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A KINETIC STUDY OF THE REACTION BETWEEN DI-h^5-CYCLOPENTADIENYLTUNGSTEN DIHYDRIDE AND BENZOTRICHLORIDE

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Summary

The reaction of di-h^5-cyclopentadienyltungsten dihydride with benzotrichloride proceeds to produce as the only observed products di-h^5-cyclopentadienyltungsten dichloride and benzal chloride. The reaction was shown to be first order with respect to Cp_2WH_2. The relative rate of reaction increases substantially with the use of 3,4-dichlorobenzotrichloride in place of benzotrichloride as the oxidizing agent.

Introduction

The reduction of carbon tetrachloride to chloroform has been used as an indication of the presence of a transition metal—hydrogen bond [1]. The di-h^5-cyclopentadienylmetal hydrides of tungsten, molybdenum, and to a lesser extent tantalum, have been shown to be converted to their respective halides by halogenated solvents [2-4] while Cp_2ReH is converted to an unknown, insoluble material [1]. However, no prior investigation of the mechanism of these reactions has been reported.

In the following study, the stoichiometry and kinetics of the reaction of Cp_2WH_2 with benzotrichloride in 1,2-dimethoxyethane (glyme) are described.

Experimental

Di-h^5-cyclopentadienyltungsten dihydride was obtained from Dr. K.S. Chen [5] and was resublimed under vacuum prior to use if the bright yellow color of the material had darkened. Benzotrichloride (Eastman) and benzal chloride (Eastman) were passed through a column of activated alumina and distilled at reduced pressure at a temperature at or below 75°C. Benzyl chloride was distilled at reduced pressure at 65°C prior to use. 3,4-Dichlorobenzotrichloride (ICN-K and K) was used without further purification. 1,2-Dimethoxyethane (MCB), b.p. 84°C, was kept at reflux over and distilled from $LiAlH_4$ immediately prior to use.

Infrared spectra were obtained on a Perkin—Elmer 21 or 421 and NMR spectra on a Varian HA-100. Mass spectra were run by Mr. R. Drake on a Varian MAT CH-5 single focusing instrument at 70 eV. Microanalyses for carbon and hydrogen were done by Mrs. K. Widiger on an F and M Model 185 C, H, N analyzer, by Mr. J. Haug on a Hewlett—Packard 185B, or by Chemalytics Laboratories, Tempe, Arizona.

Kinetic procedure

A small sample of Cp_2WH_2 (ca. 10 mg, 0.0316 mmol) was transferred (glove bag, argon) from a tared vial to a 1 ml volumetric flask. The accurate sample weight was determined by difference and the sample was then dissolved in degassed glyme, diluted to the mark, and transferred by syringe to a standard 5 mm NMR tube. Mesitylene (10 μl, 0.0719 mmol) was added as an internal standard and the tube was capped with soft plastic and dipped in paraffin. The cap could be penetrated easily by a syringe needle but would seal upon withdrawal of the needle. An appropriate volume of reactive halide (corresponding to ca. 0.9 mmol) was injected into the solution, the tube was quickly placed into the NMR spectrometer (probe at 29 ± 1°C), and the cyclopentadienyl signal of the Cp_2WH_2 was scanned every 30 sec for 15-25 min (2-3 half-lives). Signal areas were determined by use of a planimeter and by measurement of peak height × width at half-height (peaks were symmetric). Direct use of electronic integration was precluded because the small concentrations of Cp_2WH_2 necessitated high output settings on the NMR instrument. The data are summarized in Table 1.

Use of galvinoxyl

The injection of benzotrichloride (0.2 ml) into a 0.05 *M* solution of Cp_2WH_2 in glyme containing galvinoxyl (5 mg) caused the initially deep red-blue solution to turn very light yellow within 5-10 seconds. Galvinoxyl solutions in glyme, glyme and Cp_2WH_2, glyme and benzotrichloride, or benzotrichloride maintained a deep blue or red-blue color in the absence of oxygen.

Product analysis

A solution of Cp_2WH_2 (20 mg) in glyme (1 ml) was prepared as described for the kinetic runs and then 5-10 μl of a halocarbon was added. When the solu-

TABLE 1

INITIAL RATES FOR THE REACTION OF Cp_2WH_2 WITH $PhCCl_3$[a]

$[PhCCl_3]$(*M*)	$[Cp_2WH_2] \times 10^2$(*M*)	Initial rate × 10^4
1.75	4.84	4.67
3.51	4.19	11.0
1.40	3.12	2.67
2.11	3.24	8.00
2.11	4.89	10.7
1.40	5.32	6.19
2.46	4.36	13.6
1.40	4.74	3.33

[a] Disappearance of cyclopentadienyl hydrogens for Cp_2WH_2. Rates were determined graphically from the concentration versus time plots.

tion had been at 25°C for 12 h, 1 *M* hydrochloric acid (ca. 1 ml) was added to protonate unreacted Cp_2WH_2, and halocarbon products were extracted into cyclohexane and identified by NMR spectroscopy. Solutions were also subjected to VPC analysis. Cp_2WCl_2, which precipitates as a fine suspension during the reaction, was readily isolated and identified by its characteristic physical and spectral properties [4].

Results and discussion

Stoichiometry

The only metal-containing product isolated from the reaction of benzotrichloride with Cp_2WH_2 was the corresponding dichloride, Cp_2WCl_2, identified by its characteristic physical and spectral properties [4]. The benzotrichloride was reduced exclusively to benzal chloride. Even the use of excess Cp_2WH_2 failed to produce any detectable Cp_2WHCl or any reduction of the benzal chloride. Thus, under the conditions used for the kinetic study, the appropriate stoichiometry is as shown. Under the same conditions, 3,4-dichlorobenzotrichloride was reduced to 3,4-dichlorobenzal chloride.

$$Cp_2WH_2 + 2\ PhCCl_3 \xrightarrow[29^\circ C]{glyme} Cp_2WCl_2 + 2\ PhCHCl_2$$

Free radical intermediates

Limitations in the experimental procedure used to follow the reaction restricted experimentation with free radical scavengers. However, the striking color change observed upon addition of galvanoxyl [6] suggests that free radical intermediates might be involved.

Although no CIDNP effects [7,8] were observed, the NMR signal of the metal-bound hydrogens of Cp_2WH_2 disappeared immediately upon introduction of benzotrichloride to the solution of Cp_2WH_2 in glyme. The cyclopentadienyl hydrogens were unaffected. Because the kinetic data indicated that 6-7 minutes were required for one half-life under these conditions, the hydride signal was undoubtedly broadened by exchange and/or relaxation processess [9-11]. Although the exact interpretation of the broadening is unknown, its existence is consistent with the presence of free radical intermediates.

Kinetics

Kinetic measurements were made in glyme at 29 + 1°C with an approximately 30-fold molar excess of benzotrichloride to Cp_2WH_2. When data for disappearance of the cyclopentadienyl hydrogens of the starting hydride were tested with standard integrated rate expressions, plots for zero-, half-, three-halves-, and second-order in Cp_2WH_2 were clearly non-linear while that for first-order was linear through 80% reaction*. The pseudo first-order rate constant was ca. 10^{-3} sec^{-1}. Use of the method of half-lives [12] with three pairs of starting concen-

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* The fact that the product Cp_2WCl_2 precipitates as a fine suspension as the reaction progresses had no apparent effect on the kinetics but obviated optical methods of following the reaction.

trations for Cp_2WH_2 indicated that the order with respect to Cp_2WH_2 was 1.02 ± 0.01.

Assuming a free-radical chain mechanism analogous to that known for reactions between tri-n-butyltin hydride and various aryl halides [13-15], and postulating the likely intermediacy of Cp_2WHCl, one can outline possible propagation steps as shown below:

$$PhCCl_2\cdot + Cp_2WH_2 \rightarrow PhCHCl_2 + Cp_2WH\cdot$$

$$PhCCl_3 + Cp_2WH\cdot \rightarrow PhCCl_2\cdot + Cp_2WHCl$$

$$PhCCl_2\cdot + Cp_2WHCl \rightarrow PhCHCl_2 + Cp_2WCl\cdot$$

$$PhCCl_3 + Cp_2WCl\cdot \rightarrow PhCCl_2\cdot + Cp_2WCl_2$$

The fact that Cp_2WHCl could never be detected during or at the completion of any reaction indicates that its decomposition must be quite rapid, and would be consistent with the anticipated greater stability of $Cp_2WCl\cdot$ relative to $Cp_2WH\cdot$.

For experimental reasons the rate of reaction could not be followed conveniently with an excess of Cp_2WH_2. Therefore initial rate data (Table 1) were used in an effort to determine the reaction order with respect to the excess benzotrichloride*. However, the large standard deviations encountered when attempts were made to fit these data to all conceivable and reasonable rate laws did not permit a distinction to be made among the various possibilities.

It is of interest to note that the use of 3,4-dichlorobenzotrichloride as the oxidizing agent resulted in a rate much too fast to follow by the NMR procedure while both benzal chloride and benzyl chloride showed no reaction with Cp_2WH_2 in glyme at 29°C over a 24 hour period. The enhancement of reactivity upon introduction of the 3,4-dichloro substituents onto benzotrichloride may be explained as being due to the type of polar effect previously observed in the reaction of tri-n-butyltin hydride with organic halides [13,15]; The effect has been explained both in terms of stabilization of polar resonance contributions to the transition state for abstraction of halogen by a metal radical and/or reduction of electronic repulsion between the *p*-orbitals of the chlorine and the attacking radical.

The observed reactivity of di-h^5-cyclopentadienylmetal hydrides toward halocarbons is Ta > Mo > W [2]. The electronegativities for these metals are quite similar as are the ionic radii for their formal oxidation states in the hydride complexes. However, the trend in the stretching frequency for the metal—hydrogen bond (1735 cm^{-1} for Cp_2TaH_3 [2], 1847 cm^{-1} for Cp_2MoH_2 [2], and 1918 cm^{-1} for Cp_2WH_2 [5]) indicates that reactivity decreases in the order of increasing metal—hydrogen bond strength. Whether or not the tantalum and molybdenum hydrides react with halocarbons via a free radical chain mechanism has not been established.

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* Unfortunately the large changes in the ratio of reactants which would be required to change the nature of the termination step of various free radical mechanisms which could be proposed are not possible because of limitations associated with the NMR technique used to follow the reaction.

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