Journal of Organometallic Chemistry, 216 (1981) 57—63
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE HYDROGENATION OF α-METHYLSTYRENE BY TRICARBONYL(CYCLOPENTADIENYL)HYDRIDE COMPOUNDS OF TUNGSTEN AND MOLYBDENUM; SUPPORT FOR A RADICAL MECHANISM

RAY L. SWEANY *, DAVID S. COMBERREL, MAUREEN F. DOMBOURIAN, and NATASHA A. PETERS

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122 (U.S.A.)

(Received January 5th, 1981)

Summary

Rates of reaction of the hydrides of tungsten and molybdenum of the form $HM(\eta^5\text{-}C_5H_5)(CO)_3$, with α-methylstyrene have been determined. The rate law is first order in olefin and in hydride. A mechanism involving a rate limiting step of hydrogen atom transfer to the olefin is consistent with the rate law, isotope effect and the absence of CO inhibition. The activation enthalpy for the reactions of $HW(\eta^5\text{-}C_5H_5)(CO)_3$ and $HMo(\eta^5\text{-}C_5H_5)(CO)_3$ are 97.5 ± 4.2 and 89.1 ± 3.3 kJ/mol, respectively. The rate constant for the reaction of styrene and $HW(\eta^5\text{-}C_5H_5)(CO)_3$ is approximately that of α-methylstyrene, while β-methylstyrene was not observed to react under the conditions of the previous determinations. This suggests that attack by the hydride occurs at the β-carbon and this process is inhibited by substituents at that location.

Introduction

Mechanisms which have been proposed for hydrogenation reactions of olefins by transition metal hydrides have occasionally included hydrogen atom transfer reactions which yield free radical intermediates [1—5]. Experimental evidence for such hypotheses is not always available. However, the reaction of $HMn(CO)_5$ and α-methylstyrene produces CIDNP in NMR spectra at 60 MHz which is consistent with such a process [2]. Other evidence has also been cited to justify the use of similar mechanisms. Roth and Orchin proposed a radical mechanism involving hydrogen atom transfer for the reaction of $HCo(CO)_4$ and 1,1-diphenylethene [3]. The reaction exhibits no CO dependence in the rate law and an inverse isotope effect for the deuteride. The first observation was essential for eliminating from consideration a coordinatively unsaturated species. The second observation can be rationalized by postulating the transfer of a hydrogen atom from the metal to the olefin in the rate limiting step. The zero-point energy of the hydrogen—metal stretching vibration in the reactant is reasonably less than that of the hydrogen—carbon stretch in the transition state, even presuming that the transfer of hydrogen is not complete. Similar behavior was noted for the above-cited reaction of $HMn(CO)_5$ and α-methylstyrene.

The hydrogenation reaction between 9,10-dimethylanthracene and $HMn(CO)_5$ shows virtually no stereospecificity in the hydrogens added at the 9 and 10 positions, which is consistent with a two-step hydrogen atom transfer reaction [4]. Feder and Halpern [5] noted this same lack of specificity in the reaction of $HCo(CO)_4$ and 9,10-dimethylanthracene [6] as an indication of a radical mechanism. In addition, it was noted that other polycyclic aromatic hydrocarbons which were hydrogenated by $HCo(CO)_4$ varied in their reactivity in the same manner as the radical localization energies. Such behavior is consistent with a mechanism in which a rate limiting, hydrogen atom transfer reaction occurs as the initiating event.

The reactions of $HM(\eta^5\text{-}C_5H_5)(CO)_3$, where M = Cr, Mo, and W, with isoprene yields 2-methyl-2-butene [7]. This behavior suggests the possibility of similar free radical chemistry. The carbon-centered radical is stabilized by the π system in an allylic fashion, whereas the hydrogenation leading to an alkane is afforded no similar stabilization. The work which is reported herein supports such a possibility in that the reactions of these hydrides with α-methylstyrene exhibits strong evidence of a radical mechanism which is analogous to that of $HMn(CO)_5$.

Experimental

$HM(\eta^5\text{-}C_5H_5)(CO)_3$, where M = Mo and W, was prepared by standard methods [8]. The $HMo(\eta^5\text{-}C_5H_5)(CO)_3$ which had been purified only by sublimation contained an impurity which caused exchange broadening of the proton signal due to the hydridic proton. This impurity could be removed satisfactorily by recrystallization from hexane followed by sublimation. The presence of the impurity did not affect the kinetics of the reaction with α-methylstyrene to a significant extent.

$DM(\eta^5\text{-}C_5H_5)(CO)_3$ was prepared from $HM(\eta^5\text{-}C_5H_5)(CO)_3$ by exchange with a large excess of CH_3OD. The exchange process is rapid and immediately after mixing, the methanol may be vacuum distilled from the deuteride. Enrichments in excess of 95% were attained as determined by NMR. Styrene, α-methylstyrene, β-methylstyrene, and the several anthracenes were obtained from Aldrich Chemical Co. The former three were distilled before use to remove trace radical inhibitors.

Mixtures of the reactants were prepared in a N_2-filled inert atmosphere box in C_6D_6. The mixtures were then vacuum sealed in NMR tubes. The NMR spectrum of the solutions was observed at intervals at ambient conditions using either an Hitachi R20B 60 MHz or a JOEL FX90Q spectrometer. The quenching and subsequent reheating of the solutions occur essentially in a minute so that the time during which the mixture is not either stopped or at reaction temperature is small with respect to the total time of the experiment. The tubes were maintained at reaction temperature to ±1°C at temperatures from 65 to 120°C. As the reaction proceeds, the concentration of $M_2(\eta^5\text{-}C_5H_5)_2(CO)_6$ exceeds its solubility, especially at the measurement temperature. The presence of solids did not adversely affect the tuning of the spectrometer. Reactions which were to be run under a CO atmosphere used samples which were filled with one atmosphere of CO at room temperature and then closed by a valve located above the spot which was to be heat-sealed. The NMR tube was then cooled to 196 K. This caused the gas pressure in the tube to become small enough that the glass collapsed on heating as it normally would under more conventional conditions for making a seal.

The rate constant for the reactions were calculated by use of a least-squares fitting of the intensity data, assuming first order kinetics in each reactant and an overall 2 : 1 stoichiometry consistent with equations 1 and 2. The effective NMR sensitivity varied from spectrum to spectrum and the data was smoothed by requiring that the integral of the methyl resonance of α-methylstyrene plus half the intensity of the methyl resonance of the product, cumene, be constant throughout all spectra of a given sample. The intensities of all the signals in a particular spectrum were adjusted by a factor which would result in the above sum being constant. Implicit in this treatment is the assumption that the only product of α-methylstyrene is cumene, a fact which is consistent with NMR and GLC data.

Results

The reaction stoichiometries were found to conform to eq. 1.

$$2\ HM(\eta^5\text{-}C_5H_5)(CO)_3 + Ph(CH_3){=}CH_2 \rightarrow M_2(\eta^5\text{-}C_5H_5)_2(CO)_6 + PhCH(CH_3)_2 \quad (1)$$

The second order kinetic plots of the intensity data were linear over two half-lives. The rate law which fits the data is shown in eq. 2.

$$\text{rate} = k_{obs}[HM(\eta^5\text{-}C_5H_5)(CO)_3][Ph(CH_3){=}CH_2]\ (= -d[Ph(CH_3){=}CH_2]/dt) \quad (2)$$

Values of k_{obs} are shown in Table 1. The principal reason for scatter among the replicate determinations is the uncertainty in integral calibrations in the NMR spectra. The results of Eyring plots of the data showed the activation enthalpies to be 97.5 ± 4.2 and 89.1 ± 3.3 kJ/mol for tungsten and molybdenum, respectively. The corresponding activation entropies are —54 ± 4 and —58 ± 4 J/K mol. Rate constants from only the vacuum filled tubes were used in the determination of the activation parameters. The rates of reaction were not significantly affected by the presence of carbon monoxide at one atmosphere pressure. The deuterides of $HM(\eta^5\text{-}C_5H_5)(CO)_3$ react faster with α-methylstyrene than their protic forms. The deuterium adds across the double bond with no NMR evidence of deuterium incorporation in the methyl group of α-methylstyrene nor is there any evidence of protium substitution for deuterium in $DM(\eta^5\text{-}C_5H_5)(CO)_3$. The reaction of styrene with $HW(\eta^5\text{-}C_5H_5)(CO)_3$ proceeds at nearly the same rate as does α-methylstyrene. However, reactions of β-methylstyrene, anthracene, 9-methylanthracene and 9,10-dimethylanthracene could not be detected. Typically, small smounts of the metal—metal-bonded dimer were detected in these reactions but no organic products were detected by

TABLE 1

RATE CONSTANTS OF THE REACTION

2 $HMCp(CO)_3$ [a] + α-methylstyrene [b]

	Temp. (°C)	k_{obs} (X10^5 m^{-1} s^{-1})	Extreme values (X10^5 m^{-1} s^{-1})
$HWCp(CO)_3$	100	4.01(10%) [c]	3.48—4.48
$DWCp(CO)_3$	100	6.14(6%)	5.73—6.50
$HWCp(CO)_3$ with CO	100	3.92(<1%)	3.91—3.92
$HWCp(CO)_3$	110	8.64(6%)	8.12—9.32
$HWCp(CO)_3$	120	21.2(12%)	18.5—23.6
$HWCp(CO)_3$ and styrene	100	3.07 [d]	—
$HMoCp(CO)_3$	65	8.04(11%)	8.45—8.97
$DMoCp(CO)_3$	65	16.9(8%)	16.9—17.0
$HMoCp(CO)_3$ with CO	65	7.99(3%)	7.71—8.22
$HMoCp(CO)_3$	77	29.4(5%)	28.3—30.5
$HMoCp(CO)_3$	80	31.6(4%)	30.6—32.5
$HMoCp(CO)_3$	90	75.6(10%)	66.6—85.2

[a] Concentrations range from 0.286 to 1.512 *m*. [b] Concentrations range from 0.142 to 0.337 *m*. [c] One standard deviation of the data relative to the mean. [d] Single determination.

NMR. These observations can be accounted for by the decomposition of the hydride, independent of the presence of the organic substrate.

Discussion

The reactions of $HM(\eta^5\text{-}C_5H_5)(CO)_3$, where M = Mo and W, and α-methylstyrene are analogous to that of $HMn(CO)_5$ and α-methylstyrene [2] and are consistent with the following mechanism:

$$HM + Ph(CH_3){=}CH_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^{\cdot} + Ph(CH_3)_2C^{\cdot} \tag{3}$$

$$HM + Ph(CH_3)_2C^{\cdot} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M^{\cdot} + PhCH(CH_3)_2 \tag{4}$$

$$M^{\cdot} + M^{\cdot} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} M_2$$

$$M = Mo(\eta^5\text{-}C_5H_5)(CO)_3 \quad \text{and} \quad W(\eta^5\text{-}C_5H_5)(CO)_3 \tag{5}$$

In this scheme, k_4 and k_6 are considered negligible because of the endothermicity of the processes. The absence of deuterium isotope exchange between hydride and α-methylstyrene indicates that the k_2 process is kinetically slow relative to the k_3 process. Both the k_3 process and the k_5 process are presumed to be fast relative to the k_1 process. These assumptions are amply supported by work on the metal—metal-bonded species and analogous systems [9]. The observed rate constant of the reaction is therefore k_1 for most concentrations of hydride. This mechanism indicates a rate law which is first order in each reactant which is consistent with the observed behavior. In addition, the negative activation entropies are consistent with a rate limiting step which involves the formation of an activated complex from two discrete species. In the analogous reaction with $HMn(CO)_5$ the k_2 step was competitive with the k_3 step. This feature was an important aspect in the formulation of a model which is consistent with the radical pair mechanism for CIDNP. That such a process is not observed for $HM(\eta^5\text{-}C_5H_5)(CO)_3$ is sufficient reason for not seeing CIDNP in these reactions [10]. This behavior suggests that the transition state is more crowded than for $HMn(CO)_5$. As the transition state is passed along the reaction coordinate, there is significant relaxation of crowding with the formation of the radical pair (eq. 3).

The deuterium isotope effect which is observed for these reactions is described qualitatively by Bigeleisen and is consistent with a rate limiting step which involves hydrogen atom transfer from a metal to carbon [11]. Because of the relative weakness of the metal—hydrogen bond, the zero point energy of the reactant is less than that of the transition state, in which a carbon—hydrogen bond is substantially formed. Although the mechanism which has been proposed does not actually formulate the transition state for eq. 3, it is expected to resemble the intermediate free radicals, according to Polyani's rule [12]. The enthalpy change for reaction 3 is quite positive. An estimate for this enthalpy can be made based on the heat of hydrogenation of α-methylstyrene, the α carbon—hydrogen bond energy of toluene (as an estimate for that of cumene) [13], and an estimated metal—hydrogen bond energy of 250 kJ/mol [14]. These inputs lead to an estimate for the enthalpy of equation 3 of 62 kJ/mol. If the carbon—hydrogen bond is substantially formed in the transition state the zero-point energy associated with that stretching vibration will be that associated with a fundamental frequency of 2900 cm^{-1}. The metal—hydrogen stretching frequencies occur at 1790 and 1836 cm^{-1}, for molybdenum and tungsten, respectively [15]. Normally one expects the zero point energy of the transition state to exceed that of the reactants. The opposite is the case in reaction 3 and the prediction of an inverse isotope effect follows naturally from the proposed mechanism. Due regard should be paid to the more complex nature of reaction 3 than what is usually treated in descriptions of simple hydrogen atom transfer reactions. Here, for example, is a loss of bond order in the carbon skeleton as well as the breaking of a metal—hydrogen bond.

Alternative mechanisms which require the metal center to become unsaturated are not consistent with the lack of CO dependence on the rates of reaction. The possibility that the cyclopentadienyl ring might become partially uncoordinated to allow the olefin to form a π complex is also not indicated. Carbon monoxide should act in this instance as a competitive inhibitor and still slow the rate of reaction.

Of interest is the very low reactivity of β-methylstyrene with $HM(\eta^5\text{-}C_5H_5)(CO)_3$ or with $HMn(CO)_5$ [16]. The methyl group in the β position successfully blocks the reaction from occurring. The small difference in the rate of hydrogenation of styrene with respect to α-methylstyrene suggests that the α-methyl group does not drastically alter the energetics of the reaction.The stabilization which the methyl group affords the radical-like transition state is presumably cancelled by crowding. When the methyl group is switched to the β position, the electronic stabilization of the transition state is reduced but to no lesser degree than found in styrene itself. The slow rate of hydrogenation of β-methylstyrene must be due to steric crowding in the transition state. The approach of the hydride may be presumed to occur via a path along the π^* orbital of the β carbon. The hydrogen atom of the hydride is presumed to carry a large negative charge and behave as a nucleophile [17]. The π^* orbital of the olefin functions as an acceptor orbital. As charge is added to the π^* orbital a new bond is formed with a concomitant weakening of the carbon—carbon π bond. Substitution on the β carbon interferes with the ligands of the metal hydride. Such an interaction has been reported prior to the postulation of the radical mechanism but was not believed to lead to products [18].

One would like to obtain from these data some information about the relative metal—hydrogen bond energies in $HM(\eta^5\text{-}C_5H_5)(CO)_3$ and $HMn(CO)_5$ from the activation parameters. Simplistically, this is possible if one assumes that the intermediates are the transition state. Then the activation enthalpy could be related to the energetics of hydrogen—metal bond breaking in the metal hydrides and to the hydrogen—carbon bond making process in the olefin. This latter process would be the same in all three reactions so that differences in the activation energies would reflect differences in the bond breaking process, alone. That this is not the case is evidenced by the absence of a detectable reverse reaction in equation 3. There is a sufficiently large activation barrier to the back reaction that the forward reaction in equation 4 successfully competes with the back reaction. If the barrier to this back reaction reflects the degree of crowding in going from the separated radical pair to the transition state, then the meaningful comparison can still be made between $HMo(\eta^5\text{-}C_5H_5)(CO)_3$ and $HW(\eta^5\text{-}C_5H_5)(CO)_3$ because the metal sizes are not greatly different. From these assumptions it must be concluded that the metal—hydrogen bond energies are not greatly different. Estimates of these bond energies from thermochemical data of $H_2M(\eta^5\text{-}C_5H_5)_2$ have been made in two instances for M = Mo and W. They are 251 and 305, and 259 and 287 kJ/mol, respectively [14,19]. A difference of 54 kJ/mol in bond energy for the two metal—hydrogen bond energies is difficult to reconcile with the kinetic evidence reported herein. The 9 kJ/mol difference in activation energies which is ascribed to differences in the metal—hydrogen bond energies still is less than the 28 kJ/mol difference derived from the data of Tel'noi but is close to agreement within experimental error [19]. The effects of bond strengths on the position of the transition state have not been included in this analysis and may account for some of the difference between the kinetic and thermochemical evaluations of the bond energies. Both estimates of the molybdenum—hydrogen bond energy and estimates of the manganese—hydrogen bond energy in $HMn(CO)_5$ are quite similar [20]. Fortuitously, the activation energies for the hydrogenation reactions of α-methylstyrene and these hydrides are also nearly identical [2]. Because the back reaction analogous to that of equation 3 is observed for $HMn(CO)_5$, the activation energy will contain a contribution from the activation barrier for the back reaction. Thus, it would appear that the activation energies cannot be directly compared.

Acknowledgments

The authors wish to thank the National Science Foundation for the funds made available for the purchase of the JOEL FX90Q spectrometer under a matching grant CHE78-02081.

The author wishes to thank the Donors of the Petroleum Research Fund and the University of New Orleans Research Council for the support of this work.

References

1 J. Kwiatek, J. Catal., 1 (1967) 37; J. Kwiatek and J.K. Sayler, Adv. Chem. Ser., 70 (1968) 207; J. Halpern and L.Y. Wong, J. Amer. Chem. Soc., 90 (1968) 6665.
2 R.L. Sweany and J. Halpern, J. Amer. Chem. Soc., 99 (1977) 8335.
3 J.A. Roth and M. Orchin, J. Organometal. Chem., 182 (1979) 299 and a related study: T.E. Nalesnik and M. Orchin, J. Organometal. Chem., 199 (1980) 265.
4 R.L. Sweany, S.C. Butler and J. Halpern, J. Organometal. Chem., 213 (1981) 487.
5 H.M. Feder and J. Halpern, J. Amer. Chem. Soc., 97 (1975) 7186.
6 P.D. Taylor and M. Orchin, J. Org. Chem., 37 (1972) 3913.
7 A. Mikaya and H. Kondo, Angew. Chem., Int. Ed., 7 (1968) 880.
8 E.O. Fischer, in J. Kleinberg (Ed.), Inorganic Synthesis, Vol. 7, McGraw-Hill, New York, 1963, pp. 136—139.
9 M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 4246; J.L. Hughey IV, C.P. Anderson and T.J. Meyer, J. Organometal. Chem., 125 (1977) C49.
10 A.R. Lepley and G.L. Closs, Chemically Induced Magnetic Polarization, Wiley, New York, 1973.
11 J. Bigeleisen, Pure Appl. Chem., 8 (1964) 217.
12 H.S. Johnston, Gas Phase Reaction Rate Theory, Ronald Press, New York, 1966.
13 D.R. Stull, E.F. Westrum, G.C. Sinka, The Chemical Thermodynamics of Organic Compounds, Wiley, New York, 1969.
14 J.C.G. Calado, A.R. Dias, J.A. Martinho Simoes and M.A.V. Ribeiro da Silva, J. Organometal. Chem., 174 (1979) 77.
15 A. Davison, J.A. McCleverty and G. Wilkinson, J. Chem. Soc., (1963) 1133.
16 R.L. Sweany, unpublished data.
17 H. Chen, W.L. Jolly, J. Kopf and T.H. Lee, J. Amer. Chem. Soc., 101 (1979) 2607.
18 A. Nakamura and S. Otsuka, J. Amer. Chem. Soc., 95 (1973) 7262.
19 V.I. Tel'noi, I.B. Rabinovich, K.V. Kir'yanov, A.S. Smirnov, cited by ref. 14.
20 J.W. Rathke and H.M. Feder, J. Amer. Chem. Soc., 100 (1978) 3623.