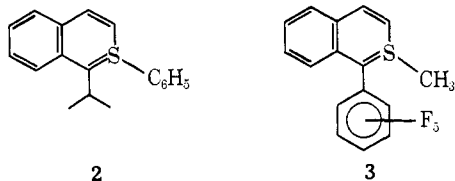


thiabenzene should be planar or have a very low bending barrier at sulfur,<sup>4-7</sup> and with related Hückel calculations on 2-phenyl-2-thianaphthalene which predict a planar structure with a barrier to out-of-plane bending at the S-phenyl bond of less than 5.0 kcal/mol.<sup>8</sup> We now wish to report our finding that 2-thianaphthalenes **2** and **3** are in fact stably pyramidal at



sulfur, with *lower limits* for the barrier to pyramidal inversion of 16.8 and 22.3 kcal/mol, respectively. These findings are consistent with our previously stated view<sup>9</sup> that thiabenzene is best described by an ylide-like model.<sup>10</sup>

Thiabenzene **2** was prepared by addition of purified phenyllithium to 1-isopropyl-2-thianaphthalenium perchlorate<sup>11</sup> under a dry nitrogen atmosphere in benzene-*d*<sub>6</sub>. The <sup>1</sup>H nmr spectrum of the purple solution thus obtained at 37° displayed a well-resolved pair of isopropyl methyl doublets ( $\delta$  1.35, 1.42;  $J$  = 6.5 Hz), as well as a doublet at  $\delta$  5.00 ( $J$  = 8 Hz) which is characteristic 3-proton signal of the 2-thianaphthalene ring.<sup>9</sup> On standing at 37° these absorptions disappeared and the purple color changed to light brown. The thermal decomposition mixture did not contain 1-phenyl-1-isopropyl-2-thio-3-chromene, a possible rearrangement product, which was prepared by an independent synthesis.<sup>12</sup>

The sharp diastereotopic isopropyl methyl signals in **2** demonstrate that inversion at pyramidal sulfur is slow on the nmr time scale.<sup>13</sup> This diastereotopicity ( $\Delta\nu$  = 4 Hz (60 MHz), 37°) requires a minimum barrier to pyramidal inversion of 16.8 kcal/mol. Heating the sample of **2** to *ca.* 60° results in rapid decomposition, and we were thus unable to raise the value of the lower limit by this method.

Since the calculated barrier to pyramidal inversion for **1** exceeds the limits of dnmr, an alternative approach to the problem lies in the preparation of an op-

(4) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(5) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969).

(6) C. C. Price and D. H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).

(7) C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971).

(8) C. K. Miao, M.S. Thesis, University of Pennsylvania, 1967. We thank Professor Charles C. Price for bringing this work to our attention.

(9) J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5650 (1974).

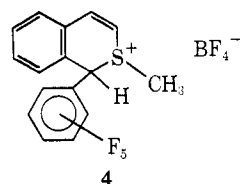
(10) See also A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

(11) Prepared by analogy with the reported synthesis of 1-*tert*-butyl-2-thianaphthalenium perchlorate.<sup>6</sup>

(12) In contrast to the thermal decomposition of 1-phenyl-2-methyl-2-thianaphthalene,<sup>9</sup> the decomposition of **2** does not entail migration (Stevens rearrangement) of the S-substituent to the 1-position.

(13) Pyramidal sulfur is the only reasonable element of chirality in **2** on this time scale of observation.

tically active thiabenzene. It had previously been shown<sup>9</sup> that **3** possesses a markedly enhanced thermal stability resulting from incorporation of the strongly electron withdrawing pentafluorophenyl group; therefore this compound was chosen for the present study. Optically active **3** was prepared by partial deprotonation of 0.050 mmol of **4**<sup>9,14</sup> with 0.028 mmol of brucine



in anhydrous dimethyl sulfoxide (5.0 ml) under a dry nitrogen atmosphere. The optical activity of the orange solution of **3** thus generated was detected by circular dichroism (CD)<sup>15</sup> in the region of the characteristic thiabenzene absorption band ( $\lambda_{\text{max}}$  480 nm, DMSO). The Cotton effect is positive, with the maximum at 480 nm,  $\theta$  = +0.0112  $\pm$  0.0008° ( $l$  1.0 cm),<sup>16</sup> and with  $\theta$  = 0.0000  $\pm$  0.0008° at 540 and at 400 nm.<sup>17</sup> The observation of optical activity (less than a 20% change in optical activity on standing at 27° for 10 min) assures that the barrier to pyramidal inversion in **3** must be at least 22.3 kcal/mol. The CD band decreases in rotational strength with time, and ultimately vanishes, paralleling a similar decrease in the intensity of the characteristic absorption in the visible region.<sup>18</sup>

Prior studies have established a pyramidal structure for the sulfur center in acyclic sulfonium ylides,<sup>19,20</sup> and the pyramidal inversion barrier for ethylmethylsulfonium phenacylide (**5**) has been determined to be 23.3 kcal/mol.<sup>20</sup> Our estimate of a lower limit for pyramidal inversion in **2** of 16.8 kcal/mol and in **3** of 22.3 kcal/mol is therefore consistent with the view that thiabenzene is ylide-like in character.<sup>9,10</sup>

(14) Although two diastereomers (*cis* and *trans*) are possible for this compound, <sup>1</sup>H nmr spectroscopic evidence suggests that one predominates to the virtual exclusion of the other in recrystallized **4**.

(15) By employing CD, interference from other optically active substances which do not have absorptions in the visible region is precluded.

(16) Assuming a quantitative yield (0.028 mmol) of thiabenzene, one obtains  $[\theta]_{480}^{20} + 204$ .

(17) In a control experiment, racemic **3** was generated by deprotonation of **4** with dimethyl lithium. Addition of brucine did not yield the observed Cotton effect.

(18) A detailed discussion is reserved for the full account of this work.

(19) H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, **23**, 4279 (1967); K. W. Ratts, *Tetrahedron Lett.*, 4707 (1966); A. Hochrainer and W. Silhan, *Monatsh. Chem.*, **97**, 1477 (1966); A. F. Cook and J. G. Moffatt, *J. Amer. Chem. Soc.*, **90**, 740 (1968); B. M. Trost and R. F. Hammen, *ibid.*, **95**, 962 (1973).

(20) D. Darwish and R. L. Tomlinson, *J. Amer. Chem. Soc.*, **90**, 5938 (1968).

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*Received May 4, 1974*

### Fixation of a Spin Labeled Organic Ion to Ion Exchangers

Sir:

It is generally considered that the affinity and fixation of ions, both inorganic and organic, in aqueous

solutions to ion exchangers with opposite fixed charges is in part related to the shape and extent of the hydration layer surrounding the ions.<sup>1</sup> However, more detailed information about the mechanism of fixation seems to be rather scanty.

This communication describes some experiments performed by use of the spin label technique<sup>2</sup> with the aim of obtaining further information about the mechanism involved in the fixation of organic ions to ion exchangers. The experiments were performed by use of the stable nitroxide radical 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid, dissolved in water solutions of different pH values. The concentration of the nitroxide radicals was kept relatively low, so that the exchange capacity of the exchanger resins was far from being exceeded ( $3 \times 10^{-6}$  to  $3 \times 10^{-8}$  mol/g resin). The anion exchanger used was AG 1-X4 (minus 400 mesh, chloride form), a strong exchanger with quaternary ammonium exchange groups attached to a styrene-divinylbenzene polymer lattice. The cation exchangers were Bio-Rex 70 (minus 400 mesh, sodium form), a weakly acidic resin containing carboxylic acid exchange groups on an acrylic polymer lattice, and AG 50W-X4 (minus 400 mesh, hydrogen form), a strongly acidic cation exchange resin composed of nuclear sulfonic acid exchange groups attached to a styrene-divinylbenzene lattice. No radicals could be detected in the ion exchangers themselves when suspended in water solutions at pH values below 9 or in organic solvents.

The experimental results were as follows.

(1) The esr spectrum of the nitroxide radicals observed in a water solution in the absence of resin is shown in Figure 1A. When water solutions of the nitroxide radicals were filled into a flat aqueous solution cell of the esr spectrometer together with the anion exchanger AG 1-X4, the esr spectra indicated a slowing down of the motion of the radicals as seen from the reduced height and broadening of the two outer lines, especially of the high field one (Figure 1C). The equilibria seemed to be established in a few minutes in the experiments concerned. The actual pH value of the aqueous phase was about 6. The radicals were completely removed from the resin after rinsing several times with water.

Under the assumption that the line shape of the esr spectra so far discussed (Figure 1A and C) was Lorentzian and that the molecular motion, rotational and translational, was isotropic, the correlation times  $\tau_c$  were calculated according to the method described by Waggoner, *et al.*<sup>3</sup> The parameters used in these calculations were  $A_z \simeq 95$  MHz, measured in water solution at 77 K without resin,  $a = 45$  MHz, measured in a water solution at  $+20^\circ$  without resin, and  $A_x = A_y \simeq 20$  MHz (calculated). This value was obtained under the assumption of axial symmetry which is valid for most nitroxide radicals. In lack of experimentally

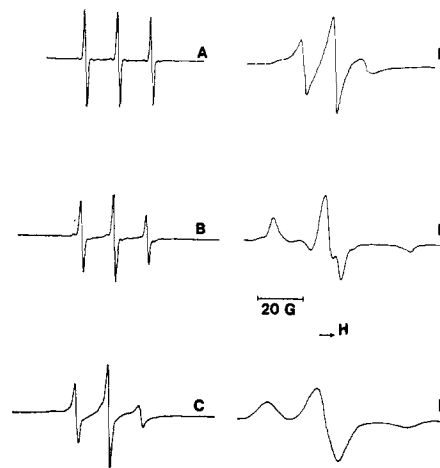


Figure 1. ESR spectra of the nitroxide radical 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid in solution and in the presence of ion exchangers: A,  $3 \times 10^{-7}$  mol in a water solution, no ion exchanger was present ( $+20^\circ$ ); B,  $3 \times 10^{-7}$  mol/g resin in a water solution in the presence of the strong cation exchanger AG 50W-X4 ( $+20^\circ$ ), the pH value of the supernatant solution was 2.6; C,  $3 \times 10^{-7}$  mol/g resin in a water solution in the presence of the strong anion exchanger AG 1-X4 ( $+20^\circ$ ), the pH value of the supernatant solution was 6.2; D,  $3 \times 10^{-6}$  mol/g resin (AG 1-X4) after rinsing with *n*-propyl alcohol ( $+20^\circ$ ); E,  $3 \times 10^{-6}$  mol/g resin (AG 1-X4) after rinsing with acetone ( $+20^\circ$ ); F, E at 77 K.

obtained  $g$  values for the actual radical, the  $g$  values of di-*tert*-butyl nitroxide were used, *i.e.*,  $g_x = 2.0089$ ,  $g_y = 2.0061$ , and  $g_z = 2.0027$ .<sup>4</sup> The correlation times calculated were  $2.2 \times 10^{-11}$  and  $1.9 \times 10^{-9}$  sec for the nitroxide radicals here concerned in the absence and presence of anion exchanger, respectively. The corresponding value obtained at pH 1.2 in the presence of the anion exchanger was  $1.2 \times 10^{-10}$  sec; *cf.* under (2).

(2) The esr spectra obtained with water solutions of the radicals in the presence of the anion exchanger were found to be dependent on the actual pH value of the supernatant solution obtained by the addition of HCl or NaOH. By use of the ratio between the peak-to-peak amplitude of the high field line and that of the center line ( $A(-1)/A(0)$ ) as a relative index of the motion of the nitroxide radicals, it was found that this ratio plotted against pH gave rise to an S-shaped curve, Figure 2. The amplitude ratio was rather constant, about 0.25, at pH values above about 4, but increased rapidly with decreasing pH values to become about 0.80 at pH 1.2, thus indicating an increasing restriction of the molecular motion with increasing pH values. The amplitude ratio corresponding to the spectrum of the nitroxide radicals in a water solution at pH 1 in the absence of resin was 0.93 (unfilled ring in Figure 2). The pH dependence of the esr spectra in the presence of the anion exchanger was also reflected in the calculated correlation times as seen under (1).

(3) The addition of substances such as sodium salicylate or NaCl to the anion exchanger-nitroxide system at pH values above 4 in increasing concentrations successively changed the esr spectrum of Figure 1C into the spectrum shown in Figure 1A.

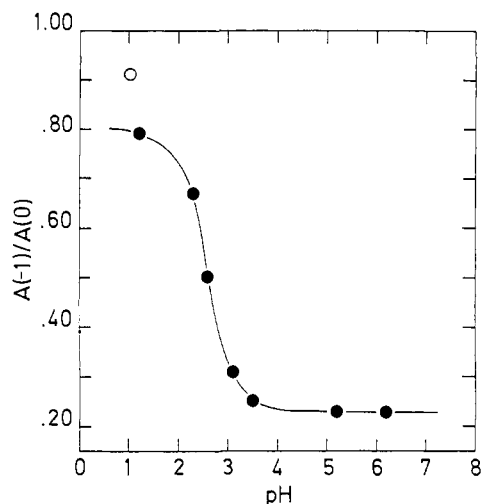
(4) When the anion exchanger previously loaded with nitroxide radicals from a water solution had been rinsed several times with acetone, the esr spectrum of the

(1) R. Kunin, "Ion Exchange Resins," Wiley, New York, N. Y., 1958; R. M. Diamond and D. C. Whitney, "Ion Exchange," Vol. 1, J. A. Marinsky, Ed., Marcel Dekker, New York, N. Y., 1966, Chapter 8; J. Feitelson, "Ion Exchange," Vol. 2, J. A. Marinsky, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 4.

(2) See, *e.g.*, I. C. P. Smith, "Biological Applications of Electron Spin Resonance," H. M. Swartz, J. R. Bolton, and D. C. Borg, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 11.

(3) A. S. Waggoner, O. H. Griffith, and C. R. Christensen, *Proc. Nat. Acad. Sci. U. S. A.*, 57, 1198 (1967).

(4) O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, 43, 2909 (1965).



**Figure 2.** The amplitude ratio,  $A(-1)/A(0)$ , between the peak-to-peak amplitude of the high field line and that of the center line plotted against the pH value for the nitroxide radical 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid in the presence of the strong anion exchanger AG 1-X4 (+20°), filled circles. The unfilled circle represents the amplitude ratio observed in the absence of exchanger resin.

resin phase suspended in acetone exhibited a highly anisotropic spectrum (Figure 1E). The spectrum of Figure 1E obtained at room temperature changed into an almost complete powder spectrum at 77 K (Figure 1F). The anisotropic spectrum could be reversed to the original one, *i.e.*, Figure 1C, after treatment of the acetone-rinsed resin with water.

(5) Rinsing of the resin loaded with nitroxide radicals with methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol, or dimethyl sulfoxide produced spectra of the suspended resin which changed their shape successively from that observed in water solution, Figure 1C, to that obtained in acetone, Figure 1E. A spectrum of an intermediate shape obtained in *n*-propyl alcohol is shown in Figure 1D.

(6) In the presence of the cation exchanger Bio-Rex 70, the nitroxide radicals dissolved in water solutions exhibited a completely isotropic esr spectrum with an almost equal height of the three  $^{14}\text{N}$  hfs lines at room temperature. However, in the presence of the strongly acidic cation exchanger AG 50W-X4, there was a minor decrease in the amplitude ratio as shown in Figure 1B. No change of the amplitude ratio could be observed in the pH range between 2.6 and 9. The esr signals disappeared completely from both cation resins after treatment with acetone in contrast to the case of the anion exchanger as described under (4) and (5).

The experimental results described under (1) and (2) indicated that the slowed down or restricted motion was due to an attachment of the nitroxide radicals to the anion exchanger. The pH dependence of the amplitude ratio (Figure 2) and the correlation times indicated that the radicals became attached to the anion exchanger much more efficiently when the carboxylic groups of the nitroxide radicals had been dissociated and the radicals were present as anions. Obviously, the fixation mechanism involved a charge-charge interaction in this case.

However, a minor degree of attachment was also

present when the carboxylic groups were undissociated, as seen from the difference in the amplitude ratios observed at pH 1 in the presence and absence of anion exchanger (Figure 2). Such a noncharge fixation was also observed with the strongly acidic cation exchanger AG 50W-X4 as shown in Figure 1B but not with the weakly acidic resin Bio-Rex 70. The observation of a noncharge fixation made with the former exchanger was in conformity with the results obtained by Chesnut and Hower<sup>5</sup> in their study of the interaction of the neutral nitroxide radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl-4-ol with the strong cation exchanger Dowex 50.

The S-shaped curve obtained by plotting the amplitude ratio  $A(-1)/A(0)$  against pH is very similar to the curves generally obtained for acid-base titrations. In analogy with such curves, the inflection point of Figure 2 indicated the pH value at which half the number of the radicals was attached to the resin by the mechanism of charge-charge interaction in the anion form. Consequently, it was expected that the pH value of the inflection point of Figure 2 (pH 2.6) would have been equal to the pK value of the radical acid concerned. However, the pK value obtained by titration of the radical acid was 3.8. This discrepancy seems to be explained, at least qualitatively, by the presence of the noncharge fixation of the radicals to the resin which induced a shift of the apparent inflection point of the S-shaped curve toward a lower pH value, as well as a reduction of the amplitude ratio actually observed at pH 1.2 in Figure 2.

The mechanism of charge-charge fixation was further supported by the results of the competition experiments described under (3) and by the rinsing experiments (4) and (5), which showed that the anion radicals fixed by charge-charge interaction could not be removed by organic solvents. No such fixation was present in the case of the cation exchangers (6), as expected.

In water solutions the attached radicals were still allowed to move rather easily, even if their motion had been slowed down to a considerable extent as compared with completely free ions. This freedom of motion is considered to be due to the presence of hydration layers surrounding the ionized carboxylic group of the nitroxide radical and probably also the charged sites on the exchanger resin.

Rinsing the resin with organic solvents (4 and 5) removed the hydration layers. The alcohols were considered to replace the water in part and to form double layers between the anion and the cation sites on the resin. No double layers remained after rinsing with acetone. The radical anions and the fixed positive charges on the resin now come much closer to each other, a situation which produced a firm fixation with an immobilization of the radical anions (Figure 1E).

A comparison with the spectrum taken at 77 K (Figure 1F), a temperature at which there is a complete immobilization of the radicals, indicated that there was some motion of the radicals at room temperature (Figure 1E). This motion might be an anisotropic *z*-axis rotation, as seen from the similarity of our anisotropic spectrum to that obtained by Birrell, *et al.*<sup>6</sup>

(5) D. B. Chesnut and J. F. Hower, *J. Phys. Chem.*, **75**, 907 (1971).

(6) G. B. Birrell, O. H. Griffith, and D. French, *J. Amer. Chem. Soc.*, **95**, 8171 (1973).

A further analysis, including spectra taken at 35 GHz, seems to be needed before a complete model could be given of the anion radicals fixed to the resin by the carboxylic group.

Further investigations are in progress with ion exchangers with different exchange groups and with other nitroxide radicals in addition to that so far used.

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### Intermediacy of Metal-Olefin Complexes in Cycloaddition and Insertion Reactions at Transition Metal- $\eta^1$ -Allyl Bonds

Sir:

Synthetic aspects of cycloaddition and insertion reactions of transition metal- $\eta^1$ -allyl complexes have been the subject of a number of investigations.<sup>1,2</sup> More recently, interest has developed in the mechanism of these processes.<sup>2-4</sup> Although it is generally accepted<sup>2-4</sup> that they proceed through a dipolar metal-olefin intermediate, no direct evidence has been presented in support of this hypothesis.<sup>5</sup> Herein we wish to report spectroscopic detection and isolation as the cationic  $\eta^2$ -(allyl sulfone) complexes of such zwitterionic intermediates.

Reactions of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>( $\eta^1$ -allyl) (**1a-d**) with SO<sub>2</sub> are known to afford S-bonded sulfinato complexes (**2a-d**, respectively).<sup>7-9</sup> We now find that freshly prepared (5-10-min old) solutions of **1a-d** ( $\sim 7 \times 10^{-3}$  M) in neat SO<sub>2</sub> at -35 to -18° show two intense  $\nu_{C=O}$  ir bands at 2085-2078 and 2050-2040 cm<sup>-1</sup>.<sup>10</sup> These frequencies are much too high to be attributed to the parent  $\eta^1$ -allyl complex (2018-2005, 1962-1945 cm<sup>-1</sup>)<sup>6,7</sup>

(1) (a) F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 289 (1968); (b) Y. Yamamoto and A. Wojcicki, *Inorg. Chem.*, **12**, 1779 (1973).

(2) (a) W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, **93**, 5299 (1971); (b) W. P. Giering, S. Raghu, M. Rosenblum, A. Cutler, D. Ehntholt, and R. W. Fish, *ibid.*, **94**, 8251 (1972); (c) A. Rosan, M. Rosenblum, and J. Tancrede, *ibid.*, **95**, 3062 (1973); (d) M. Rosenblum, *Accounts Chem. Res.*, **7**, 122 (1974).

(3) A. Wojcicki, *Advan. Organometal. Chem.*, **12**, 31 (1974).

(4) C. V. Magatti and W. P. Giering, *J. Organometal. Chem.*, **73**, 85 (1974).

(5) However, protonation of iron- $\eta^1$ -allyl complexes to the corresponding iron- $\eta^2$ -olefin cations has been known for some time.<sup>6</sup>

(6) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

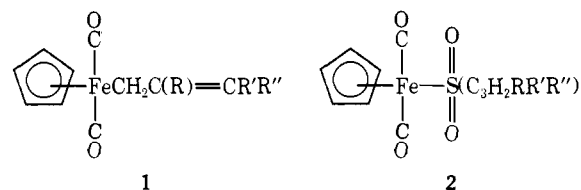
(7) (a) R. L. Downs and A. Wojcicki, *Inorg. Chim. Acta*, to be submitted for publication; (b) R. L. Downs, Ph.D. Thesis, The Ohio State University, 1968.

(8) J.-Y. Merour, *C. R. Acad. Sci.*, **271**, 1397 (1970).

(9) A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Amer. Chem. Soc.*, **94**, 4354 (1972). These authors reported the formation of **2a** from **1a** but did not furnish any spectroscopic properties.

(10) Recorded using a modified VLT-2 variable low-temperature cell unit from Research and Industrial Instruments Co., London, England. For details see S. E. Jacobson and A. Wojcicki, *J. Amer. Chem. Soc.*, **95**, 6962 (1973).

but are virtually identical with those of several cationic complexes containing  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>( $\eta^2$ -olefin)<sup>+</sup> or



- 1  
2
- a, R = R' = R'' = H  
b, R = R' = H; R'' = CH<sub>3</sub>  
c, R = H; R' = R'' = CH<sub>3</sub>  
d, R = CH<sub>3</sub>; R' = R'' = H

$\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>( $\eta^2$ -allene)<sup>+</sup>.<sup>6,11</sup> Storage of these solutions leads to the appearance and growth of the  $\nu_{C=O}$  absorptions of **2a-d**<sup>7,8</sup> at 2066-2065 and 2022-2020 cm<sup>-1</sup>, as the intensities of the original bands decrease. The two sets of the  $\nu_{C=O}$  absorptions attain comparable intensities as a function of the allyl fragment in the order: **1c** (100 min, -35°)  $\sim$  **1d** (110 min, -35°)  $>$  **1b** (120 min, -18°)  $>$  **1a** ( $\sim$ 200 min, -18°). In the spectra of **1a** in SO<sub>2</sub> there also appear, and increase in intensity, a broad band at 1967-1960 cm<sup>-1</sup> and a shoulder at  $\sim$ 2005 cm<sup>-1</sup>; corresponding absorptions are not discernible for SO<sub>2</sub> solutions of **1b-d**.

Low-temperature nmr spectra of freshly prepared SO<sub>2</sub> solutions of **1a-d** in the C<sub>5</sub>H<sub>5</sub> proton region ( $\tau$  4.0-5.5) show a strong resonance at  $\tau$  4.30-4.40 which is assigned to the reaction intermediate. The position of this signal is compatible with the positive charge on the iron as, e.g., in  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>( $\eta^2$ -olefin)<sup>+</sup>.<sup>6</sup> Upon storage of the solutions of **1b-d** at -40 to -22°, the resonance at  $\tau$  4.30-4.40 decreases and another resonance, due to **2b-d**,<sup>7,8</sup> respectively, appears and grows at  $\tau$  4.75-4.78. The nmr spectrum of the SO<sub>2</sub> solution of **1a** undergoes the following changes with time at -22°.<sup>12</sup> The signal at  $\tau$  4.36 decreases in intensity and resonances appear at  $\tau$  4.78 (due to **2a**) and 5.00. This is followed by a gradual appearance of yet another signal, at  $\tau$  5.03, and diminution of intensity of the peak at  $\tau$  5.00. After the signal at  $\tau$  4.36 has virtually disappeared, the combined intensity of the resonances at  $\tau$  5.00 and 5.03 remains constant, with the latter increasing and the former decreasing. The limiting spectrum ( $\sim$ 5 days) shows only the peaks at  $\tau$  4.78 and 5.03.

On the basis of the above spectroscopic data and virtual lack of conductivity of a freshly prepared SO<sub>2</sub> solution of **1a**,<sup>13</sup> the observed reaction intermediates are assigned zwitterionic structures **3a-d**. This assignment is strengthened by the preparation and characterization of **4a** via reaction of **3a** (from 1.0 g, 4.7 mmol, of **1a**) in neat SO<sub>2</sub> (5 ml) with (CH<sub>3</sub>)<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> ( $\sim$ 6

(11)  $\nu_{C=O}$  absorptions occur at 2090-2080 and 2060-2040 cm<sup>-1</sup>: (a) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963); (b) J. Benaim, J.-Y. Merour, and J.-L. Roustan, *C. R. Acad. Sci.*, **272**, 789 (1971); (c) D. W. Lichtenberg, Ph.D. Thesis, The Ohio State University, 1973.

(12) Only a qualitative description of changes in the  $\tau$  4.0-5.5 region is given herein. Details of the nmr spectra will be provided in our full paper.

(13) A freshly prepared  $1.2 \times 10^{-2}$  M solution of **1a** in SO<sub>2</sub> at -70° exhibits  $\Delta_M = 2.24$  ohm<sup>-1</sup>cm<sup>2</sup>. By comparison,  $\Delta_M = 84$  ohm<sup>-1</sup>cm<sup>2</sup> for [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>PC(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sup>+</sup>PF<sub>6</sub><sup>-</sup>,<sup>14</sup> which is in the region expected for 1:1 electrolytes.

(14) S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Inorg. Chem.*, **12**, 717 (1973).