Journal of Organometallic Chemistry, 213 (1981) 487—492
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE HYDROGENATION OF 9,10-DIMETHYLANTHRACENE BY HYDRIDOPENTACARBONYLMANGANESE(I). EVIDENCE FOR A FREE-RADICAL MECHANISM

RAY SWEANY *, STEVEN C. BUTLER and JACK HALPERN

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637 (U.S.A.)

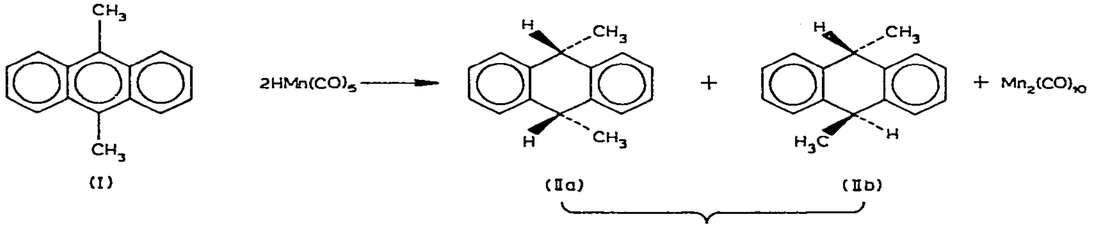
(Received October 27th, 1980)

Summary

The reaction of 9,10-dimethylanthracene with $HMn(CO)_5$ yields a nearly equimolar mixture of *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracene. The results of kinetic and isotopic tracer studies provide support for a free-radical mechanism in which the rate-determining step is the transfer of a hydrogen atom from $HMn(CO)_5$ to 9,10-dimethylanthracene.

Introduction

$HMn(CO)_5$ was found to react with 9,10-dimethylanthracene (DMA, I) to yield a nearly equimolar mixture of *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracene (IIa and IIb, respectively) according to eq. 1.



(1)

This paper reports the results of kinetic and isotopic tracer studies that bear on the mechanism of this reaction. These studies constitute an extension of an earlier investigation of the related reaction of $HMn(CO)_5$ with α-methylstyrene (eq. 2) [1]. They also are pertinent to the understanding of the mechanism of

---

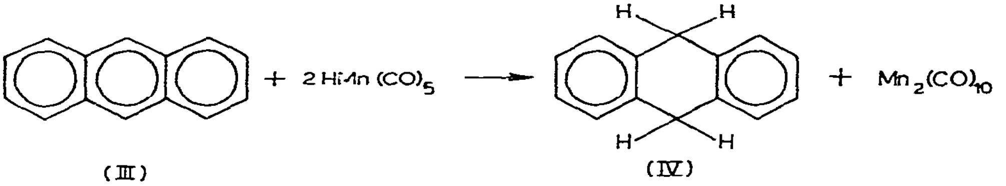
* Present address: Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70122.

the $HCo(CO)_4$-catalyzed hydrogenation of anthracene [2] and 9,10-dimethylanthracene (eq. 3) and the stoichiometric hydrogenation of the latter by $HCo(CO)_4$ for which alternative proposals have previously been advanced [3,4].

$$C_6H_5C(CH_3)=CH_2 + 2\ HMn(CO)_5 \rightarrow C_6H_5CH(CH_3)_2 + Mn_2(CO)_{10} \qquad (2)$$

$$I + H_2 \xrightarrow{HCo(CO)_4} IIa + IIb \qquad (3)$$

A few measurements also are reported on the related reaction of anthracene (III) with $HMn(CO)_5$ (eq. 4)



(4)

Experimental

$HMn(CO)_5$ and $DMn(CO)_5$ (87% isotopic purity) were prepared from $Mn_2(CO)_{10}$ (Pressure Chemical Co.) by the procedure of King and Stone [5]. Diethyl ether was used instead of tetrahydrofuran and was removed from the product (with some volatilization of the latter) by pumping under vacuum at 0° C. No ether was detectable by NMR in the final product used in these studies.

The kinetics of the reaction in deuterobenzene solution were followed by ^1H NMR using a Varian A60 or Brucker F-270 spectrometer. A weighed amount of DMA (or anthracene) together with the deuterobenzene solvent were placed in a NMR tube, fitted with a stopcock, and the resulting solution degassed by three freeze-thaw cycles. $HMn(CO)_5$ (or $DMn(CO)_5$) was then distilled into the tube, the amount transferred being determined (to a precision of ca. 2%) by weighing and confirmed by the intensity of the resulting ^1H NMR signals. The tube was sealed under vacuum and placed in a constant temperature bath thermostatted by a refluxing solvent. The tube was removed at periodic intervals, the reaction quenched by cooling, and the NMR spectrum determined. Quenching and reheating of the tubes were sufficiently rapid, relative to the rate of reaction, so that the uncertainty in the reaction time introduced by this procedure was negligible. Integrated peak intensities were measured for the metal hydride signal, for all the methyl signals, and for the 9,10-proton signals. To eliminate errors due to variations in spectrometer tuning (and hence absolute intensities) from sample to sample, the measurements were scaled by assuming the sum of the intensities of all the methyl proton signals during the course of the DMA reaction (eq. 1) to remain constant during a given experiment. Similarly, in the case of the hydrogenation of anthracene (eq. 4) the sum of the intensity of the 9,10-protons of III and one-half the intensity of the 9,10-protons of IV was assumed to be constant during a given experiment. No other products could be detected by NMR or by gas chromatography.

Rate-constants (k) were deduced for the reactions by treating the intensity data according to the second-order rate law given by eq. 5. The standard deviation in the value of the rate-constant deduced from an individual experiment was approximately 2—3% over two half-lives. Variation among rate constants for different experiments was somewhat greater, principally because of uncertainties in the initial reactant concentrations.

Gas chromatographic analyses were performed using the procedures of Taylor and Orchin [3]. Infrared spectra were determined with a Perkin-Elmer 283 spectrophotometer.

$$-d[\mathrm{DMA}]/dt = k[\mathrm{DMA}][\mathrm{HMn(CO)_5}] \quad (5)$$

Results

Reaction 1 was found to proceed in C_6D_6 solution at conveniently measurable rates at temperatures of the order of 100°C. Following the reaction by ^{1}H NMR, it was found that the intensity of the resonance at δ —7.8 ppm due to $HMn(CO)_4$ decreased at a rate approximately one-third of that of the signal at δ 2.5 ppm due to the methyl protons of DMA, in accord with the stoichiometry of eq. 1. $Mn_2(CO)_{10}$ was identified spectrophotometrically. 9,10-dihydro-9,10-dimethylanthracene ($DMAH_2$) was analyzed by GLC and found to be a nearly equimolar mixture (52 : 48) of the *cis* and *trans* isomers.

The kinetics of the reaction were found to conform to the rate-law of eq. 5. Second order kinetic plots were consistently linear for at least two half-lives. Values of the second order rate constant, k, are listed in Table 1. Kinetic measurements over the temperature range 82.3 to 110.6°C yielded the activation parameters, $\Delta H^{\ddagger} = 21.7 \pm 1.3$ kcal/mol, $\Delta S^{\ddagger} = -18.9$ cal/mol deg.

$DMn(CO)_5$ was found to react more rapidly with DMA than $HMn(CO)_5$, corresponding to an inverse isotope effect, $k(HMn(CO)_5)/k(DMn(CO)_5) = 0.41$ (see Table 1). No isotopic exchange between $DMn(CO)_5$ and the methyl protons of DMA could be detected during the reaction, based on (a) the absence of formation of $HMn(CO)_5$, and (b) the constancy (to within ±4%) of the sum of the unscaled intensities of the methyl proton signals of the unreacted DMA and the product $DMAH_2$ during the course of a given reaction.

The presence of an atmosphere of CO (instead of a vacuum) above the reaction solution resulted in only a slight (ca. 15—20%) apparent increase in the reaction rate. This may be due to a reduction in the volatilization of $HMn(CO)_5$, resulting in a slightly higher effective concentration of the latter in solution.

$HMn(CO)_5$ also was found to react in an analogous manner with anthracene, to form 9,10-dihydroanthracene, in accord with eq. 4. The rate-constant for this reaction ($k = 4.4 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$ at 100°C) was determined to be about one-half the corresponding rate-constant for reaction with DMA ($9.2 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$ at 100°C; see Table 1). The reaction of $DMn(CO)_5$ with anthracene also exhibited an inverse kinetic isotope effect ($k(HMn(CO)_5)/k(DMn(CO)_5) = 0.49$). No isotopic exchange (i.e., formation of $HMn(CO)_5$ or deuterated anthracene) could be detected during the reaction of $DMn(CO)_5$ with anthracene.

No CIDNP effects, analogous to those reported earlier for the corresponding reaction of $HMn(CO)_5$ with α-methylstyrene [1] could be detected during the reactions of $HMn(CO)_5$ with either DMA or anthracene.

TABLE 1

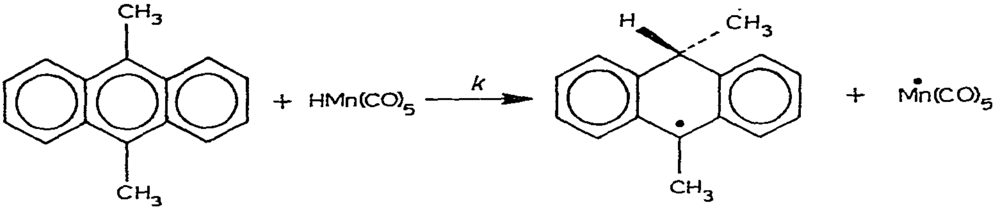
SUMMARY OF KINETIC DATA

Temp. (°C)	Initial reactant concentrations (M)				$10^4\ k$ (M^{-1} sec^{-1})
82.3	3.06	$HMn(CO)_5$	0.099	DMA	0.19
82.3	2.23	$HMn(CO)_5$	0.088	DMA	0.20
82.3	1.96	$HMn(CO)_5$	0.129	DMA	0.18
82.3	1.24	$HMn(CO)_5$	0.108	DMA	0.22
82.3	1.03	$HMn(CO)_5$	0.062	DMA	0.18
					$10^4\ k_{av} = 0.19 \pm 0.02$
88.2	1.94	$HMn(CO)_5$	0.086	DMA	0.42
88.2	1.71	$HMn(CO)_5$	0.062	DMA	0.42
88.2	1.56	$HMn(CO)_5$	0.117	DMA	0.38
88.2	1.20	$HMn(CO)_5$	0.074	DMA	0.38
88.2	1.01	$HMn(CO)_5$	0.074	DMA	0.44
					$10^4\ k_{av} = 0.41 \pm 0.03$
100.0	2.20	$HMn(CO)_5$	0.104	DMA	0.91
100.0	1.74	$HMn(CO)_5$	0.103	DMA	0.89
100.0	1.65	$HMn(CO)_5$	0.134	DMA	0.86
100.0	1.61	$HMn(CO)_5$	0.146	DMA	0.87
100.0	1.50	$HMn(CO)_5$	0.130	DMA	0.89
100.0	1.13	$HMn(CO)_5$	0.125	DMA	0.94
100.0	0.97	$HMn(CO)_5$	0.087	DMA	0.98
100.0	0.68	$HMn(CO)_5$	0.081	DMA	1.00
					$10^4\ k_{av} = 0.92 \pm 0.05$
110.6	2.70	$HMn(CO)_5$	0.136	DMA	2.08
110.6	2.34	$HMn(CO)_5$	0.064	DMA	2.07
110.6	1.66	$HMn(CO)_5$	0.084	DMA	2.25
110.6	0.99	$HMn(CO)_5$	0.117	DMA	2.30
					$10^4\ k_{av} = 2.18 \pm 0.12$
100.0	2.20	$HMn(CO)_5$	0.134	DMA	1.13 [a]
100.0	1.84	$HMn(CO)_5$	0.136	DMA	0.97 [a]
100.0	1.75	$HMn(CO)_5$	0.111	DMA	1.17 [a]
					$10^4\ k_{av} = 1.09 \pm 0.08$
100.0	1.13	$DMn(CO)_5$	0.153	DMA	2.30
100.0	0.92	$DMn(CO)_5$	0.129	DMA	2.15
					$10^4\ k_{av} = 2.23 \pm 0.08$
100.0	1.44	$HMn(CO)_5$	0.095	Anthracene	0.46
100.0	1.36	$HMn(CO)_5$	0.089	Anthracene	0.45
100.0	1.36	$HMn(CO)_5$	0.089	Anthracene	0.46
100.0	1.17	$HMn(CO)_5$	0.107	Anthracene	0.43
100.0	1.11	$HMn(CO)_5$	0.092	Anthracene	0.44
100.0	1.05	$HMn(CO)_5$	0.088	Anthracene	0.38
					$10^4\ k_{av} = 0.44 \pm 0.02$
100.0	1.47	$DMn(CO)_5$	0.111	Anthracene	0.84
100.0	1.16	$DMn(CO)_5$	0.102	Anthracene	1.04
100.0	1.09	$DMn(CO)_5$	0.089	Anthracene	0.84
					$10^4\ k_{av} = 0.90 \pm 0.10$

[a] Reaction solution under 1 atm CO instead of under vacuum.

Discussion

The results of this study are most readily accommodated by the free-radical mechanism, depicted by eq. 6—8, analogous to that previously deduced for the hydrogenation of α-methylstyrene by $HMn(CO)_5$ [1]. An analogous mechanism presumably accommodates the hydrogenation of anthracene.



(V)

(6)

$$(V) + HMn(CO)_5 \xrightarrow{fast} \underbrace{IIa + IIb} + \dot{M}n(CO)_5 \qquad (7)$$

$$2\ \dot{M}n(CO)_5 \xrightarrow{fast} Mn_2(CO)_{10} \qquad (8)$$

The following observations are consistent with and explained by this mechanism.

1. The formation of an approximately equimolar mixture of IIa and IIb. This is expected in view of the essential loss of stereochemistry at the stage of the intermediate radical, V.

2. The inverse kinetic isotope effect reflected in the higher reactivity of $DMn(CO)_5$, compared with $HMn(CO)_5$. Similar inverse kinetic isotope effects have been reported for the reactions of $DMn(CO)_5$ with α-methylstyrene [1] and of $DCo(CO)_4$ with 1,1-diphenylethylene [6], and have been interpreted in terms of similar mechanisms.

3. The higher reactivity of DMA compared with that of anthracene. This may be attributed to the enhanced stability of the methyl-substituted radical V, formed in the rate-determining step (eq. 6), compared with the unsubstituted 9-hydroanthracyl radical formed in the corresponding reaction of anthracene.

The only feature of the results which needs to be reconciled with the proposed mechanism is the absence of CIDNP effects analogous to those observed in the corresponding reaction of $HMn(CO)_5$ with α-methylstyrene [1] (but not in the related reaction of $HCo(CO)_4$ with 1,1-diphenylethylene [6]). While various other factors (e.g., excessive differences in the *g* values of the geminate radical pairs, inefficient singlet-triplet mixing due to small hyperfine coupling, etc.) may contribute to diminution of the CIDNP effects expected for a mechanism such as that depicted by eq. 6—8 [7], we consider the most likely cause to be failure of the back-reaction of the intermediate geminate radical pair in reaction 6 (eq. 9a) to compete with radical separation (eq. 9b). Support for this is provided by the absence of isotopic exchange (analogous to that observed in the corresponding reaction of α-methylstyrene which does exhibit CIDNP effects [1]) in the reaction of anthracene with $DMn(CO)_5$.

$$\overline{V, \dot{M}n(CO)_5} \begin{cases} \rightarrow HMn(CO)_5 + DMA & (9a) \\ \rightarrow V + \dot{M}n(CO)_5 & (9b) \end{cases}$$

The conclusions of the present study also lend support to an earlier proposal [4] that the $HCo(CO)_4$-catalyzed hydrogenation of DMA (and other arenes) which exhibits many similarities to the corresponding stoichiometric reaction of $HMn(CO)_5$ (similar kinetics, product distribution and deuterium kinetic isotope effects) proceeds through the related mechanism depicted by eq. 10—13.

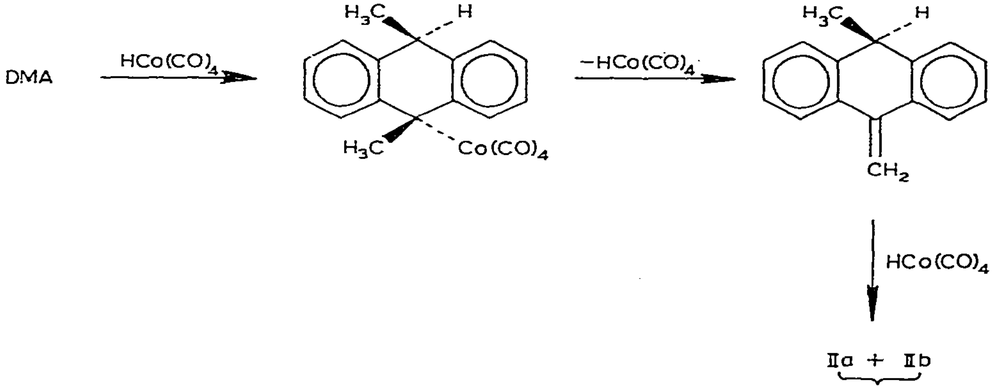
$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\ HCo(CO)_4 \tag{10}$$

$$HCo(CO)_4 + DMA \rightarrow V + \dot{C}o(CO)_4 \quad \text{(Rate-determining)} \tag{11}$$

$$V + HCo(CO)_4 \xrightarrow{\text{fast}} \underbrace{IIa + IIb}_{} + \dot{C}o(CO)_4 \tag{12}$$

$$2\ \dot{C}o(CO)_4 \xrightarrow{\text{fast}} Co_2(CO)_8 \tag{13}$$

In the light of these results and conclusions, an alternative mechanistic proposal for the hydrogenation of DMA by $HCo(CO)_4$, depicted by eq. 14 [3], is considered unlikely. This mechanism involves several features which are not readily accommodated by our observations on the corresponding stoichiometric hydrogenation of DMA by $HMn(CO)_5$, notably (a) the absence of isotopic exchange between $DMn(CO)_5$ and the methyl protons of DMA, and (b) the higher reactivity of DMA compared with that of anthracene, a result contrary to that expected for the mechanism depicted by eq. 14 on the basis of steric effects.



(14)

Acknowledgments

We thank Dr. Alexander Belyi for his contributions to some preliminary experiments related to this work. Support of this research through a grant from the National Science Foundation is gratefully acknowledged. The NMR facilities used in this research were supported in part through The University of Chicago Cancer Center Grant No. NIH-CA-14599.

References

1 R.L. Sweany and J. Halpern, J. Amer. Chem. Soc., 99 (1977) 8335.
2 S. Friedman, S. Metlin, A. Svedi and I. Wender, J. Org. Chem., 24 (1959) 1287.
3 P.D. Taylor and M. Orchin, J. Org. Chem., 37 (1972) 3913.
4 H.M. Feder and J. Halpern, J. Amer. Chem. Soc., 97 (1975) 7186.
5 R.B. King and F.G.A. Stone, Inorg. Synth., 7 (1963) 196.
6 J.A. Roth and M. Orchin, J. Organometal. Chem., 182 (1979) 299.
7 A.R. Lepley and G.L. Closs, Chemically Induced Dynamic Nuclear Polarization, Wiley, New York, 1973.