Tropylium Ligands in the Mass Spectra of Substituted Ferrocenes

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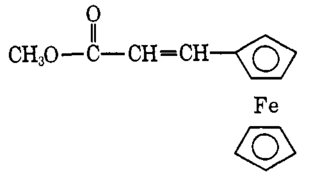
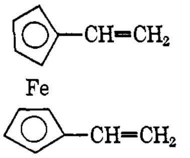
Abstract: Prominent $C_7H_7Fe^+$ ions in the mass spectra of substituted ferrocenes may derive their stability from formation of a symmetrical species. Labeling studies with 1,1′-divinylferrocene suggest that fragmentation of the ligand ring competes with formation of a species with equivalent hydrogens.

In the more recent of our studies[2,3] of the fragmentation patterns of substituted ferrocenes, the observation of intense peaks of nominal masses corresponding to $C_6H_6Fe^+$ and $C_7H_7Fe^+$ suggested that the structure of the ligands must contribute to a special stability of these ions. The former ion had been noted before.[4] The latter, however, has not been studied, although it is very frequently observed in ferrocene spectra. For example, it appears as a fairly intense ion in all of the spectra of more than 24 ferrocenes containing at least a two-carbon side chain which we have recently examined. The hydrogens need not be initially attached to the first two carbons; the peak is observed, for example, even in the spectrum of methyl β-ferrocenylacrylate (I), in which the seventh hydrogen must come from the methyl group.[5] In all of these spectra there were found a sufficient number of normal and metastable peaks in the vicinity of the regions of interest to complicate the quantitative interpretation of labeling results, and so the simplest possible ferrocene, 1,1′-divinylferrocene (II), in which the rearrangement could be studied was prepared. This molecule gives a spectrum with no extraordinary complications, so that the transformations of eq 1–3 could be used to study the structure of the C_7H_7 ligands. In addition to Fe^+



I



II

$$C_7H_7FeC_7H_7^+ \longrightarrow C_7H_7FeC_5H_5^+ + C_2H_2 \quad (1)$$

$$C_7H_7Fe^+ \xrightarrow{m^*} C_5H_5Fe^+ + C_2H_2 \quad (2)$$

$$C_7H_7^+ \xrightarrow{m^*} C_5H_5^+ + C_2H_2 \quad (3)$$

these ions are the principal ions contributing to the spectrum (Table I); a few small satellites containing one or two fewer hydrogens often accompany them.

Table I. Fragmentation of Divinylferrocenes Corrected for Isotope Impurity

Divinylferrocene *m/e*	%	Divinylferrocene-d_2 *m/e*	%
238	100	240	100
213	0.18	215	0.37
212	2.5	214	0.6
148	1.8	213	1.7
147	8.0	149	2.4
146	5.2	148	7.8
145	8.9	147	3.1
122	2.4	146	8.6
121	16.8	145	3.7
120	2.4	123	2.4
119	4.7	122	8.5
91	9.6	121	10.2
65	6.1	120	5.3
56	24	119	1.7
		92	9.1
		66	5.0
		65	2.8
		56	26

Structure of the $C_7H_7^+$ Ion. Of all the studies of the structures of organic ions in the mass spectrometer, perhaps the best known is the classical study of $C_7H_7^+$ in the spectra of ethylbenzene and toluene by deuterium labeling, in which this ion was demonstrated to be the symmetrical tropylium ion rather than the benzyl ion or some other ion of lower symmetry.[6] In the present case, the more likely routes of formation of $C_7H_7^+$ are loss of FeC_7H_7 as a unit and sequential loss of C_7H_7 and Fe. A metastable peak at *m/e* 46.4 indicates that these ions (*m/e* 91) decompose with loss of acetylene to produce $C_5H_5^+$, analogously to the classical cases. In the spectrum of α,α′-dideuteriodivinylferrocene the *m/e* 91 ion is shifted cleanly to *m/e* 92, and $C_5H_5^+$ (*m/e* 65 in the original compound) is split between *m/e* 66 and *m/e* 65 in a ratio of 64:36. This should be compared with the expected value of 5:2, or 71:29, for the symmetrical tropylium ion (III), which may lose C_2H_2 five ways (a) and C_2HD two ways (b). The dis-

a b

III

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[1] Du Pont Teaching Fellow, 1966–1967; Enka Summer Fellow, 1966.

[2] D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **89**, 4917 (1967).

[3] D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *ibid.*, **89**, 6156 (1967).

[4] (a) G. W. Wilcox and R. W. Geiger, Anachem Conference, Detroit, Mich., 1963. We thank Dr. Wilcox for informing us of this observation. (b) H. Egger, *Monatsh. Chem.*, **97**, 602 (1966).

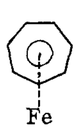
[5] That it indeed does is indicated by the shift of this peak (*m/e* 147) to *m/e* 148 in the mass spectrum of the trideuteriomethyl ester.

[6] For a review, see H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 453.

crepancy may result from contributions from other sources to the intensities of these ions, sources which might not involve the intermediacy of symmetrical species. In order to test this possibility, the intensities of the metastable peaks themselves were examined; fortunately, the metastable transition 91 → 65 of the unlabeled compound does not produce a wide metastable, and the two metastables resulting in the spectrum of the labeled compound (92 → 66, 47.3; 92 → 65, 45.9) are nearly completely separated. The integrated intensity ratio, corrected for the small amount of overlap, is 71:29. In addition, when the intensities of the normal daughter ions are measured only a few volts above their appearance potential (at several points between 25 and 30 V nominally), the intensities are found to be 70:30. The voltage dependence of the isotopic distribution again suggests a multiple pathway leading to nominally common products.[7] The small discrepancy in the intensities of the normal $C_5H_5^+$ ions at 75 V is therefore attributable to other interfering sources, and it seems safe to conclude that the $C_7H_7^+$ which decomposes to $C_5H_5^+$ is tropylium. If the bonding in the precursor ions is similar to that in the original molecule, this represents the first case of formation of tropylium by cleavage of a π bond rather than a σ bond, but in view of the ubiquity with which tropylium is formed in the electron impact induced fragmentation of other molecules,[8] it is not extraordinary, nor does this information indicate what the structure of C_7H_7 bonded to iron might be, for the rearrangement to a seven-membered ring might have occurred either before or after the bond to iron had been broken.

The $FeC_7H_7^+$ Ion. In order to answer this last question, we examined the *m/e* 147 peak, which is formed in the mass spectrum of II by the loss of C_7H_7. As eq 2 indicates, this also decomposes by loss of acetylene to give $FeC_5H_5^+$ (*m/e* 121), an ion usually of considerable importance in the mass spectra of monosubstituted ferrocenes (where it can form by loss of the substituted ring), but one which can arise only by a hydrogen rearrangement (at the minimum) in the present case. A metastable peak at *m/e* 99.6 confirms the decomposition. As Table I indicates, there is an accompanying collection of ions of slightly lower mass about either ion, but the assumption that only *m/e* 147 produces *m/e* 121 allows a ratio of 54:46 to be obtained for the loss of C_2H_2 *vs.* C_2HD in the spectrum of the deuterated compound. There is an important discrepancy between this set of values and the theoretical 71:29.

It was again possible to examine the integrated intensities of the metastable peaks. In the undeuterated compound, the metastable at *m/e* 99.6 is only slightly wider than that at 46.4, and no other metastables are near it. In the deuterated compound, then, the metastables at *m/e* 100.6 (148 → 122) and *m/e* 98.9 (148 → 121) overlap only a little, sufficiently to occasion measurement of only the outer half of each metastable for comparison, however. The ratio for loss of C_2H_2 *vs.* loss of C_2HD in this case is 66:34, a value which suggests that again the symmetrical seven-membered ring for the C_7H_7 unit occurs in the best single structure IV.



IV

Nevertheless the fit is not perfect. The fact that the intensities of the normal and metastable ions give such different ratios suggests an explanation, namely, that isomeric C_7H_7 ligands exist, and that they have different rates of decomposition. The low-voltage isotopic distribution is once again different from the high-voltage distribution: at nominal values of 18 and 20 V, the distribution is shifted to 50:50. Apparently the two processes are not easily separated, although the corresponding metastable intensities are in the ratio of 70:30 at 18 V. The existence of two or more processes is once again supported by the low-voltage behavior. One of these processes involves tropylium, and almost all of the metastable $C_7H_7Fe^+$ ions have this for a ligand. Some other structure contributes a few per cent to the metastable peak and rather more to the intensity of the *m/e* 122 and 121 ions, so that their ratio is considerably distorted from the expected value. It is possible that this other structure resembles the unrearranged ligand, which presumably would lose acetylene preferentially from the side chain[9] so that the amount of C_2HD should be increased. In this case, the process could be viewed as a competition between the loss of C_2H_2 from the unrearranged molecule and the rearrangement reaction.

The $(C_7H_7)_2Fe^+$ Ion. Loss of acetylene is a minor process in the decomposition of the molecular ion itself and the process is not confirmed by a metastable ion. The spectrum is fairly free of interference around *m/e* 212 ($C_7H_7FeC_5H_5^+$), so that an estimation of the relative losses of C_2HD and C_2H_2 in the dideuterio compound can be attempted without loss of confidence because of a large number of corrections to the intensity. In the dideuterio derivative, the ratio of the $(M - C_2H_2)^+$ peak at *m/e* 214 to that of the $(M - C_2HD)^+$ peak at *m/e* 213 is approximately 2:5. Therefore the loss of deuterium is significantly favored. Presumably this reflects a loss of carbons and hydrogens of the vinyl group before equilibration of all the carbons and hydrogens can occur. The fact that some C_2H_2 is lost suggests that at least an approach to equilibration is begun, but the absence of a metastable peak might be taken to indicate that the reaction is relatively fast, with no population of ions remaining to decompose in this fashion as metastable ions. This interpretation would support the explanation that fragmentation of this ion precedes complete equilibration.

It appears, then, that there is strong evidence for the formation of tropylium ions from divinylferrocene ions. Whether or not these structures are ligands for iron depends on the relative rates of isomerization and fragmentation. The molecular ion loses acetylene faster than it can rearrange, but there is sufficient time for practically all of the C_7H_7 ligand of $FeC_7H_7^+$ to be reorganized to a symmetrical structure.[9a]

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(7) *Cf.* S. Meyerson and H. Hart, *J. Amer. Chem. Soc.*, **85**, 2358 (1963).

(8) For a recent review, see S. Meyerson, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **26**, 257 (1965).

(9) Note that C_2H_2 is not lost to a significant extent from ferrocene itself, or from $C_5H_5Fe^+$; loss of C_2H_2 by analogy might come only from the vinyl group.

(9a) NOTE ADDED IN PROOF. Tropylium ligands have been postulated in solution chemistry: M. Cais and A. Eisenstadt, *J. Amer. Chem. Soc.*, **89**, 5468 (1967).

Experimental Section

General. Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were recorded from samples in KBr pellets with a Perkin-Elmer Model 237 grating infrared spectrophotometer. Nmr spectra were recorded on a Varian Model A-60 spectrometer with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer, at 75 V ionizing voltage and 80 μA emission current. The oven was maintained at 185° and the source at 175°. The analyses were performed by Alfred Bernhardt, 433 Mulheim (Ruhr), Germany.

1,1′-Bis(α-deuterio-α-hydroxyethyl)ferrocene was prepared by reduction of 1.0 g of 1,1′-diacetylferrocene (0.0037 mol) and 0.1 g of $LiAlD_4$ (0.0024 mol) by the standard procedure[10] yielding 0.095 g (94%) of a yellow solid. Recrystallization from hexane yielded a pure compound, mp 70–72° (lit.[10] mp 69–71°).

1,1′-Divinylferrocene was prepared from 1,1′-bis-1-hydroxylethylferrocene (mp 70–72°; lit.[10] 69–71°) by the method of Rausch.[11]

1,1′-Bis(α-deuteriovinyl)ferrocene was made by the above procedure.

Ethyl *trans*-Ferrocenylacrylate. To a solution of 4.0 g of ethylferrocenoylacetate (mp 52.5–4.5°; lit.[12] 50–51°) (0.013 mol) in 50 ml of absolute ethanol was added 1.0 g of $NaBH_4$ (0.026 mol) in 5 ml of H_2O.[13,14] The reaction mixture was stirred at 0° for 24 hr, then taken to pH 5 with dilute HCl in EtOH, then stirred 1 hr at room temperature. The ethanol was stripped off at room temperature yielding 2.95 g (78%); washing through a plug of alumina and recrystallization from hexane yielded a pure compound, mp 63–64°, 70–70.5°; ν^{KBr} 3080, 1700, 1633, 1105, 1003, and 977 cm^{-1}; nmr τ 8.67 (t, CH_3), 5.85 (s, C_5H_5), 5.76 (q, CH_2), 4.56 (2t, C_5H_4), and 2.40 and 3.95 (AB doublet, J = 19 cps, CH=CH). The vinyl coupling constant of 19 cps and the ir peak at 977 cm^{-1} indicate a *trans* double bond rather than a *cis*.[15]

Anal. Calcd for $C_{15}H_{16}FeO_2$: C, 63.40; H, 5.67. Found: C, 63.53; H, 5.64.

***trans*-Ferrocenylacrylic Acid.** This compound was prepared by saponification of 500 mg of ethyl *trans*-ferrocenylacrylate (0.0018 mol) yielding 350 mg (78%), recrystallized from CH_2Cl_2–hexane, mp 188–191 dec (lit.[16] 186–187° dec).

Trideuteriomethyl *trans*-Ferrocenylacrylate. To 1.5 ml of CD_3OH in 4 ml of ether was added 50 mg of *trans*-ferrocenylacrylic acid (0.002 mol) and 0.5 ml of $BF_3 \cdot Et_2O$. The solution was refluxed for 24 hr and worked up as before yielding 35 mg (66%), recrystallized from hexane, mp 100–103°.

Methyl *trans*-Ferrocenylacrylate. To 5 ml of CH_3OH was added 150 mg of *trans*-ferrocenylacrylic acid (0.00059 mol) and 1 ml of $BF_3 \cdot Et_2O$. The solution was refluxed for 4 hr and worked up as before yielding 121 mg (77%); recrystallization from hexane gave a pure compound, mp 102–103°; ν^{KBr} 3085, 1700, 1627, 1104, and 975 cm^{-1}; nmr τ 6.27 (s, CH_3), 5.83 (s, C_5H_5), 5.53 (2t, C_5H_4), and 2.45 and 3.92 (AB doublet, J = 19 cps, CH=CH).

Anal. Calcd for $C_{14}H_4FeO_2$: C, 62.25; H, 5.23. Found: C, 62.54; H, 5.39.

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(14) W. F. Little and R. Eisenthal, *ibid.*, **26**, 3609 (1961).

(15) Two crystal modifications, as seen before in ref 2 and 3.

(16) C. D. Broadhead, J. M. Osgerby, and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).

Chemistry of Singlet Oxygen. IV.[1] Oxygenations with Hypochlorite–Hydrogen Peroxide[2a]

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Abstract: Good acceptors for the dye-sensitized photooxygenation can be oxygenated efficiently by metal hypochlorites and hydrogen peroxide to give products identical with those of photooxygenation. Oxygenations of 2,3-dimethyl-2-butene, $\Delta^{9,10}$-octalin, 2,5-dimethylfuran, tetraphenylcyclopentadienone, 1,3-cyclohexadiene, and anthracene are described. The reactive intermediate is probably $^1\Delta_g$ molecular oxygen. The yield of singlet oxygen depends on solvent and other factors, for reasons which are not yet understood.

Dye-sensitized photooxygenations of organic compounds have been studied extensively.[3] Among the acceptors studied, two types have received particular attention. Conjugated dienoids (cyclic and a few other *s-cis* dienes, polycyclic aromatics, and some heterocycles) undergo addition of oxygen to give (at least as the primary products) 1,4-*endo*-peroxides, in a reaction analogous to Diels–Alder addition (reaction 1). Many olefins with allylic hydrogens produce allylic hydroperoxides with an attendant specific shift of the double bond to the allylic position (reaction 2), in a reaction analogous to the "ene" reaction.[4]

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(1) Part III: C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Letters*, 4111 (1965).

(2) (a) Supported by National Science Foundation Grants No. G-25086, GP-3358, and GP-5835, and by a grant from the Upjohn Company; taken in part from S. Wexler, Ph.D. Thesis, UCLA, 1966; (b) Alfred P. Sloan Research Fellow, 1965–1967.

(3) For leading references, see: (a) G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957); (b) K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); (c) E. J. Bowen, *Advan. Photochem.*, **1**, 23 (1963); (d) A. Nickon, N. Schwartz, J. B. DiGiorgio, and D. A. Widdowson, *J. Org. Chem.*, **30**, 1711 (1965); (e) Yu. A. Arbuzov, *Russ. Chem. Rev.*, **34**, 558 (1965); (f) K. Gollnick and G. O. Schenck in "1,4-Cycloadditon Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967, p 255.

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