Journal of Organometallic Chemistry, 54 (1973) 247–253

ISOMERIZATION OF 1,3,5-CYCLOOCTATRIENEIRON TRICARBONYL TO BICYCLO[4.2.0]OCTA-2,4-DIENEIRON TRICARBONYL*

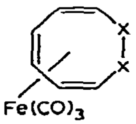
MAURICE BROOKHART**, NORMAN M. LIPPMAN, and EDWARD J. REARDON, JR.
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514 (U.S.A.)
(Received September 14th, 1972)

SUMMARY

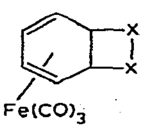
1,3,5-Cyclooctatrieneiron tricarbonyl, (VI), has been shown to undergo electrocyclic ring closure to bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl, (VII), at 102°. The first-order rate constant for this process at 102° was determined to be 7×10^{-5} sec^{-1} corresponding to $\Delta F^{\neq} = 29.3$ kcal/mol. Less than 1% of (VI) remains at equilibrium, thus K_{eq} must be greater than 100 for (VI)$\rightleftharpoons$(VII) and ΔF must be less than -3.4 kcal/mol. The iron complexed system is compared to the previously studied free ligand system where 1,3,5-cyclooctatriene, (VIII), is favored over the bicyclo[4.2.0]octa-2,4-diene, (IX), with $K_{eq} = 0.18$ for (VII)$\rightleftharpoons$(IX) and $\Delta F = +1.1$ kcal/mol. The large shift in the equilibrium in favor of (VII) is explained by considering the relative distortions and consequent ring strain introduced into the ligands (VIII) and (IX) upon bonding to the iron tricarbonyl moiety.

INTRODUCTION

The thermal reactions of cyclic trienes with iron carbonyls can lead to formation of either monocyclic trieneiron tricarbonyls of general structure (I), bicyclic dieneiron tricarbonyls of general structure (II), or mixtures of both (I) and (II). For example, bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl [(II), $X = CH_2$] is obtained from reaction of $Fe(CO)_5$ with 1,3,5-cyclooctatriene at temperatures of 140° [1], while mixtures of (I) and (II) ($X = CH_2$) are obtained when 1,3,5-cyclooctatriene is treated with $Fe_3(CO)_{12}$ at 80–100° in hydrocarbon solvents[2]. Reaction of $Fe(CO)_5$ with cyclooctatetraene yields only the monocyclic cyclooctatetraeneiron tricarbonyl



(I)



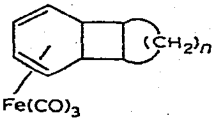
(II)

---

* Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972.

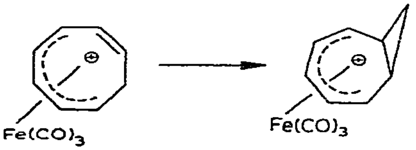
** To whom correspondence should be addressed.

[(I), X–X = –CH=CH–) while with 1,3,5,7-tetramethylcyclooctatetraene the only reported mononuclear product is the bicyclic complex[3]. Most recently, Cotton[4] has reported the isolation of tricyclic diene complexes (III) ($n = 2,3,4$) via reaction of the olefinic ligands with $Fe_2(CO)_9$.



(III)

Although there are extensive studies and detailed quantitative data concerning the equilibrium between uncomplexed cyclic trienes and bicyclic dienes[4,5] none of the presently available data indicates whether such a dynamic equilibrium exists for the iron complexed species. Neither is it clear whether the bicyclic dieneiron complexes, (II), must form entirely from selective reaction of the iron carbonyls with the bicyclic tautomers, or whether they are formed in part from electrocyclic ring closure of the monocyclic trieneiron complexes, (I). In view of these facts, we felt it would be of considerable interest to attempt to observe the isomerization via electrocyclic ring closure of a cyclic trieneiron tricarbonyl complex to a bicyclic dieneiron tricarbonyl complex. This appeared especially feasible since we have recently observed the cationic analog of such a process, the ring closure of the cyclooctatrienyliron tricarbonyl cation (IV) to the bicyclo[5.1.0]octadienyliron tricarbonyl cation (V)[6].



(IV) (V)

In this paper we wish to report a study of the isomerization of 1,3,5-cyclooctatrieneiron tricarbonyl, (VI), to bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl, (VII), and, in addition, quantitative rate and equilibrium data which yield considerable insight into the effect of the bound iron tricarbonyl moiety on the cyclic triene–bicyclic diene rates of interconversion and position of equilibrium.

RESULTS AND DISCUSSION

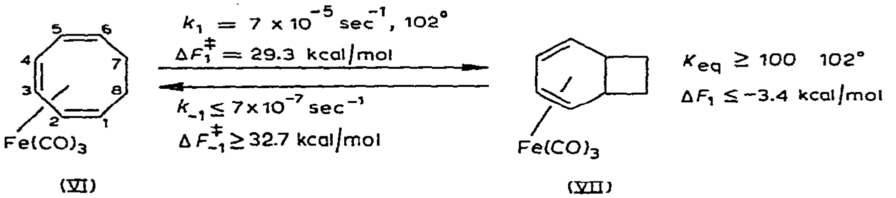
Pure samples of cyclooctatrieneiron tricarbonyl, (VI), were prepared by photolysis through Pyrex of equimolar mixtures of iron pentacarbonyl and cyclooctatriene in benzene followed by chromatography on alumina. Initial studies indicated that when (VI) was heated for 20 h in degassed heptane at 99° complete conversion to (VII) was obtained.

The rate of thermal isomerization of (VI) to (VII) could be measured in several ways; however, the most accurate and convenient technique for monitoring the isomerization proved to be direct gas chromatographic analysis of complexes (VI) and (VII). A kinetic run consisted of heating a degassed octane solution of (VI) at

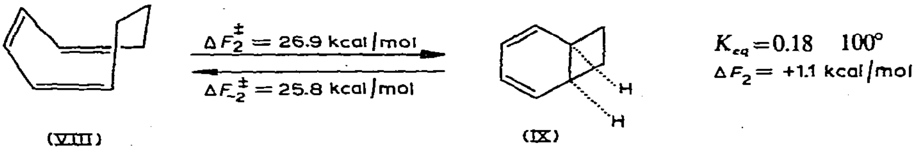
102°, taking aliquots at twenty minute intervals and analyzing each for the ratio of (VI)/(VII) by gas chromatography*. Standard treatment of the data yielded a first-order rate constant for the conversion of (VI) to (VII) at 102° of $7 \pm 1 \times 10^{-5}$ sec^{-1} ($t_{1/2} = 2.7$ h) which corresponds to a free energy of activation, $\Delta F^{\ddagger} = 29.3 \pm 0.1$ kcal/mol.

A second, less accurate method for measuring the rate of isomerization of (VI) to (VII) was also used and provided a check on the data quoted above. This method consisted of heating degassed heptane solutions of (VI) at reflux (99°) for various time periods. The two complexes (VI) and (VII) generated were isolated as a mixture, high vacuum dried free of any volatile material and cleaved with ceric ammonium nitrate at 0° in acetone[7]. The resulting mixture of 1,3,5-cyclooctatriene, (VIII), and bicyclo-[4.2.0]octa-2,4-diene, (IX), were analyzed by gas chromatography. The ratio of (VIII)/(IX) was assumed to correspond to the original ratio of (VI)/(VII). Control experiments indicated that when a 1.0/1.0 molar ratio of complexes (VI) and (VII) was cleaved, a 1.0/1.0 ratio of (VIII)/(IX) was generated. The first-order rate constant obtained at 99° using this method was $8 \pm 2 \times 10^{-5}$ sec^{-1} ($\Delta F^{\ddagger} = 29.0 \pm 0.2$ kcal/mol) which is within experimental error of that expected based on the value obtained above at 102°.

By heating samples of (VI) in octane for 24 h (9 half-lives) at 102° and analyzing by GLC, an upper limit of 0.02 could be placed on the ratio of (VI)/(VII) at equilibrium. In a similar experiment using the cerium technique described above for analysis, an upper limit of 0.01 could be placed on the ratio of (VI)/(VII) at equilibrium**. The latter experiment implies that K_{eq} for (VI)$\rightleftarrows$(VII) must be greater than 100 at 102° ($\Delta F \leqslant -3.4$ kcal/mol) and that k_{-1} must be less than 7×10^{-7} sec^{-1}. This data provides an interesting comparison with the corresponding parameters for the free ligand summarized below[5].



(1)



(2)

---

* Approximately 2% isomerization of (VI) to (VII) occurs on the GLC column but this has no significant effect on the accuracy of the rate measurements. As determined by GLC, the total amount of (VI) and (VII) which remains after 80% isomerization is ≥95% of the initial amount of (VI). After 22 h at 102° the yield of (VII) is ≥95%.

** In the GLC analysis of the complexes, peaks were sufficiently broad that 2% was the limit of detection. In the GLC analysis of the free ligands, ca. 0.8% of triene (VIII) can be detected. It is not clear whether this amount of triene arose from 0.8% of (VI) present at equilibrium or from thermal isomerization of (IX) to (VIII) during the cerium cleavage reaction and subsequent work-up, or whether each possibility contributes significantly to the 0.8%.

It should be noted that in the case of the free ligands, the equilibrium at 100° favors the monocylic triene (VIII) over the bicyclic diene (IX). Clearly, for the iron complexed species the equilibrium is shifted substantially toward the diene complex with the difference in free energies for the two equilibria ($\Delta F_2 - \Delta F_1$) being greater than 4.5 kcal/mol at 100°. However, even though the equilibrium is dramatically shifted, the actual rate of electrocyclic ring closure of (VI) to (VII) is substantially less than that for (VIII) to (IX). For ring closure of (VI) to (VII) a 1,2 iron shift must occur and at least part of the increase in activation energy for closure perhaps could be attributed to the barrier for such a 1,2 shift.

Although electronic factors may be important, probably the most significant factor responsible for the shift in the equilibrium toward the complexed diene is that the iron tricarbonyl moiety distorts the cyclooctatriene ring in (VI) into an energetically unfavorable conformation. Whereas the uncomplexed triene (VIII) prefers a tub structure, bonding of (VIII) to the $Fe(CO)_3$ group forces the bound diene moiety into a nearly planar configuration thereby introducing considerable strain into the cyclooctatriene ring*. In comparing the complex (VII) with the free diene (IX), there must be considerably less distortion of the organic ligand away from the energetically preferred conformation since the four carbon diene moiety in (IX) is already planar**.

An important question which should be considered is whether the isomerization of (VI) to (VII) is truly intramolecular or whether the conversion might proceed via a mechanism involving closure of the *free* triene, (VIII). One such mechanism is the reversible dissociation of (VI) into cyclooctatriene (VIII) and $Fe(CO)_3$ followed by ring closure of (VIII) to (IX) and recombination of (IX) with $Fe(CO)_3$ to yield (VII). Kinetically these two pathways would be indistinguishable; however, the latter dissociative pathway can be ruled out by a consideration of the energetics involved. If this mechanism applied, the measured free energy of activation, $\Delta F_1^{\neq}$, (29.3 kcal/mol) would represent the sum of ΔF_3 for the dissociative equilibrium

$$\text{(VI)} \rightleftarrows \text{(VIII)} + Fe(CO)_3 \tag{3}$$

and $\Delta F_2^{\neq}$, the free energy of activation for isomerization of (VIII) to (IX). Since $\Delta F_2^{\neq}$ is known to be 26.9 kcal/mol, ΔF_3 would then have to be ca. 2.4 kcal/mol. Such a low value of ΔF for the dissociation of (VI) is clearly unreasonable. If this low value were to obtain, complex (VI) would be expected to undergo extremely rapid exchange with other dienes. It does not. Treatment of (VI) with a five fold excess of cyclooctatetraene results in no exchange (no production of cyclooctatetraeneiron tricarbonyl) after standing 24 h at 25°. In addition, the PMR spectrum of (VI) would be expected to be characteristic of a rapidly fluxional system in which there is rapid exchange between the uncomplexed 5,6 double bond and the complexed 1,2 double bond resulting in averaging of H_1 with H_6, H_2 with H_5 and H_3 with H_4. Such an averaging does not occur; all signals are sharp and distinct at 35°.

Another alternative mechanism involves the function of low concentrations of diene (IX) in a catalytic fashion to generate triene (VIII). Such a mechanism could

---

* The bound diene moiety of (VI) would be expected to assume approximately the same configuration as that for cyclooctatetraeneiron tricarbonyl, a complex whose crystal structure is known[8].

** The exact configuration of the cyclobutane ring in (IX) is not known with certainty but based on steric grounds it is almost surely *trans* to the metal.

be envisioned to proceed by essentially a ligand exchange process in which any small amounts of (IX) present react with triene complex (VI) in the rate determining step to yield the bicyclic complex (VII) and free triene (VIII). The triene (VIII) could then undergo equilibration via ring closure to yield more (IX) and the newly generated (IX) could then react with additional (VI) to generate more diene complex (VII) and triene (VIII). This mechanism is viewed as highly unlikely for the following two reasons. First, the exchange reaction of dieneiron tricarbonyl complexes with other dienes is known to be second order, first order in complex and first order in free diene[9,10]. To account for the observation of good first-order kinetics, the concentration of (IX) would obviously have to remain small relative to (VI) (pseudo first-order kinetics), but in addition this small concentration of (IX) must also remain *constant*. No (IX) is present initially in the pure complex (VI), so it would be necessary to make the highly unlikely assumption that some (IX) is produced by decomposition of (VI) in the very early stages of the isomerization and that its concentration then remains *constant* through the course of the isomerization*. Secondly, the thermal rearrangement of (VI) occurs on GLC columns at ca. 110° under conditions where the retention times of the free ligands (VIII) and (IX) are extremely short compared to the complexes. It seems unlikely that the catalytic mechanism could operate under these conditions where any free (IX) generated would be rapidly separated from (VI).

Although the present study does not answer the question as to how in general the cyclic diene complexes, (II), are formed, it does suggest that such complexes may be formed at least in part via ring closure of triene complexes, (I), under appropriate experimental conditions. From the rate of ring closure of (VI) to (VII) at 102°, it is clear why mixtures of (VI) and (VII) can be obtained from reactions carried out at 80–100°[2] but only (VII) can be isolated from reactions carried out at 140°[3].

These results as well as those recently reported by Cotton[4] suggest that the pronounced effects of transition metals upon tautomeric equilibria could be of considerable synthetic utility. Since generally mild methods are available for the cleavage of metal π-complexes, the use of such complexes may prove to be advantageous in preparing pure diene tautomers otherwise difficult to obtain.

In this regard, we are currently exploring the effects of transition metals on rates and equilibria in other cyclic triene–bicyclic diene systems, especially those in which the triene is substantially lower in energy than the bicyclic diene.

EXPERIMENTAL

General

Gas chromatography was performed on an Hewlett–Packard 5750 Research Chromatograph using a thermal conductivity detector and helium as the carrier gas. IR spectra were recorded on a Perkin–Elmer 421 spectrometer while PMR spectra were obtained using the Jeolco-C-60HL spectrometer. Nitrogen gas was purified by passing it first through concentrated sulfuric acid and then through a heated column of BASF catalyst R3-11.

---

* In addition, based on known rates of diene exchange reactions of dieneiron tricarbonyl complexes measured at 165°[10], the rate of isomerization of (VI) appears to be much too rapid to be accommodated by this exchange mechanism, although these rates were measured for acyclic diene exchanges.

1,3,5-Cyclooctatrieneiron tricarbonyl, (VI)

A photolytic procedure for the preparation of (VI) has previously been reported by Nakamura and Hagihara[11]. The procedure used in this work was as follows. Cyclooctatriene[12] (1.2 g, 0.011 moles) and iron pentacarbonyl (2.90 g, 0.015 moles) in 200 ml of degassed benzene were irradiated through Pyrex in a standard photochemical well at room temperature for 3 h using a Hanovia 450 W lamp. The orange solution was concentrated and chromatographed under nitrogen using degassed hexane as eluant on Woelm alumina (grade 3, neutral). The first orange band to elute proved to be (VI) while the second band to elute was a small amount of the binuclear complex C_8H_{10}-$Fe_2(CO)_6$. The first band was concentrated and rechromatographed. Removal of hexane at reduced pressures yielded 1.52 g (56 %) of (IV) as a viscous orange oil which was stored cold under nitrogen. The spectral data (IR, NMR) for the complex were identical to those previously reported[2b].

Bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl, (VII)

An authentic sample of this complex could be prepared as previously reported[2b] by heating at reflux a mixture of (VIII) and (IX) with triiron dodecacarbonyl in heptane. The PMR and IR spectral data were identical to those previously reported for this complex[2,13].

Rate measurements

(*a*). *From direct analysis of complexes (VI) and (VII)*. To a small Schlenk tube which had been soaked in an ammonium hydroxide solution, rinsed with distilled water and dried under high vacuum at 250° was added 0.42 g of (VI) and 1.8 ml of degassed, redistilled octane. This solution was rigorously degassed on a high vacuum line using three freeze-pump-thaw cycles. The Schlenk tube was blanketed with oxygen-free nitrogen and kept under a slight positive pressure of nitrogen. This tube was then immersed in an oil bath maintained at a constant temperature of 102 ± 1°. At 20 min intervals the tube was quenched by immersion in ice water and under a flow of nitrogen a 6.0 μl sample was withdrawn by syringe. The tube was then recapped and replaced in the oil bath. The withdrawn sample was analyzed by GLC on a 6′ × 1/4″ column packed with 3 % UC-W98 on Chromosorb W60-80 (oven 90°, injection port 110°, He flow 85 ml/min). Under these conditions the retention times of (VI) and (VII) were 11.7 and 7.8 min, respectively. Kinetics were followed over the course of 6 h (2.2 half-lives). No decomposition ($<$ 5 %) of the complexes to free ligands could be observed after 6 h.

(*b*). *From analysis of (VIII) and (IX)*. In a typical run, 0.30 g of triene complex (VII) was dissolved in 50 ml of degassed spectral grade heptane contained in a three-necked flask. This solution was then degassed on a high vacuum line using the freeze-pump-thaw method. After blanketing with oxygen-free nitrogen, the solution was heated to reflux (99°) for the desired period of time. The solution was then passed through a short alumina column and the collected mixture of complexes pumped free of any volatile material on a high vacuum line. The complexes were then cleaved with ceric ammonium nitrate using a method similar to that described by Paquette[7]. Ceric ammonium nitrate was slowly added to a solution of 200–300 mg of the mixture of complexes in 50 ml of acetone at 0° until gas evolution ceased. The reaction mixture was poured into hexane and extracted twice with a saturated salt solution. The hexane layer was then dried over anhydrous potassium carbonate and concentrated at reduced pressure. These room temperature operations were done quickly so as to avoid any thermal equilibration of the diene and triene. The hexane solution of (VIII) and (IX) was analyzed by GLC using a 6′ × 1/8″ column packed with 3% Carbowax 20 M on 80–100 Chromosorb W (column oven 50°, injection port 55°, He flow 50 ml/min). Under these conditions the retention times of (VIII) and (IX) were 4.3 and 3.8 min, respectively. Rate constants were determined for reaction times of 1,2,4 and 8 h. To check the validity of this method of analysis a mixture of 51% (VIII) and 49% (IX) was cleaved with ceric ion and worked up using the above procedure. The GLC analysis of the resulting mixture of diene and triene tautomers indicated 52% (VIII) and 48% (IX).

ACKNOWLEDGEMENTS

The authors are grateful to the National Science Foundation (Grant GP-29080) and the Materials Research Center of the University of North Carolina contract no. DAHC-15-67-C-0223 with the Advanced Research Projects Agency for support of this work.

REFERENCES

1 T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 82 (1960) 366.
2 (a) T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 82 (1960) 6241;
(b) W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1963) 2162;
(c) E. O. Fischer and H. Werner, *Metal π-Complexes*, Vol. 1, Elsevier, New York, 1966, p. 136–143.
3 F. A. Cotton and A. Musco, *J. Amer. Chem. Soc.*, 90 (1968) 1444.
4 (a) F. A. Cotton and G. Deganello, *J. Amer. Chem. Soc.*, 94 (1972) 2142;
(b) F. A. Cotton and G. Deganello, *J. Organometal. Chem.*, 38 (1972) 147.
5 (a) A. C. Cope and F. A. Hochstein, *J. Amer. Chem. Soc.*, 72 (1950) 2515;
(b) A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumball, *J. Amer. Chem. Soc.*, 74 (1952) 4867;
(c) R. Huisgen, F. Mietzsch, G. Boche and H. Seidl, *Spec. Pub. of the Chem. Soc.* No. 19 (1965), *Organic Reaction Mechanisms* pp. 3–20;
(d) R. Huisgen, G. Boche, A. Dahmen and W. Hechtl, *Tetrahedron Lett.*, (1968) 5215;
(e) D. S. Glass, J. W. H. Watthey and S. Winstein, *Tetrahedron Lett.*, (1965) 377;
(f) D. S. Glass, J. Zirner and S. Winstein, *Proc. Chem. Soc.*, (1963) 276.
6 (a) M. Brookhart and E. R. Davis, *J. Amer. Chem. Soc.*, 92 (1970) 7622;
(b) M. Brookhart, E. R. Davis and D. L. Harris, *J. Amer. Chem. Soc.*, 94 (1972) 7853.
7 L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, 89 (1967) 6659.
8 B. Dickens and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 83 (1961) 4862.
9 H. W. Whitlock, Jr. and R. L. Markezich, *J. Amer. Chem. Soc.*, 93 (1971) 5290.
10 M. Cais and N. Maoz, *J. Chem. Soc. A*, (1971) 1811.
11 A. Nakamura and N. Hagihara, *J. Chem. Soc. Jap., Pure Chem. Sect.*, 82 (1961) 1389.
12 W. O. Jones, *J. Chem. Soc.*, (1954) 1808.
13 R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, (1951) 594.