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CONVERSION OF THE DIAMAGNETIC NONAMETHYLFERROCENYLCARBENIUM SALTS INTO THE PARAMAGNETIC SALTS OF BIS(NONAMETHYLFERROCENIUMYL)ETHANE *

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Summary

Conversion of the diamagnetic salt of the nonamethylferrocenylcarbenium primary cation into the paramagnetic salt of bis(nonamethylferroceniumyl)ethane has been studied by high-resolution NMR in solution and, mainly, by spin–lattice and spin–spin relaxation in solids. For the first time the dependence of the conversion rate on the nature of the anions BF_4^-, PF_6^-, $AlBr_4^-$ and the aggregate state of the sample has been established. Possible mechanisms of the conversion are discussed.

Introduction

Ferrocenylcarbenium ions are diamagnetic species and are well studied by various methods [1]. Some ferrocenylcarbenium ions have been observed to form dimeric products [2–4]. This formation was assumed to proceed through the intramolecular redox process resulting in conversion of the diamagnetic carbenium ions (Ia) into paramagnetic species (Ib). The subsequent recombination of the latter results in the dimeric products (II) (see Scheme 1) [5,6].

We now report isolation of the relatively stable primary ferrocenylcarbenium ion and its conversion to a dimeric substance. High-resolution NMR and spin–lattice and spin–spin relaxation methods have been used for the study of this conversion. Until now the researchers dealt with either very stable cations which did not convert into the paramagnetic substances [1,7,8] or, with unstable diamagnetic cations whose

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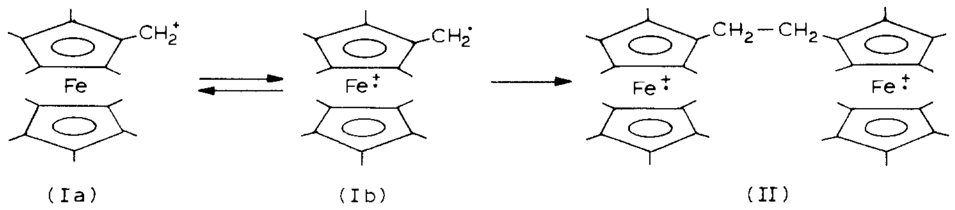
* Dedicated to Professor O.A. Reutov on the occasion of his 65th birthday in recognition of his outstanding research in organometallic chemistry.



SCHEME 1 *

conversion into the paramagnetic substance was so rapid that isolation was impossible [4].

Results

Recently we have demonstrated that the nonamethylferrocenylcarbenium ion is readily produced from the corresponding carbinol III under the action of various acids [9]. This diamagnetic ion can easily be precipitated as a salt with suitable anions ($A = BF_4^-$, PF_6^-, $AlBr_4^-$, ClO_4^-). Its tetrafluoroborate ($IV \cdot BF_4$) is stable at 20°C for approximately 0.5 h **. Reduction of the cation by $NaBH_4$ in aqueous ethanol resulted in decamethylferrocene [9].

This diamagnetic salt ($IV \cdot A$) is rather easily transformed into a paramagnetic substance both in the solid state and in solutions with time. The paramagnetic compound obtained was identified by analytical data, ^1H and ^{13}C NMR spectra, electron impact (EI) and field desorption (FD) mass spectra (see below).

On the basis of these results it can be assumed that the paramagnetic substance is a dimeric form of the salt 1,2-bis(nonamethylferroceniumyl)ethane ($V \cdot A_2$). It must be pointed out that reduction of the paramagnetic salt $V \cdot A_2$ with $NaBH_4$ in aquous ethanol resulted in 1,2-bis(nonamethylferrocenyl)ethane (VI). Further evidence for the dimeric structure of $V \cdot A_2$ was obtained from studies of spin–spin relaxation in solids (see below). Unfortunately, none of the numerous attempts to grow single crystals of the salts $V \cdot A_2$ (with $A = BF_4^-$, PF_6^- and ClO_4^-) were succesful ***.

In this work we studied qualitatively the conversion of the diamagnetic salts $IV \cdot A$ into the paramagnetic salts $V \cdot A_2$ in solutions, using high-resolution NMR. The kinetics of this conversion were also studied in solids by using spin–lattice and spin–spin relaxation (SLR and SSR).

^1H and ^{13}C NMR spectra of ($IV \cdot A$) and ($V \cdot A_2$) salts

We studied the ^1H and ^{13}C NMR spectra of the cation IV, obtained by dissolving carbinol III in acids, and the solution of the freshly precipitated compounds (see Tables 1 and 2).

Analysis of the data in Tables 1 and 2 shows that the spectra of compounds $IV \cdot A$ in various acids are practically identical.

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* Since Ia and Ib are in different spin states, they are not resonance hybrids.

** The solid salt of the cation $C_5H_5FeC_5H_4CH_2^+ BF_4^-$ was reported to be produced at −50°C [10]. In solution this compound was found to be stable for several hours below −20°C and for 10–20 min at +20°C. It was identified only by the ^1H NMR spectrum.

*** Hence, dimerisation occurring during reduction or in the mass spectrometer can not be excluded.

TABLE 1

^1H NMR SPECTRA OF IV·A (carbinol in acids)

Solvent	Chemical shifts [a] (integral intensity)			
	(α- or β-Me)	1′-Me	(β- or α-Me)	CH_2^+
$CF_3COOH/CDCl_3$	1.319(3)	1.620(7.5)	1.940(3)	5.265(1)
H_2SO_4	1.10(3)	1.43(7.5)	1.67(3)	4.98(1)

[a] Relative to internal TMS.

TABLE 2

^{13}C-{^1H} NMR SPECTRA OF IV·A (carbinol in acids)

Solvent	Chemical shifts		
	Me groups	CH_2^+	C of the ring carbon
$CF_3COOH/CDCl_3$ [a]	7.10 [d], 9.19 [d]	90.73 [e]	92.09, 93.46, 107.30
FSO_3H/SO_2 liq. [b]	7.14, 9.25	90.75	92.73, 93.86, 107.62
CH_2Cl_2 [a,c]	7.10, 9.19	91.23	92.13, 93.46, 107.34

[a] At room temperature. [b] At −70°C. [c] A solution of freshly precipitated $C_5Me_5FeC_5Me_4CH_2^+ BF_4^-$ (IV·BF_4). [d] In the undecoupled ^{13}C NMR spectrum, these lines are observed in the form of two identical quadruplets with $J(^{13}C-^1H)$ equal to 129.4 Hz. [e] In the undecoupled ^{13}C NMR spectra the signal is a triplet with $J(^{13}C-^1H)$ 164.1 Hz.

We have also identified compounds of the type V·$(BF_4)_2$ by ^1H and ^{13}C NMR spectra. The corresponding chemical shifts in ppm and linewidths ($\Delta\nu$) in Hz of signals observed are given in Tables 3 and 4.

Examination of Tables 3 and 4 shows that chemical shifts of the diamagnetic IV·BF_4 and paramagnetic V·$(BF_4)_2$ are typical of the diamagnetic ferrocenylcarbenium ions [1] and paramagnetic salts of polymethylferrocenium [11]. The weak solvent dependence of chemical shifts and usual temperature dependence (see, for instance, ref. 12) suggest that V·$(BF_4)_2$ is indeed an individual compound and does not dissociate into monomer species in the solution.

Repeated recording of the spectrum of the solution of carbinol III in $CF_3COOH/CDCL_3$, after storing for three days gave the picture shown in Fig. 1. It represents a superposition of the dimagnetic salt IV·A and paramagnetic compound V·A_2 (A = $OCOCF_3^-$) spectra. The relative integral intensity of the latter increases

TABLE 3

^1H AND ^{13}C NMR SPECTRA OF V·$(BF_4)_2$ AT ROOM TEMPERATURE [a]

Solvent	Chemical shifts (linewidths in Hz)	
CH_3NO_2	−28(1650)	−35(650)
CD_3CN	−30(1650)	−35(650)
$CD_3CN+CDCl_3$	−29(1650)	−34(650)
CD_3CN	−15(272) [b], −11.3(136) [b]	+252(434) [c]

[a] Bruker-WP-200-SY (200.13 MHz) NMR spectrometer. [b] ^{13}C-{^1H} spectra. ^{13}C signals of the Me group (at 50.327 MHz). [c] ^{13}C-{^1H} spectra. ^{13}C signals of the ring carbon.

TABLE 4

^{1}H NMR SPECTRA OF V·$(BF_4)_2$ IN CD_3CN AT DIFFERENT TEMPERATURES [a]

Temperature	Chemical shifts (linewidth, Hz)		
−30°C	−32.5(1100)	−36.2(1200)	−43.0(700)
+23°C	−26.8(800)	−29.8(800)	−35.5(500)
+70°C	−23.6(850)	−26.2(850)	−31.1(400)

[a] Bruker-WH-250 NMR spectrometer.

with time. Under such conditions (A = $OCOCF_3^-$, excess of CF_3COOH) the conversion proceeds slowly enough and the amount of V · A_2 in 16, 40 and 75 h is 5, 11, and 19%, respectively.

Investigation of SLR and SSR of salts IV · A and V · A_2

In studying SLR and SSR we took into account the following considerations. The reaction mechanism and, therefore, the SLR rate are sensitive even to insignificant paramagnetic impurities [13]. Since the final product is paramagnetic, studies of the kinetics of the conversion IV · A → V · A_2 become feasible. Both SLR and SSR might be sensitive to molecular motions of different kinds (reorientations and diffusion) so that determination of the motion character and of the relevant thermodynamic parameters may be a source of structural information of the compounds studied.

If there are different SLR mechanisms, the observed relaxation rate is the sum of the rates for separate mechanisms. In our case, SLR can be contributed by the

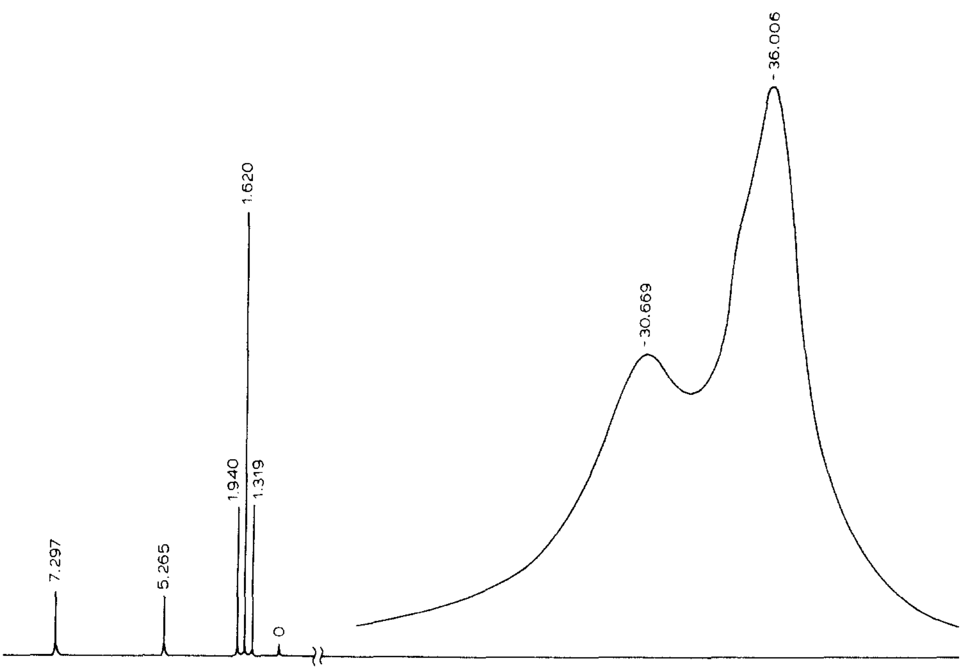


Fig. 1. ^{1}H NMR spectrum of IV·$OCOCF_3$ after partial conversion into V·$(OCOCF_3)_2$.

molecular motions and interaction with the paramagnetic centres:

$$\frac{1}{T_{1\,\text{obs.}}} = \frac{1}{T_{1\,\text{mol.mot.}}} + \frac{1}{T_{1\,\text{param.}}} \tag{1}$$

Here T_1 is the SLR time.

In order to evaluate the individual rates, we have measured the temperature dependence of the SLR time in decamethylferrocene (VII) (Fig. 1). It was assumed that under our experimental conditions its conversion into the paramagnetic ferrocenium salt could be neglected, so that paramagnetic contribution to SLR could also be neglected, while molecular motions must be similar to those in the cation IV. Figure 2 shows that SLR in VII is induced by motions of two kinds. At high temperatures ($T > 170$ K), the main contribution to the relaxation comes from rotation of the cyclopentadienyl rings around the 5-fold axis. T_1 is minimum and the SLR rate is maximum at 233 K: T_1 106 msec. The corresponding reorientation thermodynamical parameters are E_a 3.1 ± 0.2 kcal/mol and τ^{∞} $(1.4 \pm 0.8) \times 10^{-12}$ sec. They agree with the results of ref. 14 (E_a 3.3 kcal/mol and τ^{∞} 9×10^{-11} sec) and of ref. 15 (E_a 3.2 kcal/mol), both based on ^{13}C NMR spectra. At $T < 170$ K, SLR is determined by the rotation of the methyl groups around the 3-fold axis (E_a 1.3 ± 0.1 kcal/mol).

In the initial compound IV · BF_4 the relaxation proved to be temperature-independent and much faster than that in VII (Fig. 2). This means that already in IV · BF_4 the relaxation is determined by intraction with the paramagnetic centres. At high temperatures ($T > 295$ K) the SLR time drops approximately 50 times (Fig. 2).

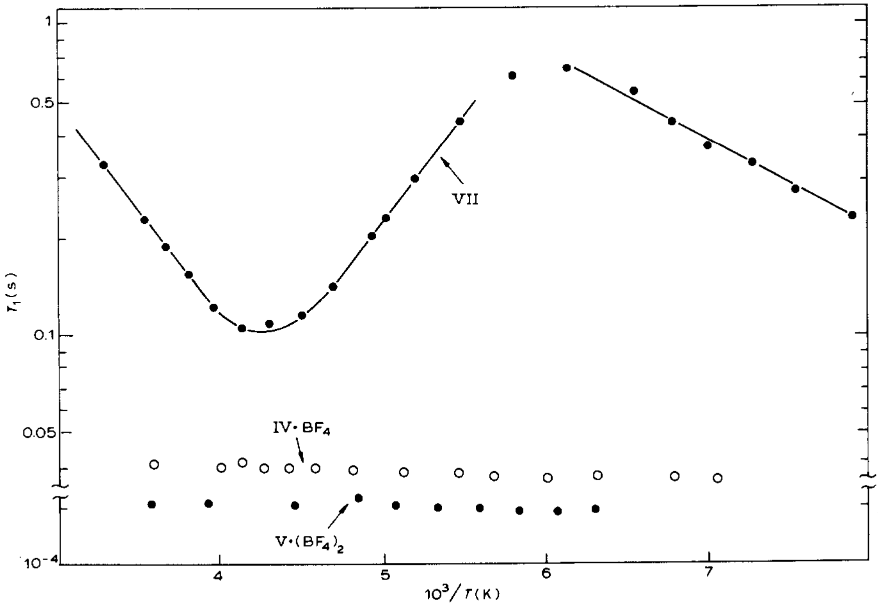


Fig. 2. Temperature dependence of SLR time T_1 in IV·A, V·A_2 and VII. Note the break on the ordinate axis indicating the 50-fold reduction of T_1 after the conversion IV·A → V·A_2. The solid line represents T_1 for VII calculated assuming E_a^{Cp} 3.1 kcal/mol, τ^{∞} 1.4×10^{-12} s and E_a^{Me} 1.3 kcal/mol.

This correlates with the complete conversion $IV \cdot BF_4 \rightarrow V \cdot (BF_4)_2$. Similar behaviour was observed for other anions (PF_6^- and $AlBr_4^-$).

If we assume that SLR is dominated by interaction with the paramagnetic centres, then [13]:

$$\frac{1}{T_1} \sim N \tag{2}$$

where N is the concentration of the paramagnetic centres. If N rises with temperature by the exponential law:

$$N = 1 - \exp(-t/t_0) \tag{3}$$

then it is conventient to plot the time dependence of the quantity

$$\ln(1 - N) = \ln\frac{1/T_1^{\infty} - 1/T_1}{1/T_1^{\infty}} \quad \text{vs. } t$$

Here t is the conversion time, and $1/T_1^{\infty}$ is the SLR time in the purely paramagnetic compound $V \cdot A_2$. The corresponding anamorphosises are shown in Fig. 3. The time dependence of the paramagnetic centre concentration is nonlinear. Hence, the production of compound $V \cdot A_2$ is kinetically complex and at least a two-stage process. We have tried to evaluate the energetics on the basis of the half-conversion time $\tau_{1/2}$ (Fig. 4). The values of the effective activation energies and the pre-exponential factors are presented in Table 5.

From our studies of salts $IV \cdot A$ and $V \cdot A_2$ we conclude that SLR is determined solely by interaction with the paramagnetic centres. The above data have enabled us

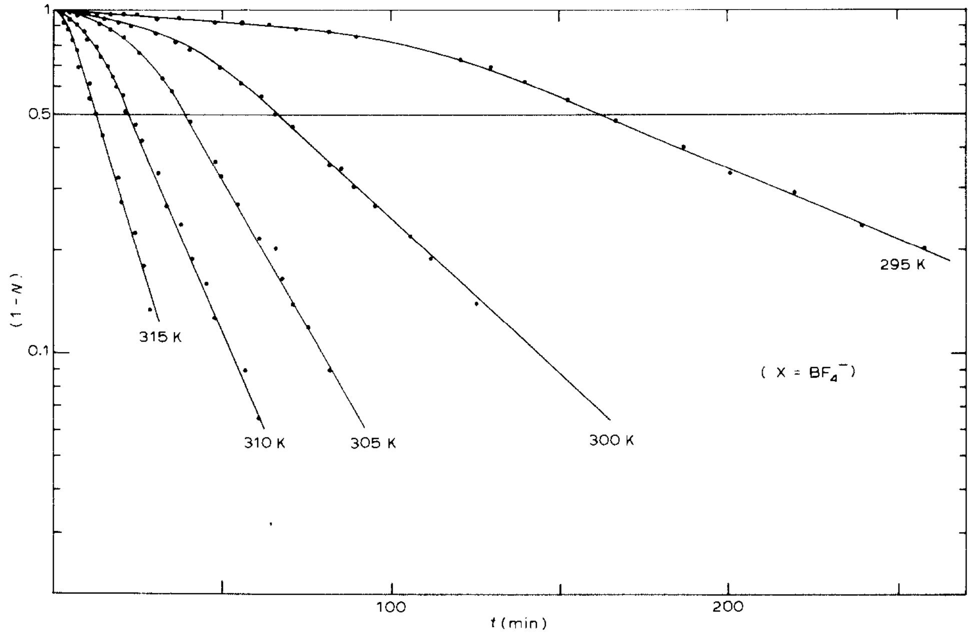


Fig. 3. Kinetics of accumulation of the paramagnetic centres in IV·A ($A = BF_4^-$). Plotted along the vertical axis is a quantity $(1/T_1^{\infty} - 1/T_1(t))/(1/T_1^{\infty})$ equal to $(1 - N)$ where N is the relative concentration of the paramagnetic centres (see text).

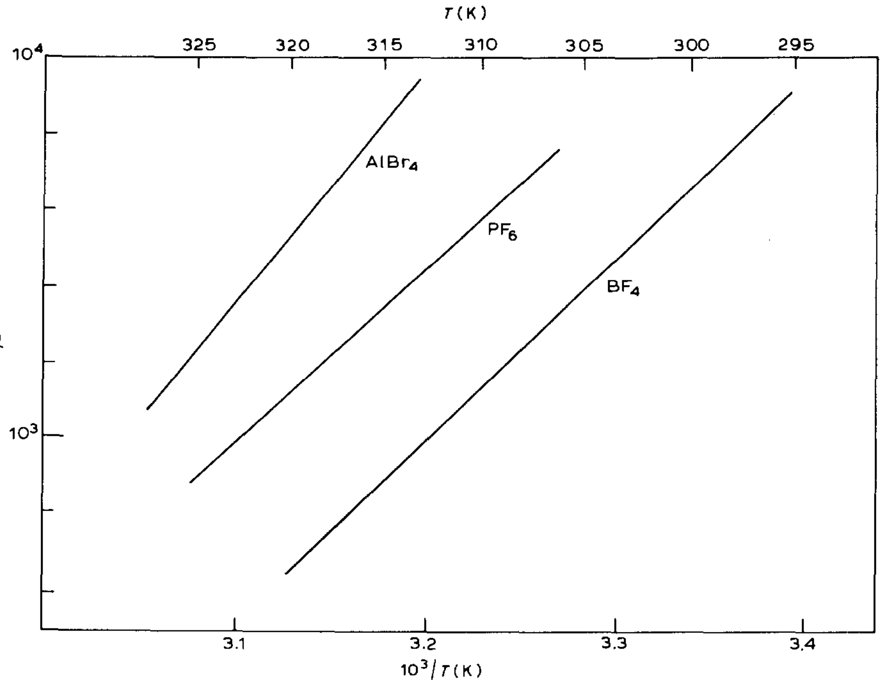


Fig. 4. Half-conversion time as a function of reverse temperature for three different anions.

to determine the kinetics of the process and to find the relevant thermodynamic parameters. However, they do not give any information on the molecular motions. For this reason we have investigated SSR in the same compounds.

The temperature dependence of the SSR time in compounds IV · A and V · A_2 is shown in Fig. 5. An abrupt line broadening in the curve of decamethylferrocene(VII) in the temperature range 160–110 K is due to freezing of the rotation of cyclopentadienyl rings around the 5-fold axis. The principal conclusions from the above data on SSR are as follows:

(i) At high temperature the line in IV · A is broader than in VII due to either the intermolecular dipole–dipole interaction of $^1H-^{19}F$ and $^1H-^{10,11}B$ ($^1H-^{31}P$, $^1H-^{27}Al$) in V · A_2 or to different reorientational behaviour of the cyclopentadienyl rings.

(ii) Completion of the conversion IV · A → V · A_2 is followed by further line broadening and its subsequent broadening with decrease in temperature becomes less pronounced.

TABLE 5

THERMODYNAMICAL PARAMETERS OF THE CONVERSION PROCESS 2 IV·A → V·A_2[a]

Anion	E_a (kcal/mol)	$-\lg(\tau_{0(s)})$	$\tau_{1/2}$ (min) (T 315 K)
BF_4^-	23.2±0.8	13.3±0.7	12
PF_6^-	20±2	10.5±1.5	40
$AlBr_4^-$	30±2	14.7±1.5	115

[a] The half-conversion time was supposed to obey the Arrhenius law $\tau_{1/2} = \tau_{1/2}^0 \cdot e^{Ea/RT}$

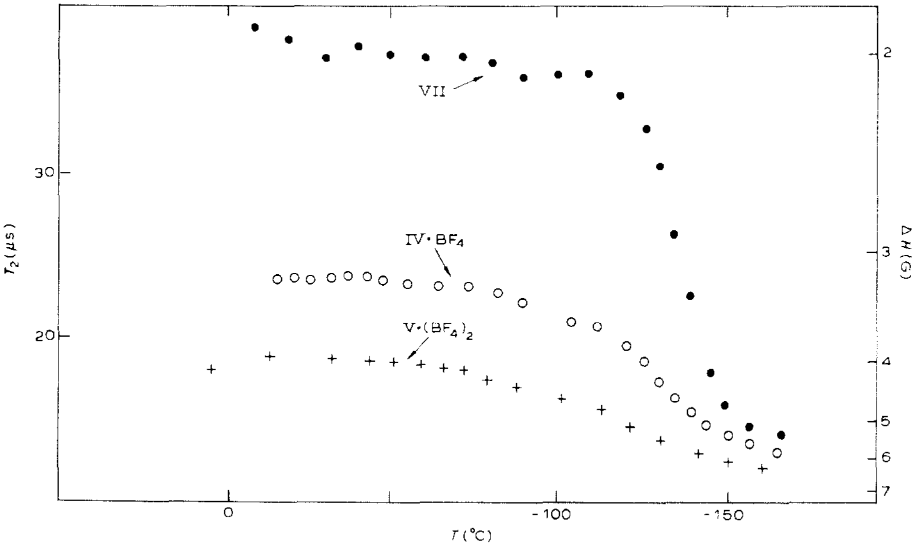


Fig. 5. Temperature dependence of SSR time T_2 for IV·A, V·A_2 and VII. Plotted on the right-hand vertical axis is the line-width, calculated from T_2 under assumption of the Gaussian shape of the line.

These results suggest the change in the character of the molecular motions in compound V · A_2 is induced by structural transformation of the molecule and the crystal lattice. Our data on SSR and linewidths in compounds IV · A and V · A_2 (Fig. 5) agree with the dimeric, rather than the monomeric, structure of the green paramagnetic substance V · A_2.

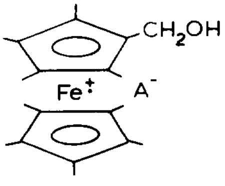
Line broadening during the IV · A → V · A_2 conversion (linewidths change from 5 to 9 G at $T < 170$ K) suggests less intensive molecular motion in V · A_2. This is possibly due to the absence of the rotation of one of the cyclopentadienyl rings due to dimerization and formation of the fragment $-CH_2-CH_2-$, which gives a broader spectrum than the isolated methyl groups. Unfortunately, in our case exact calculation of the linewidths is impossible since there is no information on the lattice structure.

Discussion

Having studied the behaviour of salts IV · A and V · A_2 in solutions by high-resolution NMR and the kinetics of the conversion IV · A → V · A_2 (A = BF_4^-, PF_6^-, $AlBr_4^-$) in solids by SLR and SSR, we have demonstrated that the conversion rate depends on the nature of the anion (see Table 5). In earlier investigations of this conversion (Scheme 1) the role of anions was ignored, and the process was supposed to be a purely intra-molecular redox-process [4,5,6], followed by dimerisation of the generated particles [2–4].

In general, conversion depends on size, oxidation potential and nucleophilicity of the anion. Therefore, we have confined ourselves to anions A = BF_4^-, PF_6^-, $AlBr_4^-$, which hardly have any nucleophilic reactivity and do not possess oxidizing properties [16].

SLR studies of the conversion kinetics in solids have shown, that the conversion rate decreases with increasing anion size in the sequence $BF_4^- > PF_6^- > AlBr_4^-$ (see Table 5). The migration of ions is probably a limiting stage of the reaction. The data also show that the kinetics of the conversion $IV \cdot A \rightarrow V \cdot A_2$ are complex (at least a two-stage process) and may be complicated by the reconstruction of the crystal lattice. It should be noted that all the samples studied contained a small impurity of paramagnetic particles (< 1%) even when SLR recording began. There may be several sources of these paramagnetic centres. The most probable is production of the paramagnetic molecules $V \cdot A_2$ during the synthesis of the substance and its preparation for SLR measurements. It is also possible, that production of the initial salt is accompanied by another process, leading to the formation of the ferrocenium salts of carbinols (VIII).

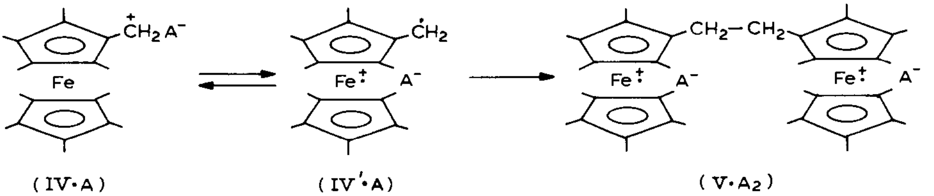


(VIII)

This may be due to the rather high oxidation capacity of iron atoms in ferrocenes. It is noteworthy that the oxidation potential of decamethylferrocene is ~ 0.5 V lower than that of unsubstituted ferrocene [17]. However, attempts to prepare such salts have not yet been successfull.

It is also possible that the initial paramagnetism of the samples is due to the presence of the stationary concentration of the salt $IV' \cdot A$, formed as a result of migration of anion A from the carbon to the iron atom. This can facilitate subsequent dimerization $IV' \cdot A \rightarrow V \cdot A_2$. Hence we propose Scheme 2 for the process which includes migration of anions.

Scheme 2 is consistent with kinetic data on the dependence of the process rate and the nature of the anion. The charge transfer induced by the anion diffusion begins at high temperatures. This is confirmed by effective "activation energies" and pre-exponential factors (see Table 5) typical for diffusion of ions in solids [18] and by higher formation temperatures of $V \cdot A_2$ with increasing size of the anion. Hence, the first stage of the process presumably is accumulation of $IV' \cdot A$, while at concentrations 0.1–0.2 dimerization $IV' \cdot A \rightarrow V \cdot A_2$ begins (see Fig. 3). Thus, the



SCHEME 2

migration of anions from the carbon eliminates the steric hindrance for dimerization of the species and favours the electronic conditions for this process.

There have been several attempts to prove the existence of paramagnetic species of the type IV′ · A by EPR spin trapping [5,6] and Mössbauer spectroscopy [19]. However, the interpretation of these results is ambiguous. Our scheme for the process agrees with qualitative results obtained in studying the conversion IV′ · A → V · A_2 in solutions by high-resolution ^{1}H and ^{13}C NMR spectra. The spectrum of the freshly prepared samples contains only narrow signals, corresponding to the diamagnetic compound IV · A. This may be due to a low stationary concentration of IV′ · A in solution. Diffusion in liquid is, obviously, more rapid than in the crystal lattice, but because of the low concentration of IV′ · A the conversion rate is decreased drastically, so that even after three days at room temperature the concentration of the paramagnetic substance V · A_2 is only ~ 20%.

The above assumption that the initial paramagnetism of the samples is due to the equilibrium IV · A ⇄ IV′ · A had to be checked for the salts with stable cations containing sterically screened carbenium centres in which the dimerization is hindered. We chose diferrocenylcarbenium tetrafluoroborate, whose structure had previously been determined by X-ray analysis [8]. According to the ^{1}H NMR spectra in solutions, it is a diamagnetic compound and can be stored for a long time in the solid state. SLR and SSR studies of freshly prepared samples of this salt have shown that the concentration of the paramagnetic centres is $\leqslant 1\%$. The number of these centres remains constant for a long time with increasing temperature. It may be assumed that in the solid state the equilibrium IV · A ⇄ IV′ · A occurs. This equilibrium was not observed in solution by ^{1}H NMR probably because of a relatively low concentration of the paramagnetic substance.

It is less likely that the initial paramagnetism of samples should be attributed either to impurities or to reaction products, e.g. V · A_2 or ferrocenium carbinols of type VIII, as in these cases not only dimerization would have been hindered. However, the oxidation capacity would have decreased, since the cyclopentadienyl rings do not contain methyl substituents. The initial paramagnetism is consistent with the first stage of reaction scheme 2, the equulibrium IV · A ⇄ IV′ · A. However, the available data are not sufficient to support the existence of such an equilibrium. We shall continue our study with other salts with stable sterically screened ferrocenylcarbenium salts.

Experimental

The high-resolution NMR spectra were recorded on Bruker-WP-200-SY and Bruker-WH-250 spectrometers. Relaxation measurements were performed on a Bruker-SXP-4-100 pulsed spectrometer at a proton resonance frequency of 88.1 Hz. The EI and FD mass spectra were measured with a CH-5-FD (Varian MAT) spectrometer, supplemented by the combined ion source FD/FI/EI.

Preparation of samples for NMR studies. A modified method [20] was used to prepare salts IV · A ($A = BF_4^-$, PF_6^-) from carbinol III. Initial carbinol III was earlier prepared by us [9].

Synthesis of IV · A ($A = BF_4^-$, PF_6^-). A solution of "anhydrous" HBF_4 or HPF_6 (previously prepared by careful dropwise addition of 0.8 ml of a 48% aqueous solution of HBF_4 or a 70% solution of HPF_6 to a −20°C cooled solution of 4 ml $(CF_3CO)_2O$ and 10 ml dry ether) was added dropwise to 30 ml of an ethereal solution of 0.5 g (1.46 mmol) of III, containing 1 ml of $(CF_3CO)_2O$ at −20°C during 5 min. The red precipitate thus formed was filtered off on a cooled glass filter. The precipitate was carefully washed with dry ether, dissolved in ~ 5 ml of cooled (~ −20°) CH_2Cl_2 and again precipitated in 200 ml of dry ether and filtered. It was then washed 3–5 times with dry ether and with cooled pentane, dried in vacuum, and transferred to the SLR/SSR spectrometer's ampule which was sealed. All the above operations were performed in argon. Analysis. IV · BF_4 Found: C, 57.15; H, 6.89; Fe, 12.18, $C_{20}H_{29}BF_4Fe$ calcd.: C, 58.28; H, 7.09; Fe, 13.55%. V · $(BF_4)_2$ Found: C, 57.73; H, 6.96; Fe, 14.30; F, 17.92. $C_{40}H_{58}B_2F_8Fe_2$ calcd.: C, 58.28; H, 7.09; Fe, 13.55; F, 18.44%. The substance was recrystallized from MeOH. V · $(PF_6)_2$ Found: C, 51.48; H, 6.28; Fe, 11.73; F, 23.12. $C_{40}H_{58}F_{12}Fe_2P_2$ calcd.: C, 51.08; H, 6.22; Fe, 11.83; F, 24.24%. The substance was recrystallized from a MeCN/MeOH mixture.

The FD mass spectrum of V · $(BF_4)_2$ contains ions with m/z 650 and 651 corresponding to the molecular ion for the cationic part of this salt, $[M_V^+]$ and $[M_V^+ + 1]$, respectively. The EI mass spectrum contains the ion with m/z 650 $[M_V^+]$ and an ion with m/z 325 ($C_{20}H_{29}Fe^+$).

Synthesis of $HAlBr_4$. Excess HBr obtained by dropwise addition of 1 ml (3.1 g, 19.4 mmol) Br_2 to a suspension of 2 g red phosphorus in 3 ml H_2O, dried in a U-shaped tube above a mixture of red P and P_2O_5 on glass wool, was bubbled into a solution of 2.7 g (10.1 mmol) $AlBr_3$ in 20 ml dry ether.

Synthesis of IV · $AlBr_4$. An ethereal solution of $HAlBr_4$ was added to a solution of 0.5 g (1.46 mmol) III in 30 ml dry ether. The precipitate was separated on the filter, washed with ether and repricipitated from CH_2Cl_2. All procedures were carried out in argon at −20°C (see above). Other procedures were similar to those for preparation of tetrafluoroborate and hexafluorophosphate. Analysis. IV · $AlBr_4$. Found: C 31.84; H, 5.01; Br, 42.89; Al, 5.92; Fe, 7.22. $C_{40}H_{58}Al_2Fe_2Br_8$ calcd.: C, 35.71; H, 4.32; Br, 47.61; Al, 4.03; Fe, 8.35%. More satisfactory analytical data were not obtained. Perhaps the compound contained an impurity of the initial carbinol III or of partially hydrolyzed products of the $AlBr_4^-$ ion. The ^1H NMR spectrum of this compound in $(CD_3)_2CO$ contains signals at 4.780, 1.673 and 1.451 ppm, with relative intensities 1/3/10.5, which is typical for IV · A (see Tables 1 and 2). Reduction of a mixture of IV · $AlBr_4$ + $V(AlBr_4)_2$ by the action of $NaBH_4$ in 80% aqueous ethanol results, according to mass spectrometric data, in a mixture of VII (M_1^+, 326), VI (M_2^+, 650), and $C_5Me_5FeC_5Me_4CH_2OEt$ (M_3^+, 370).

Measurements of the relaxation time. The 180°–τ–90°C sequence technique was used to measure the SLR time. The relaxation followed the exponential law in the whole temperature range. Kinetic measurements were performed using the null-point method [21]. The SLR time T_2 was determined directly from free induction decay after the 90°C pulse. The spectrometer was supplemented by a home-made temperature-control unit which enabled fixing the temperature within an accuracy of ~ 0.5 K and keep it stabilized with drift not exceeding 0.2 K/h in the temperature range 80–400 K.

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