100	toluene	1	45	53

an organic radical and a metal-based radical (V). The organic radical could then initiate the radical polymerization of vinyl monomers, whereas the metal-based radical could undergo further degradation to produce additional organic radicals or catalytically inactive species such as R_2.

The photo-induced polymerizations of other vinyl monomers such as methyl acrylate, styrene, and vinyl acetate in the presence of I were also successful, and typical examples are given in the Experimental section.

Polymerization of ethylene

Solutions of either I or II upon irradiation have also been found to function as active polymerization catalysts under very mild conditions *. Prior to light exposure, these solutions are catalytically inactive towards ethylene. Thus, photolysis of a 0.5% solution of I in toluene at 35°C and at 1 atmosphere ethylene pressure results in the production of 0.8 g of high molecular weight polyethylene (m.p. 137°C) per mmol of I over a 4 h period. Likewise, a solution of II under the same conditions yields 0.15 g of polyethylene per mmol of II. The catalytic activity of either I or II towards ethylene polymerization can be

$$CH_2{=}CH_2 \xrightarrow[\text{1 atm, 35°C, solvent}]{h\nu,\ \text{I or II}} (CH_2CH_2)_x$$

significantly increased by the addition of various metal halides such as $AlCl_3$, $CrCl_3$, $TiCl_3$, etc., prior to photolysis. Thus irradiation of a mixture of I, $TiCl_3$, and ethylene in toluene under the above conditions produces 1.8 g of polymer per mmol of I. In preliminary experiments, we have observed that the photolysis of I and certain metal halides likewise produces a catalysis system also capable of polymerizing propylene under very mild conditions [22].

The above findings are especially noteworthy in view of the known thermal stabilities of compounds such as I and II, and their reported general inertness to many chemical reactions under thermal conditions [14—17,19]. Our results also suggest that other β-elimination-stabilized alkyl- and aryl-transition metal

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[*] The photo-initiated polymerization of ethylene by means of tetra-t-butylchromium and related complexes under low ethylene pressures has been mentioned in patents [25].

compounds can be activated by photolysis under mild conditions, and that such activated species might be useful as catalysts for the photo-curing of inks and coatings. Studies designed to examine the scope and mechanism of photo-induced activation of such compounds are in progress in our laboratory.

Experimental

All operations were conducted under argon using Pyrex Schlenk tubes. Argon, solvents, and alumina were purified by techniques previously described [5]. Photolyses were conducted with either a 450 W Hanovia photochemical lamp located in a quartz, water-cooled immersion well, as previously described [5], or with a 275 W G.E. sun lamp.

Methyl acrylate, methyl methacrylate, styrene, and vinyl acetate were used as commercially obtained. Neopentane for GC comparison was prepared by hydrolysis of a solution of neopentyllithium, and 2,2,5,5-tetramethylhexane was prepared by a literature procedure [23]. A solution of $Cr(CO)_6$ and $Cr(CO)_5$-THF was prepared by photolysis of a solution of $Cr(CO)_6$ in THF for IR comparison with experimental samples [18].

Polymer samples were characterized by their ability to be cast into films; as well as by their NMR and IR spectra. The tacticities of poly(methyl methacrylate) samples were determined from their NMR spectrum at 120°C in *o*-dichlorobenzene at 90 MHz [24].

Gas chromatographic analyses were performed on a Varian Series 2400 gas chromatograph equipped with a flame ionization detector. GLC/MS analyses were performed on a Perkin—Elmer—Hitachi RMU-6L mass spectrometer interfaced with a Perkin—Elmer 990 gas chromatograph. Proton NMR spectra were recorded on a Varian A-60, Perkin—Elmer R-12A, or Perkin—Elmer R-32 spectrometer. IR spectra were recorded on Perkin—Elmer 237B infrared spectrophotometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Mass.

Photolysis of $Cr(neo\text{-}C_5H_{11})_4$ in toluene

A solution of $Cr(neo\text{-}C_5H_{11})_4$ (0.2 g, 0.6 mmol) in 150 ml of toluene was irradiated in a Schlenk tube (4 × 30 cm) for three days with a 275 W sun lamp to give a dark brown solution, together with a black highly pyrophoric precipitate, and a faint chromium mirror on the Schlenk tube. The brown solution was found to contain neopentane and 2,2,5,5-tetramethylhexane by GLC comparison with authentic samples and GLC/MS analyses. The black pyrophoric solid was found to contain carbon, hydrogen, and chromium in varying amounts depending on the run. Found: C, 28.06—29.14; H, 4.91—5.53; Cr, 50.9—60.1%.

Photolysis of $Cr(neo\text{-}C_5H_{11})_4$ in THF in the presence of CO

A solution of $Cr(neo\text{-}C_5H_{11})_4$ (0.1 g, 0.3 mmol) in 100 ml of THF was cooled to 0°C and saturated with CO by bubbling through a slow stream of CO gas for 15 min. The solution was then photolyzed with a 450 W medium pressure mercury lamp for 30 min at 0°C while continually bubbling CO through the solution. The solution was allowed to warm to room temperature while the CO stream was maintained. An aliquot of the resulting solution was removed and comparison of its IR spectra with those of authentic samples indicated the presence of $Cr(CO)_6$ and $Cr(CO)_5(THF)$. Triphenylphosphine (0.2 g, 0.8 mmol) was added to the reaction mixture and the solution stirred in the dark at 23°C for 2 h. An IR spectrum of an aliquot of the resulting solution indicated the presence of $Cr(CO)_6$ and $Cr(CO)_5(PPh_3)$ by comparison with IR spectra of authentic samples.

Polymerization of methyl methacrylate with $Cr(neo\text{-}C_5H_{11})_4$ under photochemical conditions

In a typical polymerization $Cr(neo\text{-}C_5H_{11})_4$ (0.1 g, 0.3 mmol) was dissolved in methyl methacrylate (50 ml, 48.8 g, 0.49 mol) and the resulting solution photolyzed for 2 h with a 275 W sun lamp placed a distance of 15 cm from the reaction vessel. The resulting clear solution was poured into 300 ml of methanol and the resulting precipitate filtered and dried to give 14.5 g of poly(methyl methacrylate).

In a control experiment $Cr(neo\text{-}C_5H_{11})_4$ (0.10 g, 0.3 mmol) was dissolved in 50 ml of methyl methacrylate (48.8 g, 0.49 mol) and the resulting solution allowed to stand in the dark for 12 h. Upon work-up of this solution in a manner similar to that above, no poly(methyl methacrylate) was obtained.

In another control experiment 50 ml of methyl methacrylate (48.8 g, 0.49 mol) was photolyzed for 2 h with a 275 W sun lamp as described above. Work-up similar to that above gave no poly(methyl methacrylate).

Polymerization of methyl acrylate with $Cr(neo\text{-}C_5H_{11})_4$ under photochemical conditions

In a typical polymerization $Cr(neo\text{-}C_5H_{11})_4$ (0.01 g, 0.03 mmol) was dissolved in 20 ml of benzene and methyl acrylate (6 ml, 66 mmol). The resulting violet solution was then photolyzed at room temperature with a 275 W sun lamp for 15 min to give a clear yellow solution. Upon methanol work-up as described above, 0.71 g of poly(methyl acrylate) were produced.

Polymerization of methyl methacrylate with $Cr(2,4,6\text{-}Me_3C_6H_2)_3(THF)$ under photochemical conditions at 100°C

In a typical polymerization, $Cr(2,4,6\text{-}Me_3C_6H_2)_3(THF)$ (0.070 g, 0.15 mmol) was dissolved in a solution of 50 ml of toluene and 24 ml of methyl methacrylate (22.4 g, 0.22 mmol). After photolysis at 100°C with a 125 W low pressure mercury lamp for 2 h, work up in a manner similar to that above produced 1.06 g of poly(methyl methacrylate). The results of control experiments with $Cr(2,4,6\text{-}Me_3C_6H_2)_3THF$ are summarized in Table 1.

Polymerization of methyl methacrylate at low temperature with $Cr(neo\text{-}C_5H_{11})_4$ under photochemical conditions

In a typical polymarization $Cr(neo\text{-}C_5H_{11})_4$ (0.1566 g, 0.466 mmol) and 10 ml of methyl methacrylate (9.36 g, 93 mmol) were dissolved in 15 ml of toluene. The resulting solution was cooled to −78°, and photolyzed for 8 1/2 h with a 450 W medium pressure mercury lamp. Upon methanol work-up as described above 0.22 g of poly(methyl methacrylate) were obtained.

Polymerization of styrene with $Cr(neo\text{-}C_5H_{11})_4$ under photochemical conditions

In a typical polymerization $Cr(neo\text{—}C_5H_{11})_4$ (0.1171 g, 0.35 mmol) was dissolved in 50 ml of styrene (45.4 g, 0.43 mmol) and photolyzed for 15 min with a 275 W sun lamp. Upon work-up of the resulting pale-yellow solution in a manner similar to that described above 0.62 g of polystyrene were obtained.

Polymerization of ethylene with $Cr(neo\text{-}C_5H_{11})_4$ under photochemical conditions

In a typical experiment ethylene was bubbled through a solution of $Cr(neo\text{-}C_5H_{11})_4$ (0.10 g, 0.3 mmol) in 20 ml of toluene while photolyzing at 35°C with a 250 W medium pressure mercury lamp for 4 h. Upon methanol work-up 0.24 g of polyethylene (m.p. 137°C) was obtained.

Polymerization of ethylene with $Cr(2,4,6\text{-}Me_3C_6H_2)_3(THF)$ under photochemical conditions

In a typical polymerization ethylene was bubbled through a solution of $Cr(2,4,6\text{-}Me_3C_6H_2)_3(THF)$ (0.10 g, 0.2 mmol) in 200 ml of toluene while photolyzing with a 275 W sun lamp at 35°C for 2.5 h. Upon methanol work-up 0.03 g of polyethylene was obtained.

Polymerization of ethylene with $Cr(neo\text{-}C_5H_{11})_4$ in the presence of Lewis acids under photochemical conditions

In a typical polymerization ethylene was bubbled through a mixture of $Cr(neo\text{-}C_5H_{11})_4$ (0.10 g, 0.3 mmol) and $TiCl_3$ (0.10 g, 0.65 mmol) in 20 ml of toluene while photolyzing at 35°C with a 275 W sun lamp for 4 h. Upon methanol work-up 0.54 g of polyethylene was obtained.

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