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THE STABILITIES OF THE 2-FERROCENYL-2-PROPYL AND FERROCENYLMETHYL CATIONS

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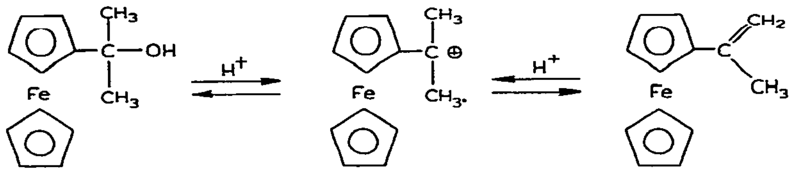
SUMMARY

The pK_R of the 2-ferrocenyl-2-propyl cation has been evaluated by a spectrophotometric indicator acidity study. The observed value, -0.01, is in substantial disagreement with a previous report of the stability of this carbonium ion. In the equilibrium between 2-ferrocenyl-2-propanol and 2-ferrocenylpropene in dilute acid, the alcohol predominates. Redetermination of the absorption spectrum of the ferrocenylmethyl cation demonstrates that the cation is completely formed in 38 to 70% sulfuric acid, in contrast with a previous pK_R determination for this cation of -4.94.

INTRODUCTION

In a recent paper, Horspool, Sutherland and Sutton[1] report that 2-ferrocenyl-2-propanol (I) and 2-ferrocenylpropene (III) are half converted to the 2-ferrocenyl-2-propyl cation (II) in 37 and 44% sulfuric acid respectively. This result appeared to us to be questionable on two grounds. First, if both alcohol and alkene are in rapid equilibrium with carbonium ion, they will simultaneously be in equilibrium with each other. The carbonium ion should then be half formed at a single acidity, independent of the starting material. Second, in earlier work[2], we determined pK_R values for the ferrocenylmethyl and 1-ferrocenylethyl cations in equilibrium with the corresponding alcohols by a Hammett–Deno type indicator acidity study[3]. From the values found, -1.28 and -0.66, the assumption of constant methyl substituent effect would lead to a predicted pK_R of -0.04 for the 2-ferrocenyl-2-propyl cation. In contrast, half conversion to carbonium ion in 37 or 44% sulfuric acid would correspond to pK_R values of -4.3 or -5.5 respectively. No experimental details



(I) (II) (III)

were given to indicate the methods used by Horspool and co-workers[1].

Another report in the literature is markedly in disagreement[2] with our earlier study of ferrocenylcarbonium ion stability. Nesmeyanov and co-workers[4] found a value of -4.94 for the pK_R of the ferrocenylcarbonium ion, which may be compared with our value of -1.28.

The present paper reports efforts aimed at resolving the discrepancies mentioned above, in order to eliminate any ambiguity concerning the stabilities of ferrocenylcarbonium ions.

RESULTS AND DISCUSSION

The 2-ferrocenyl-2-propyl cation

A spectrophotometric indicator acidity study of the 2-ferrocenyl-2-propyl cation has been carried out with 2-ferrocenyl-2-propanol and 2-ferrocenylpropene as starting materials. In 40% and more concentrated sulfuric acid solution, a new absorption spectrum is observed, different from either the alcohol or the alkene: λ_{max} 227 mμ (log ε 4.00), 259 (4.07), 407 (2.85). This spectrum appears to correspond to carbonium ion (II). In dilute acid (< 0.1% H_2SO_4), either starting material exhibits a spectrum similar to that of the alcohol. A plot of $\log([R^+]/[ROH])$ *vs.* H_R at intermediate acidities (Table 1) has a slope of 0.85, and an intercept $pK_R = -0.01$.

TABLE 1

pK_R DETERMINATION FOR 2-FERROCENYL-2-PROPYL CATION

H_2SO_4(%)	H_R[a]	log Q[b]	pK_R[c]
15.43	−1.37	+1.30	−0.07
11.98	−0.97	+0.72	−0.15
10.04	−0.73	+0.55	−0.18
7.15	−0.37	+0.28	−0.09
5.65	−0.15	+0.12	−0.03
4.49	+0.04	−0.05	−0.01
2.81	+0.41	−0.31	+0.10
0.82	+1.01	−0.95	+0.06
0.20	+1.55	−1.35	+0.20

[a] Ref. 3. [b] $Q=[R^+]/[ROH]$. [c] pK_R determined from plot of log Q *vs.* H_R, taken as the value of H_R where log $Q=0$, is -0.01.

The non-unit slope of the plot may reflect some unusual activity coefficient behavior for this system, or may be an artifact resulting from a solvent effect on the spectrum, or a side reaction, such as oxidation to a ferrocenium ion (see experimental section). However, errors introduced in the pK_R determination should be minor. It is clear that the result is in complete disagreement with the values reported by Horspool, Sutherland and Sutton[1], and in essential agreement with earlier pK_R work[2].

Another feature of the present work which may be at variance with the results of Horspool, Sutherland and Sutton[1] is the predominance of alcohol (I) in equilibrium with alkene (III) in aqueous solution. The alcohol may be converted to the alkene in nearly quantitative yield by shaking it in carbon tetrachloride solution with 20% sulfuric acid. Horspool and co-workers conclude that the alcohol is more basic than the alkene, and that the carbonium ion "deprotonates to give the alkene much faster than it undergoes solvolytic attack to form the alcohol". However, we find from the UV spectrum that the alkene is present to an extent of less than 5%. A sample of alkene was equilibrated with the alcohol in 0.05% H_2SO_4 solution. The NMR spectrum of the isolated product showed no more than 5% of the alkene. Preponderance of the alcohol at equilibrium implies a greater basicity for the alkene than for the alcohol. We have also found that neutralization of a solution of the carbonium ion in 40% sulfuric acid with aqueous sodium hydroxide or sodium acetate yields a product which is less than 5% alkene. The success of the dehydration reaction may then be explained if the alcohol and alkene are in rapid equilibrium with each other and with the carbonium ion (largely carbonium ion in 20% sulfuric acid). In the heterogeneous system used in the dehydration, the alkene product predominates over alcohol because of its greater tendency to partition into the non-polar organic phase, despite preponderance of the alcohol in the aqueous phase. (Since the activity of water in 20% sulfuric acid is 0.88[5], it is unlikely that the alkene–alcohol equilibrium shifts much between water and 20% sulfuric acid). The rapidity of the alcohol–alkene equilibration is evident, since equilibria were reached within the time necessary to obtain spectra. However, in sufficiently dilute acid solution it is possible to observe conversion of alkene to the equilibrium mixture. In very rough kinetic measurements, half lives of 2 and 40 min were found in 6×10^{-4} and 6×10^{-5} M sulfuric acid solutions.

In their study, Horspool, Sutherland and Sutton[1] found that the product isolated from reaction of acetylferrocene with methylmagnesium iodide is primarily alkene (III), whereas with Grignard reagents from alkyl bromides, the alcohol predominates. They concluded that the Grignard–ketone adduct undergoes elimination to the alkene before hydrolysis. While we have not specifically studied this reaction, we might note that the alcohol predominated by at least a 10/1 ratio over alkene in our preparation utilizing methylmagnesium iodide. A good yield (75%) of the alcohol has also been reported by Schloegl and Fried in the reaction of acetylferrocene with methylmagnesium iodide[6].

The ferrocenylmethyl cation

In their report of the basicity of ferrocenylmethanol, Nesmeyanov and coworkers[4] report and UV absorption for the carbonium ion in 56 to 98% sulfuric acid essentially the same as we had observed in 54 to 97% sulfuric acid. From reductions in intensity of the carbonium ion absorption in several solutions ranging from 41.3 to 54% sulfuric acid, they deduced that the carbonium ion was formed to the extent of 84.3% to 99%. From the derived indicator ratios ($Q = [R^+]/[ROH]$), pK_R values were then calculated. However, it seems quite risky to deduce pK_R from ionization ratios all greater than 5, as in their data. Furthermore, values of pK_R derived from different sulfuric acid concentrations show a trend with acid concentration, and substantial scatter. (pK_R values vary from -5.45 in the 54% sulfuric acid solution to -4.24 in the 41.3% sulfuric acid.)

In order to check these results, we have redetermined the absorption spectrum of the ferrocenylmethyl cation in solutions bracketing those used by Nesmeyanov, 38 and 70% sulfuric acid, using a variety of techniques to prepare the solutions (see experimental section). While there was some variation in extinction coefficients in excess of the probable uncertainties inherent in the spectrometer and the sample handling, paired measurements in the two acid solutions matched within ±1%, indicating substantially complete ionization to carbonium ion in both acid concentrations. Solutions prepared by directly dissolving the carbinol in acid solutions had extinction coefficients lower than the others by about 3%. This deviation may result from a rapid bimolecular side reaction in locally concentrated solutions occurring during the solution process. (Indeed, it was observed that a 10^{-2} *M* stock solution in 38% sulfuric acid became cloudy within 20 min at room temperature, while similar solutions in 70 and 97% sulfuric acid or more dilute solutions in 38% acid were quite stable.) One solution in 38% sulfuric acid, prepared by addition of an aliquot of ethanolic stock solution to the acid, had a larger extinction coefficient by about 4%. In this case, a shoulder at 290 mμ was also prominent, suggesting some oxidation to ferrocenium ion.

We therefore conclude that the pK_R value of -4.94 reported by Nesmeyanov for the ferrocenylcarbonium ion is in error, and that the previously derived value of -1.28 is probably substantially correct.

EXPERIMENTAL

Substrates

2-Ferrocenyl-2-propanol (I) and 2-ferrocenylpropene (III) were prepared essentially as described by Horspool, Sutherland and Sutton[1], except that acetylferrocene was added in tetrahydrofuran solution to the methyl Grignard in ether, and the Grignard solution was apparently less concentrated (0.5 *M*). After chromatography, there were isolated 2-ferrocenyl-2-propanol, m.p. 63.5–64.5° (petroleum ether) (lit.[6] m.p. 64–65°) and 2-ferrocenylpropene, m.p. 63.5–64.5° (subl.) (lit.[1,7] m.p. 61–62°, 66–69°], in a ratio of about 40/1. More of the alkene was prepared by dehydration of the alcohol, m.p. 66.5–67.5° (subl.).

Ferrocenylmethanol had m.p. 77.8–78.5° (lit.[8] m.p. 80–81°).

Basicity determinations

Solutions for spectroscopic observation of the 2-ferrocenyl-2-propyl cation were prepared by injecting 50-μl aliquots of an ethanolic stock solution (ca. 5×10^{-3} *M*) of the alcohol or alkene into the appropriate acid, either in a 50-ml volumetric flask or directly in a 10-cm spectrophotometer cell (volume 29.5±0.3 ml). Spectra were immediately scanned from 700 to 210 mμ, and showed little change over periods up to 1 h. Beer's law was obeyed over a factor of ten in concentration. The results are shown in Table 1. One experiment using a 1-cm cell led to similar extinction coefficients, and a calculated pK_R value of -0.04.

Oxidation to a ferrocenium ion presents a potential complication. Ferrocenium ion is reported to have a spectrum somewhat similar to that of the carbonium ion: ferrocenium ion[9]: λ_{max} 252 mμ (log ε 4.1), 620 (2.6); 2-ferrocenyl-2-propyl cation: 227 (4.00), 259 (4.07), 407 (2.85). In concentrated solution, absence of ferrocenium ion was clear both visually and spectroscopically. In more dilute solutions, the presence of ferrocenium ion was suggested in a few cases by a shoulder at ca. 290 mμ. From published spectra, and samples of 2-ferrocenyl-2-propanol oxidized with ferric ammonium sulfate, this shoulder appears to have an extinction coefficient half to two-thirds that of the maximum at 252 mμ. An amount of ferrocenium ion equal to less than 20% of the carbonium ion is readily apparent from qualitative examination of spectra. Solutions of the carbinol in 5 and 10% sulfuric acid were not oxidized to an appreciable extent when oxygen was bubbled through for several minutes. However, some samples of sulfuric acid appeared to contain a trace impurity which produced partial oxidation to ferrocenium ion when very low concentrations of substrate ($< 10^{-5}$ M) were present. Results from such solutions were discarded. Some other unidentified side reaction may also be causing slight interferance, since there was less constancy of extinction coefficients and indicator ratios determined at wave lengths shorter than 240 mμ.

The absorption spectrum of ferrocenylmethanol was redetermined in sulfuric acid solutions. The following values of extinction coefficients at 255 mμ were obtained in 38 and 70% acid solutions respectively, when made up in the manner described: (1) Injection of ethanol stock solution into sulfuric acid solutions, 7×10^{-6} M, 10 cm path, 9240 and 8910; (2) same, 4×10^{-5} M, 1 cm path, 8825 and 8800; (3) dissolving the alcohol directly in acid and diluting to 1×10^{-3} M, 0.1 cm cell, 8540 and 8650; (4) dissolving the alcohol in 97% sulfuric acid and diluting with 38 and 70% sulfuric acids, 1 cm path, 8580 and 8580; (5) previous values, using ethanol aliquots in 54, 58, 60 and 87% sulfuric acid, 1 cm path, 8900, 8980, 8780 and 9200; (6) Nesmeyanov results in 56–98% sulfuric acid, 10 000.

Product isolation

2-Ferrocenyl-2-propanol (20 mg) was dissolved in 5 ml of carbon tetrachloride, and extracted into 40% sulfuric acid. Within less than 5 min, the acid phase was run slowly into excess cold sodium hydroxide solution, the product extracted and isolated. NMR of the residue showed it to contain no more than 5% of the alkene. An experiment with a similar result was carried out using saturated sodium acetate solution for the neutralization. The pH of the final solution was about 5.

An ethanolic stock solution of 2-ferrocenylpropene (0.75 ml, 7.6×10^{-3} M) was injected into 0.05% sulfuric acid (300 ml). After 5 min, the solution was extracted with chloroform, and the chloroform extract was washed with an aqueous sodium bicarbonate solution. Any chloroform phase remaining with the sulfuric acid was evaporated under aspirator vacuum, and the process was repeated with another aliquot of the substrate. A total of 8 ml of the 2-ferrocenylpropene solution was treated in this manner. The organic phases were combined, evaporated, and the NMR spectrum was run. The product was shown to be mainly 2-ferrocenyl-2-propanol, with possibly 5% of 2-ferrocenylpropene.

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REFERENCES

1 W. H. Horspool, R. G. Sutherland and J. R. Sutton, *Can. J. Chem.*, 47 (1969) 3085.
2 E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, 91 (1969) 509.
3 N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Amer. Chem. Soc.*, 77 (1955) 3044.

4 A. N. NESMEYANOV, M. D. RESHETOVA AND E. G. PEREVALOVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1967) 2746.
5 S. SHANKMAN AND A. R. GORDON, *J. Amer. Chem. Soc.*, 61 (1939) 2370.
6 K. S. SCHLOEGL AND M. FRIED, *Monatsh. Chem.*, 95 (1964) 558.
7 W. M. HORSPOOL AND R. G. SUTHERLAND, *Can. J. Chem.*, 46 (1968) 3453.
8 J. K. LINDSAY AND C. R. HAUSER, *J. Org. Chem.*, 22 (1957) 355.
9 P. H. HARJU AND N. C. PETERSON, *Proc. N. Dakota Acad. Sci.*, 11 (1967) 31; G. WILKINSON, M. ROSENBLUM, M. C. WHITING AND R. B. WOODWARD, *J. Amer. Chem. Soc.*, 74 (1952) 2125.