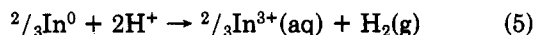
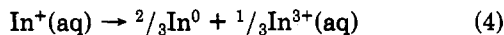
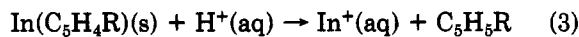
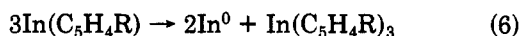


then the indium metal is oxidized. Since only 1 mol of H_2 is formed per mol of indium(I), only two-thirds of the initial indium(I) can be converted to indium metal. One possible reaction sequence (eq 3-5) that would be con-



sistent with all observations involves the initial hydrolytic cleavage of $\text{In}(\text{C}_5\text{H}_4\text{R})$ with the subsequent rapid disproportionation of the resulting indium(I) species to form indium metal and indium(III). The disproportionation reaction provides $\frac{2}{3}$ mol of indium metal/mol of indium(I) as required by the H_2 evolution measurements. An alternative sequence of reactions begins with the disproportionation of $\text{In}(\text{C}_5\text{H}_4\text{R})$ (eq 6). Then, $\text{In}(\text{C}_5\text{H}_4\text{R})_3$ would



hydrolyze, and indium metal would be oxidized by H^+ to form the observed products. Our limited data do not permit us to distinguish between the two hypotheses. However, the persistence of the indium(I) derivative in aqueous HCl for sufficient time to form $\text{In}(\text{C}_5\text{H}_4\text{R})_3$ would seem unlikely.

The physical properties of $\text{In}(\text{C}_5\text{H}_5)$ and $\text{In}(\text{C}_5\text{H}_4\text{Me})$ are surprisingly different. The parent compound $\text{In}(\text{C}_5\text{H}_5)$ is a pale yellow solid with the surprisingly high melting point of 169.3-171.0 °C. In contrast, $\text{In}(\text{C}_5\text{H}_4\text{Me})$ is a colorless solid with the relatively low melting point of 48.5-51.0 °C. It is also noteworthy that $\text{In}(\text{C}_5\text{H}_4\text{Me})$ is more volatile than

$\text{In}(\text{C}_5\text{H}_5)$. These observations of volatility at room temperature suggest that the bonding between $\text{In}(\text{C}_5\text{H}_4\text{R})$ units in the solid state is relatively weak. However, the interactions between $\text{In}(\text{C}_5\text{H}_5)$ are strong enough to substantially reduce the solubility of the compound in the non-polar solvent cyclohexane. The compound $\text{In}(\text{C}_5\text{H}_4\text{Me})$ is soluble in cyclohexane. The properties of solid $\text{In}(\text{C}_5\text{H}_5)$ and its long indium-cyclopentadienyl distances would be consistent with the earlier conclusion of significant ionic character to the bonds. The addition of a methyl group would appear to increase the covalent bonding contribution to the bonds between indium and the ring, decrease the metal-ring distance, and change the properties. In an upcoming paper additional comparisons between the significant features of $\text{In}(\text{C}_5\text{H}_5)$, $\text{In}(\text{C}_5\text{H}_4\text{Me})$, and $\text{In}(\text{C}_5\text{Me}_5)$ will be fully discussed.

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Registry No. InCl , 13465-10-6; $\text{In}(\text{C}_5\text{H}_5)$, 34822-89-4; $\text{In}(\text{C}_5\text{H}_4\text{Me})$, 38181-22-5; $\text{Li}(\text{C}_5\text{H}_5)$, 16733-97-4; $\text{Li}(\text{C}_5\text{H}_4\text{Me})$, 54061-45-9; cyclopentadiene, 542-92-7; methylcyclopentadiene, 26519-91-5.

Supplementary Material Available: Tables of anisotropic thermal parameters (2 pages); listings of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Kinetic Study of the Formation of Dihydrogen from the Reaction of [1.1]Ferrocenophanes with Strong Acids. 2.¹ Tensiometry, Spectrometry, and Deuterium Exchange Studies

Sherie Michalle and Manny Hillman*

Chemical Sciences Division, Department of Applied Science, Brookhaven National Laboratory,
Upton, New York 11973

John J. Eisch

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

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The kinetics of the reactions [1.1]ferrocenophane (I), 3,3'-trimethylene[1.1]ferrocenophane (II), and 2,2'-trimethylene[1.1]ferrocenophane (III) were studied by using tensiometric and spectrometric techniques at acid strengths that were lower than those used in the electrochemical investigation.¹ The results of these measurements are consistent with the three-step mechanism proposed for the formation of dihydrogen: a very fast initial protonation, a slower second protonation, and the elimination of dihydrogen as the rate-determining step. However, at the lower acid strengths, competing reactions occur. One of these very likely involves the comproportionation of the ferrocenophane and the dication followed by the decomposition of the resulting monocation. The nature of other competing reactions remains as an open question. Kinetic studies using deuteriated acids established a primary kinetic isotope effect, k_H/k_D , between 3 and 5, for compound I. The ring protons of the ferrocenophane undergo complete exchange in these media at a rate much faster than the rate for dihydrogen formation. No exchange of the methylene protons was observed.

Introduction

Bitterwolf and Ling reported that compound I (see Figure 1 for the structures) reacts quantitatively with a

strong acid, e.g. $\text{BF}_3 \cdot \text{H}_2\text{O}$, to yield the ferrocenophane dication and dihydrogen.² Since ferrocene derivatives are known to be protonated on the iron atom under these conditions,^{2,3} it was assumed² that the mechanism involves

(1) Hillman, M.; Michalle, S.; Feldberg, S. W.; Eisch, J. J. *Organometallics* 1985, 4, 1258-1263.

(2) Bitterwolf, T. E.; Ling, A. C. J. *Organomet. Chem.* 1973, 57, C17-C18.

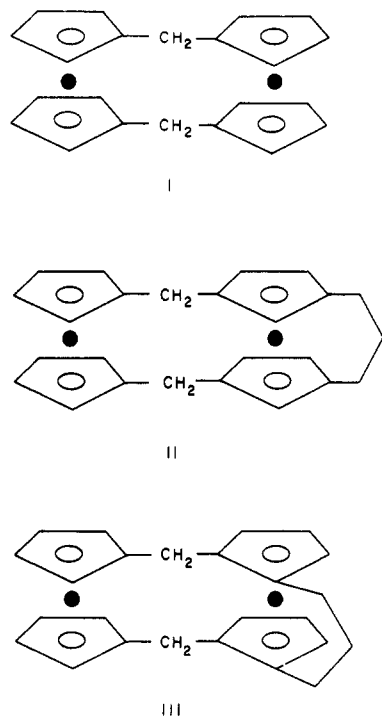
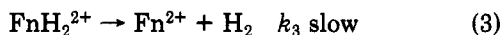
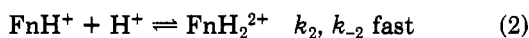
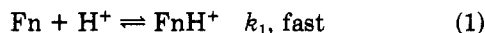


Figure 1. Structural representations of the compound used in this study.

stepwise protonation of the two iron atoms, followed by elimination of dihydrogen with concurrent formation of the ferrocenophane dication (eq 1–3), where Fn is the ferrocenophane.



A kinetic study¹ using electrochemical methods (especially chronoamperometry) at very high acid strengths ($H_0 = -7$ to -9) gave results consistent with the proposed mechanism. The equilibrium constants of the first two steps and the rate constants for the third were determined. Furthermore, since the relative rates for formation of dihydrogen ($\text{II} > \text{I} > \text{III}$) was correlated with the expected orientation of the protons on the iron atoms, the suggestion that the dihydrogen arises from a coupling of those hydrogen atoms was corroborated. Indications were noted, however, that at lower acid strengths, where an unsuccessful attempt was made to measure the rates of the protonation reactions, the reaction mechanism might be complicated by competing reactions.

The electrochemical method cannot be used to study the kinetics of the reaction of III nor of any of the compounds at acid strengths lower than $H_0 = -7$ because of the slowness of the reactions. On the other hand, tensiometry measurements are virtually impossible at the high acid strengths because the acid itself has a significantly high vapor pressure, and the relative increases in pressure due to dihydrogen evolution are very small. Spectrometry at high acidities, attempted by placing the solid ferrocenophane into the neat acid, is also impractical because the rate of dissolution of the ferrocenophane in the acid is slower than or equal to the rate of the reaction. Even resorting to a mutual solvent is difficult at high acid strengths, because the acids and the best solvents found,

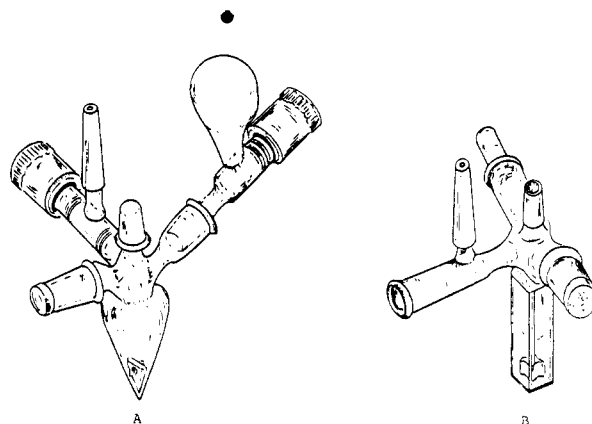


Figure 2. Reaction vessels used for the tensiometry and optical absorption experiments. The tensiometry reaction vessel is A, the optical-absorption reaction vessel is B, and the arrow points to the acid-storage bulb in the delivery position.

2,4-dimethylsulfolane and 3-methylsulfolane, are quite viscous and a significant time is required in mixing the components. Both tensiometry and spectrometry, however, are very useful techniques at much lower acid strengths. This paper discusses the results obtained by using tensiometry and spectroscopy at the lower acid strengths ($H_0 = -5$ to -7).

Experimental Section

Compounds I, II, and III were prepared in our laboratory.⁴ Samples of compound I were also donated by Dr. U. T. Mueller-Westerhoff, whose procedures were the models used in synthesizing the compounds.⁵ The PF_6^- salts of compounds I and II and the I_3^- salt of compound I were prepared in our laboratory by adaptations of literature procedures.⁶ All compounds were purified by column chromatography and/or by recrystallization.

The four Hammett indicators used 2,4,6-trinitroaniline, 2-bromo-4,6-dinitroaniline, anthraquinone, and 2,4-dinitroaniline were purchased from the Aldrich Chemical Co. Since the observed melting points were in agreement with their literature values, the indicators were used without further purification. The acidities were determined by using the Hammett acidity-function technique previously described.¹ The reproducibility of the H_0 measurements was $\pm 0.04 H_0$ units. To define the D_0 acidity scale in the deuteriated acids, it was assumed that the $\text{p}K_a$ of 2-bromo-4,6-dinitroaniline is 0.2 $\text{p}K_a$ unit larger in the deuteriated acids, as was found in the sulfuric acids.⁷

The solvents 2,4-dimethylsulfolane and 3-methylsulfolane (hereafter referred to as DMS and 3MS), assayed at 98% and 99% purity, were purchased from the Aldrich Chemical Co. and were purified by using a modified procedure for the purification of sulfolane.⁸ First, to the solvent (100 mL) was added a small amount (2–3 mL) of concentrated sulfuric acid, and the solution was mixed for approximately 1 h. The dark red color that developed as a result of this treatment presumably arose from oxidation of impurities. The mixture was first vacuum-distilled from sodium hydroxide pellets and then from calcium hydride. The purified solvent no longer becomes discolored with concentrated sulfuric or with trifluoroboric acids, even over a period of months. The solvent was stored under nitrogen and over molecular sieves to ensure dryness. Either DMS or 3MS could be used interchangeably without affecting acidity or kinetic measurements. DMS was used for the bulk of experiments described,

(4) Singletary, N. J.; Hillman, M.; Dauplaise, H.; Kwick, A.; Kerber, R. C. *Organometallics* 1984, 3, 1427–1433.

(5) Cassens, A.; Eilbracht, P.; Nazzari, A. I.; Proessdorf, W.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* 1981, 103, 6367–6372.

(6) Morrison, W. H., Jr.; Hendrickson, D. N. *Inorg. Chem.* 1975, 14, 2331–2346.

(7) Sierra, J.; Ojeda, M.; Wyatt, P. A. H. *J. Chem. Soc.* 1970, 1570–1573.

(8) Arnett, E. M.; Douty, C. F. *J. Am. Chem. Soc.* 1964, 86, 409–412.

(3) Curphey, T. J.; Santer, J. O.; Rosenblum, M.; Richards, J. H. *J. Am. Chem. Soc.* 1960, 82, 5249–5250.

and 3MS was used in the deuterium experiments.

The trifluoroboric acids referred to in these studies are mixtures of the boron trifluoride hydrates $\text{BF}_3 \cdot \text{H}_2\text{O}$ and $\text{BF}_3 \cdot 2\text{H}_2\text{O}$. Batches of acid were prepared in the manner previously described¹ and stored under nitrogen.

Two types of reaction vessels were used in connection with a vacuum line equipped with a Toepler pump: one vessel for the tensiometric experiments and the other for the optical absorption experiments (Figure 2). The vessel for the optical absorption experiments was made entirely of quartz. The acid-storage bulb (also depicted in Figure 2) was designed to hold about 3 mL of acid.

All ultraviolet and visible absorption measurements were obtained on a Cary 219 spectrophotometer. Prerecorded base lines of blank solutions were automatically subtracted from all spectra.

The temperatures for all kinetic measurements were controlled to within ± 0.03 °C by using water-jacketed cell holders connected to a constant-temperature circulating bath. Experiments were performed at 22.00 ± 0.03 °C unless otherwise noted.

Tensiometry Measurements. A 1.5-mL sample of acid was delivered to the acid-storage bulb with a 5-mL, graduated, gas-tight (Hamilton) syringe equipped with a Kel-F hub and delivery tube. The acid was degassed on the vacuum line with freeze-pump-thaw cycles by using liquid nitrogen. The weighed ferrocenophane was placed in the reaction vessel, and a 2-mL sample of the DMS (or 3MS) was added under an atmosphere of nitrogen by a volumetric pipet. The vessel was attached to the vacuum line and the ferrocenophane solution degassed. The water-jacketed cell holder was set in position, and a minimum of 15 min was allowed for temperature equilibration while the reaction solution was stirred. The acid was then transferred to the reaction vessel and a timing clock simultaneously started. At appropriate times the reaction vessel was opened to the working manifold for approximately 5 s and then reclosed. The condensable gases were condensed into a vessel on the manifold containing activated charcoal and immersed in a liquid-nitrogen bath. A period of 3–5 min (until the pressure was steady for 0.5 min) was allowed for the condensation of gases. The hydrogen gas was then collected and measured by means of the Toepler pump. The amount of dihydrogen gas collected was corrected for the portion left in the reaction vessel.

Data were collected on the order of twice each hour over the first 8 h of the reaction and once a day afterward until no additional noncondensable gas was evolved.

Optical Absorption Measurements. The same procedure described above for the tensiometric experiments was used to set up the optical absorption experiments. However, since the quartz cell could not be cooled in liquid-nitrogen without cracking, an ice bath was used in the freeze-pump-thaw cycles. Although the cell was equipped with a stirring bar, it was found that stirring alone was insufficient for initial mixing of the viscous acid and DMS mixture. Initial mixing was accomplished by pouring the liquids back and forth between the cell and the acid-storage bulb. The solution was stirred throughout the subsequent measurements to prevent the development of density and/or temperature gradients. Absorption measurements were made continuously over the wavelength range from 850 to 350 nm. Scanning was automatically repeated, and the scan rate and paper were changed periodically to ensure distinguishability of the scans.

Experiments with Deuteriated Acids. These experiments were done in a manner similar to the tensiometric experiments. However, it was of interest to recover the ferrocenophane (I) for a mass spectroscopic (Hewlett-Packard 5980A) determination of the extent of hydrogen-deuterium exchange. The reaction was quenched by immersion of the vessel in a liquid-nitrogen bath. The volume of the dihydrogen evolved was measured, the dihydrogen collected, and the reaction vessel then removed from the vacuum manifold. The reaction solution was quickly thawed and added to an aqueous solution of stannous chloride (ca. 100 mL of 1 mM concentration) under an atmosphere of nitrogen. A saturated aqueous solution of sodium bicarbonate was slowly added until a neutral pH was established. The reduced (i.e. neutral) ferrocenophane was extracted with diethyl ether and the ether evaporated to leave the ferrocenophane. The yields of recovered ferrocenophane were on the average 84%.

Three variations of this experiment were carried out. In one, compound I in 2 mL of 3MS was allowed to react with 1.5 mL

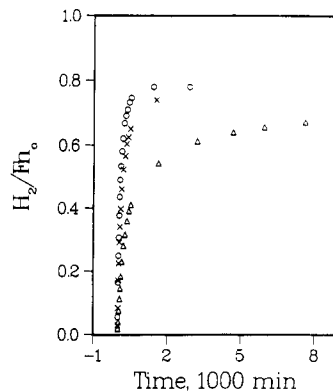


Figure 3. Tensiometry data for I: O, $H_0 = -6.19$; X, $H_0 = -5.81$; Δ, $H_0 = -5.66$.

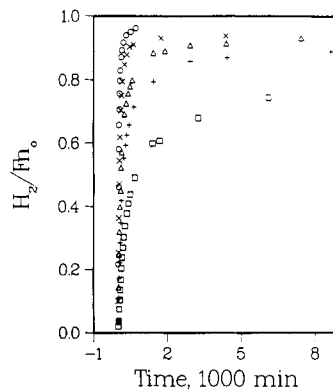


Figure 4. Tensiometry data for II: O, $H_0 = -6.13$; X, $H_0 = -5.99$; Δ, $H_0 = -5.84$; +, $H_0 = 5.70$; □, $H_0 = -5.54$.

of the deuteriated acid, and samples of dihydrogen were periodically removed. The reaction was run for various lengths of time before quenching and recovery of the ferrocenophane dication as [1.1]ferrocenophane.

In order to determine whether exchange of the ferrocenophane protons occurs during the quenching and recovery procedure, a second variation was employed. In this variation, compound I in 3MS was allowed to react with protonated acid and the quenching was carried out in D_2O media.

In a third variation, compound I reacted with a small amount (i.e. 0.1 mL) of protonated acid for 1–3 days in order to form the dication. Approximately 2 mL of deuteriated acid was added to the dication solution, and the reaction was continued for various times, e.g. 0.5–72 h, before quenching in H_2O and SnCl_2 . Whether or not the dication undergoes proton-deuteron exchange can be determined by this variation.

The variation-one experiments were carried out by using the vacuum-line techniques described for the tensiometry experiments; variations two and three were carried out in the hood under nitrogen.

Experiments with the Monocation. With use of the tensiometric technique, experiments were performed in trifluoroboric acids at $H_0 = -8.6$ using the I_3^- and PF_6^- monocation salts of compound I. The weighed monocation salt was placed in the vacuum-line reaction vessel, the air from the vessel was removed, and degassed acid (1.5 mL) from the acid-storage bulb was added to the reaction vessel containing the monocation salt. After 0.5 h reaction time, the reaction vessel was immersed in a liquid-nitrogen bath and any noncondensable gas was collected with the Toepler pump and measured. In an optical absorption experiment in DMS/trifluoroboric acids at $H_0 = -5.54$ similar to one described for neutral ferrocenophanes, the PF_6^- salt of the monocation of I was substituted for I.

Results

The kinetic data obtained from the tensiometry experiments are shown in Figures 3–5. The data obtained from

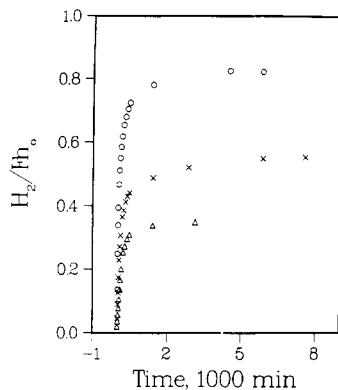


Figure 5. Tensiometry data for III: O, $H_0 = -6.74$; X, $H_0 = -6.44$; Δ , $H_0 = -5.97$.

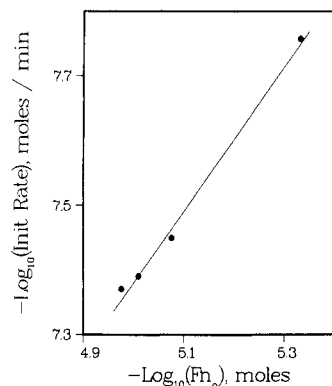


Figure 6. Reaction order determination from tensiometry data for II at $H_0 = -5.70$.

Table I. Mass Spectroscopy Results

mass, m/e	mass distribution, %			
	A ^a	B ^b	C ^c	D ^d
392	1.8	1.8		0.5
393	2.0	2.0		0.8
394	11.5	12.4		2.1
395	7.2	8.0		3.9
396	58.9	57.5		10.5
397	16.0	15.7		16.9
398	2.5	2.5		20.8
399				19.3
400				12.3
401				7.1
402				3.3
403				1.3
404				0.4
405				
406				
407				
408			2.5	
409			3.3	
410			11.0	
411			12.9	
412			53.4	
413			14.3	
414			2.3	
415				

^aA is compound I without any treatment. ^bB is compound I recovered from the dication in deuteriated acid. ^cC is compound I after reaction with deuteriated acid. ^dD is compound I after reaction with protonated acid followed in a short time by deuteriated acid.

initial rate studies using compound II are shown in Figure 6. The logarithm of the rate constants, calculated from the tensiometry data using the initial rates of dihydrogen formation, are shown plotted against the acidity (H_0 or D_0 units) in Figure 7.

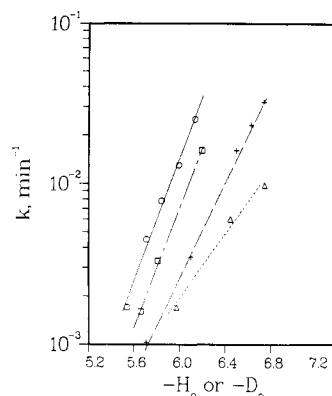


Figure 7. Acid dependence of rate constants from tensiometry experiments: Δ , compound III; O, compound II; X, compound I; +, compound I using deuteriated acids.

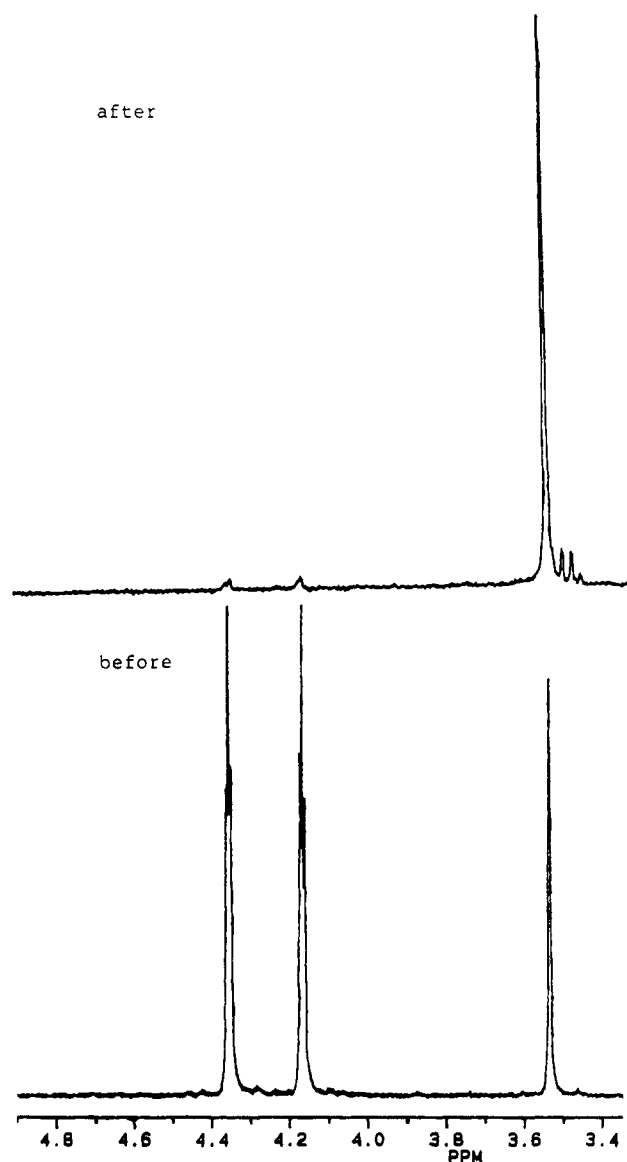


Figure 8. ^1H NMR spectra of I in CDCl_3 before and after reaction with deuteriated acid.

The pertinent part of the mass spectrum of I, (a) before reaction with deuteriated acid, (b) after complete reaction with protonated acid to form the dication followed by deuteriated acid according to the third variation, and (c) after reaction with the deuteriated acid according to the first variation, are all in Table I (columns A, B, and C,

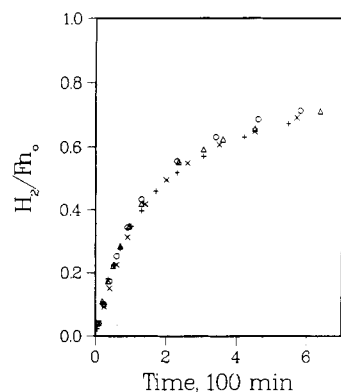


Figure 9. Tensiometry data for II at $H_0 = -5.70$ at various concentrations: O, 2.79 mM; X, 1.33 mM; Δ, 3.02 mM; and +, 2.40 mM.

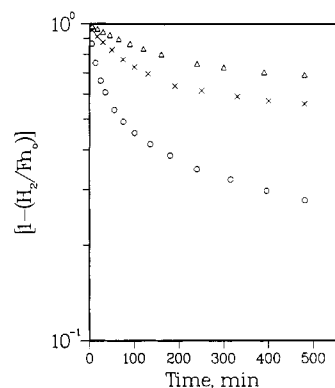


Figure 10. Tensiometry data for I plotted as a first-order process. O, $H_0 = -6.19$; X, $H_0 = -5.81$; Δ, $H_0 = -5.66$.

respectively). Also shown in Table I (column D) is the pertinent part of the mass spectrum of I after incomplete reaction with protonated acid (about 30 min) followed by reaction with deuterated acid.

The ^1H NMR spectrum (Bruker 300) of compound I, before and after reaction with deuterated acid, is shown in Figure 8. The singlet at ca. 3.5 ppm in this spectrum corresponds to the signal from the methylene protons.

Discussion

The relative reactivities observed for the ferrocenophane compounds in the tensiometry and optical absorption experiments, $\text{II} > \text{I} > \text{III}$, are in agreement with the reactivities observed in the electrochemistry experiments¹ and are in the order predicted from the hypothesis that the dehydrogenation reaction is the rate-determining step and that the direction of the ring-tilt controls the rate of the dehydrogenation reaction.¹

The details of the results obtained from the tensiometry, spectrometry, and proton/deuteron exchange reactions lend additional insight into the reaction mechanism. The consistency of the data with the proposed mechanism can be demonstrated by first showing that the reaction is first-order in ferrocenophane as determined from initial rates as illustrated for compound II in Figure 6 and then normalizing all data for initial ferrocenophane concentration. If the reaction were first-order in ferrocenophane concentration throughout the course of the reaction, all curves for a particular acidity should then coincide, as is in fact shown for compound II in Figure 9.

The initial nonzero rate of dihydrogen formation (Figures 3–5) requires that the proposed mechanism has one relatively slow and two relatively fast reaction steps. The

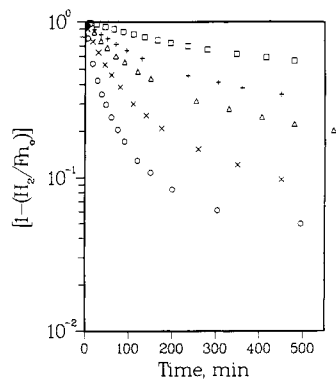


Figure 11. Tensiometry data for II plotted as a first-order process: O, $H_0 = -6.13$; X, $H_0 = -5.99$; Δ, $H_0 = -5.84$; +, $H_0 = -5.70$; □, $H_0 = -5.54$.

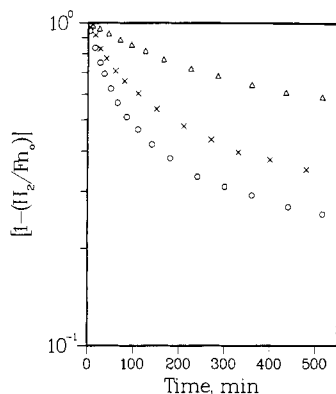
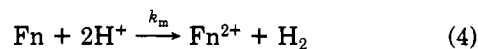


Figure 12. Tensiometry data for III plotted as a first-order process: O, $H_0 = -6.74$; X, $H_0 = -6.44$; Δ, $H_0 = -5.97$.

Table II. Rate Constants and Dihydrogen Yields

compd	$-H_0$	k, min^{-1}	H_2 yield, %
I	5.66	1.6×10^3	≥ 34
	5.81	3.3×10^3	55
	6.19	1.6×10^2	82
II	5.54	1.7×10^3	78
	5.71	4.5×10^3	89
	5.84	7.8×10^3	94
	5.99	1.3×10^2	94
	6.13	2.5×10^2	96
III	5.97	1.7×10^3	68
	6.44	6.0×10^3	≥ 75
	6.74	9.7×10^3	≥ 78

three-step mechanism (eq 1–3) can then be combined into one

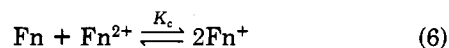


and eq 5 should hold for a large excess of H^+ . Plots of log

$$[\text{H}_2] = [\text{Fn}]_0 (1 - \exp(-kt)) \quad (5)$$

$[1 - \text{H}_2/\text{Fn}_0]$ versus time, t , should give straight lines, but they do not, as seen in Figures 10–12. This indicates that other reactions are taking place.

One possible reaction that we have already considered¹ is the comproportionation reaction.



From a standpoint of thermodynamics, this reaction is expected to occur in neutral media but has been found to be of little importance in reactions of ferrocenophanes at very high acid strengths.¹ At the lower acid strengths used in the current studies, though, the comproportionation reaction may be important. The addition of the compro-

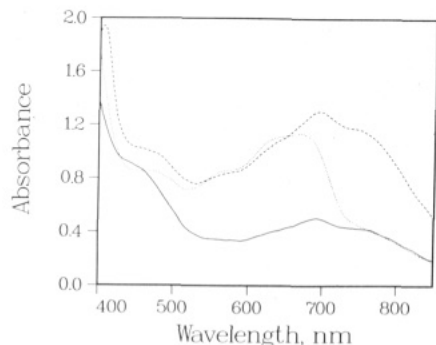


Figure 13. Optical absorption spectra of I at various times during reaction at $H_0 = -5.66$: —, 30 min; ---, 210 min; ···, 48 h.

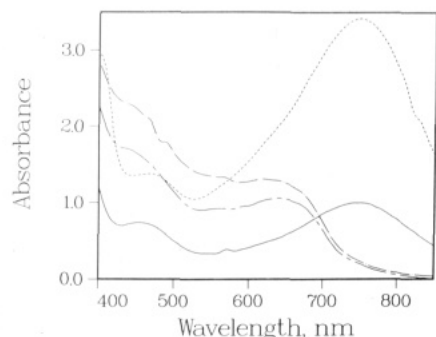
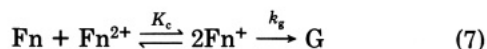


Figure 14. Optical absorption spectra of I at various times during reaction at $D_0 = -5.69$. —, 2 min; ---, 20 min; ···, 4 days; - · -, 6 days.

portionation reaction alone, however, cannot account for the observation that the ultimate yields of dihydrogen is often less than 100% and is acid-dependent (Table II). A reaction that prevents the formation of dihydrogen, such as the permanent removal of the initial ferrocenophane, must be included.

The decomposition of the monocation as reported in the electrochemical paper¹ can account for ultimate yields of dihydrogen that are acid dependent and less than 100%. The acid dependence of the dihydrogen yields can be attributed indirectly to the acid dependence of the formation of the dication. Thus in neat acid, $H_0 = -8.6$, the monocation salts of compound I rapidly form a dark brown solution that has an absorption spectrum different from compound I in any of its known oxidation states but resembling the spectrum of Rayleigh scattering from particulate matter. No dihydrogen is evolved in this reaction. In a weaker acid, DMS/trifluoroboric acids ($H_0 = -5.54$), the monocation of I undergoes decomposition to a similar dark brown solution. Furthermore, the optical spectra obtained during the reaction of I with acid, $H_0 = -5.66$, show the formation of the monocation (absorbance maximum at 750 nm) and its subsequent decay. As this reaction proceeds, the spectra appear to become those of the dication superimposed on Rayleigh scattering curves (Figure 13). The formation of the monocation is more clearly evident in the deuteriated acid, $D_0 = 5.69$ (Figure 14), possibly because the deuteration of I is not as pronounced as the protonation of I. The above phenomenon was not observed at higher acid strengths nor at similarly low acid strengths for compounds II and III.

Equation 6 can now be modified to



where G represents the decomposition products. Equations 4 and 7 represent the proposed mechanism to account for the dihydrogen formation data observed in the ten-

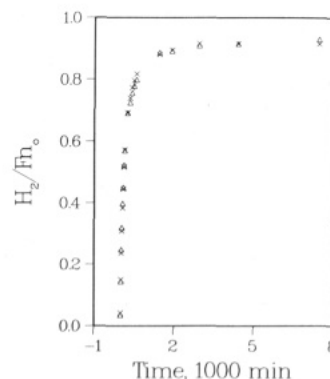


Figure 15. Tensiometry data for II at $H_0 = -5.84$ fitted by using comproportionation/monocation decomposition mechanism: O, observed data; X, fitted data.

siometry experiments. The differential equations arising from these rate equations are not soluble in closed form and therefore were solved by using a nonlinear least-squares numerical analysis using Runge-Kutta and Milne methods.⁹

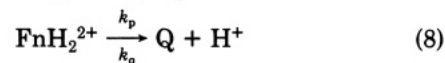
The initial estimates of k_m were taken from the electrochemical results;¹ that is, $k_m = K_1 K_2 k_3$. Estimates of K_C between 1 and 10 are consistent with the observed reduction potentials. [The equilibrium constant for the comproportionation reaction, K_C , can be calculated from

$$F\Delta E_{12} = RT \ln K_C$$

where F is Faraday's constant, R is the gas constant, T is the absolute temperature, and ΔE_{12} is the potential difference between the E° 's for the Fn^+/Fn and $\text{Fn}^{2+}/\text{Fn}^+$ redox couples. The magnitude of ΔE_{12} for the [1.1]-ferrocenophanes in neutral media is on the order of 0.2 V. However, in the DMS/acid media used in the tensiometry and optical absorption experiments, the difference between the two redox potentials is no greater than about 0.05 V, which corresponds to magnitudes for K_C on the order of 10.] Estimates of k_g on the order of 10^{-3} min^{-1} were found to give good initial results.

An example of the best fit of the data is shown in Figure 15. The calculations of the ultimate yields of dihydrogen are lower than what was observed (i.e. 91% instead of 94%) and the amounts of monocations calculated during the course of reaction are larger than what was observed. For the tensiometry data shown in Figure 15 the calculated amounts of monocation were large enough for the monocation to have been clearly observed in the corresponding optical experiment (the same H_0) where it was not observed.

The possible formation of still other compounds as intermediates was investigated. One example of such an intermediate is a compound that is formed from the iron-diprotonated ferrocenophane by removal of a proton from one of the methylene groups.



Precedence for such an intermediate comes from the observation that [1.1]ferrocenophane can lose a proton from one of the bridging methylene groups¹⁰ and from the suggestion that the [1.1]ferrocenophane dication is a strong acid.¹¹ Various modifications of the originally proposed

(9) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

(10) Mueller-Westerhoff, U. T.; Nazzari, A.; Proessdorf, W. *J. Am. Chem. Soc.* 1981, 103, 7678-7681.

(11) Mueller-Westerhoff, U. T. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 702-717.

Table III. Initial Gas Composition^a

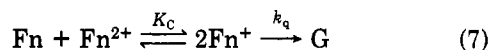
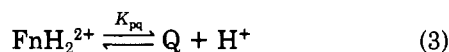
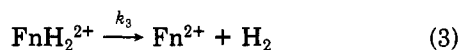
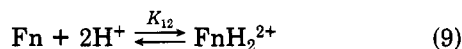
	% D ₂	% HD	% H ₂
obsd	92 (1)	7.2 (7)	0.5 (5)
calcd ^b	96	4.0	0.04

^a Acid strength, $D_0 = -6.91$, results are averages of three measurements. ^b Assuming original D₂O (99.8%) was diluted by the exchange of the 16 protons on the ferrocenophane ring, but no correction was made for any possible exchange with moisture from the air while the acid was prepared.

reaction mechanism were considered in order to account for Q, although for these purposes Q need not arise as described in 8 but could be in some form of equilibrium not involving ionization.

Equation 8 included in a numerical least-squares analysis in three ways. The first two, for purposes of simplifying the calculation, did not include eq 7. In one of these, the dihydrogen formation reaction is considered the rate-determining step (as usual), and in the second, the second protonation reaction is considered the rate-determining step. The results of the latter give miniscule amounts of Q, and that case was eliminated from further consideration. The former case gives reasonable amounts of Q.

When all of the equations are included in the calculation



the correct yields and acid dependence of the yields of dihydrogen and reasonable amounts of the unidentified compound(s) are obtained. The amounts of monocation calculated, however, are still higher than those observed.

An important check of the formation of Q according to 8 is an examination of the exchange reactions that take place when deuteriated acids are used in the reaction medium. First, it is necessary to examine the reaction of I with deuteriated acid. This reaction in itself is of interest since ferrocene is known to undergo a rapid exchange of ring protons for deuterons,^{12,13} and suggestions have been made that the protonation of the iron atom proceeds first through a protonation of the ring followed by transfer of a proton from the ring to the iron.^{14,15} Finally, a determination of a kinetic isotope effect may lend insight to the overall reaction mechanism.

The results obtained indicate that the exchange reaction with the ring protons is much faster than the dihydrogen formation reaction, too fast in fact to determine if a proton transfer from ring to iron takes place as has been sug-

gested.^{11,14,15} This is indicated by the fact that all 16 ring positions are already deuteriated at the earliest stages of the reaction measured, and the initial gas obtained is essentially deuterium (Table III). A transfer of protons from ring to iron would initially put hydrogen atoms on the iron atoms, and dihydrogen should be the initial gas obtained.

Most significant as far as the nature of Q is concerned is that under no circumstances were more than 16 deuterons found in the recovered ferrocenophane (Table I, column C), which implies that the methylene protons did not undergo exchange. This was confirmed in the NMR spectrum of the recovered ferrocenophane (Figure 8). No exchange of any kind was observed for the dication (Table I, column B). No exchange was observed during the quenching procedure. This eliminates the possibility of a reverse exchange of the methylene protons that would have obscured the results. It is clear then that neither the methylene protons of the ferrocenophane, of any of the intermediates, nor of any of the products undergo exchange in these media. Q, therefore, cannot be the iron-diprotonated carbocation, as suggested. In addition, these results do not support the suggestion¹¹ that the dication of I is a strong acid, since as a strong acid, it, too, would exchange at the methylene protons. Whether or not Q is another intermediate in the reaction remains an open question.

The large kinetic isotope effect observed for I, $k_H/k_D = 3-5$, is indicative of a primary kinetic isotope effect. This demonstrates that the rate-determining step in the formation of dihydrogen involves the making or breaking of a bond with a proton or deuteron. This is consistent with the proposed reaction mechanism, but it provides no differentiation between a protonation of the iron or dehydrogenation as the rate-determining step.

As one further note we would like to offer this additional mystery. Although the [1.1]ferrocenophane exchanges ring protons very rapidly with the acid medium, the exchange reaction is quickly suppressed. This was observed in the following way: In order to study the exchange reactions of the dication, the dication was formed in protonated acid by allowing the reaction to proceed to completion (2-3 days). Then a large excess of deuteriated acid was added to the mixture. However, if the reaction with the protonated acid was allowed to proceed for only 0.5 h before adding the deuteriated acid, exchange of a few protons (ca. between two and six) was observed. Since only a few protons were involved in the exchange, the compound exchanging could not have been the [1.1]ferrocenophane since 16 protons are exchanged rapidly nor the dication since it does not exchange protons at all. The compound exchanging slowly must be an intermediate in the reaction sequence. Further study of this phenomenon is planned.

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(12) Setkina, V. N.; Kursanov, D. N. *Russ. Chem. Rev. (Engl. Transl.)* **1968**, *37*, 737-748.

(13) Bykova, E. V.; Setkina, V. N.; Kursanov, D. N. *Dokl. Akad. Nauk SSSR* **1968**, *178*, 352-358.

(14) Bitterwolf, T., private communication.

(15) Waleh, A.; Loew, G. H.; Mueller-Westerhoff, U. T. *Inorg. Chem.* **1984**, *23*, 2859-2863.