Intramolecular Cation Exchange in Ion Pairs. Part I. Alkali Metal Complexes of Heterocyclic Dicarbaldehydes

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The e.s.r. spectra of the radical anions of thiophen-2,5-dicarbaldehyde, thieno[3,2-*b*]thiophen-2,5-dicarbaldehyde, and dithieno[3,2-*b*:2',3'-*d*]thiophen-2,6-dicarbaldehyde, produced by metal reduction in ethereal solvents, showed a marked linewidth alternation which has been attributed to the migration of the counterion between the two equivalent carbonyl groups. A kinetic study of this process in dimethoxyethane and tetrahydrofuran, using sodium or potassium as the reducing agent, allowed the roles played by the size of the anion, the nature of the counterion, and the solvent to be clarified.

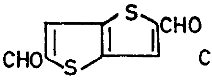
A NUMBER of heteroaromatic carbonyl compounds have recently been investigated with the aim of gaining information about their conformational properties, with the help of several spectroscopic techniques.[1] Our current interest is concerned with the study of rotational isomerism in thiophen-2,5-dicarbonyl derivatives; this investigation has been carried out both for neutral molecules using n.m.r. spectroscopy in anisotropic solvents[2] and for the corresponding anion radicals by e.s.r. spectroscopy.[1] In the latter case the radicals were produced by photolysis in a solution of methanol and sodium methoxide and their e.s.r. spectra showed the existence of two of the three possible rotational isomers. The more stable was unambiguously identified as the *O-cis-cis*; this assignment was also confirmed for the neutral molecule by a liquid crystal n.m.r. investigation.

Interestingly, ketyl radicals can exist as free ions or as associated ion pairs depending on the solvent, the free ion being favoured in polar solvents and the ion pair in solvents having a low dielectric constant. Ketyl ion pairs, although not extensively studied as those of aromatic hydrocarbons, are the subject of current interest and information concerning their structural features is accumulating.[3,4] A strong electrostatic interaction between the carbonyl group and the positive ion is expected in these radicals. In fact, e.s.r. data indicate contact ion pair structures for ketyls in ethereal solvents, with the metal lying near the oxygen atom.[3]

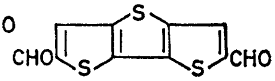
In our previous examination,[1] where methanol was used as solvent, the radicals were present as free ions. We report here the results of a new investigation on the radicals from thiophen-2,5-dicarbaldehyde (I), thieno-[3,2-*b*]thiophen-2,5-dicarbaldehyde (II), and dithieno-[3,2-*b*:2',3'-*d*]thiophen-2,6-dicarbaldehyde (III), produced by metal reduction in ethereal solvents.

As expected, e.s.r. spectra characteristic of ketyl ion pairs were detected; they presented a marked linewidth alternation due to the oscillation of the cation between the two equivalent carbonyl groups. Although similar processes have been observed in alkali metal complexes of several molecules[5,6] and particularly of semiquinones,[7-10] only a few quantitative determinations of the activation parameters have been reported. Recently Warhurst and Wilde[11] attempted to rationalize the factors determining the rate of the intramolecular cation exchange in the ion pairs formed by 2,5-di-t-butyl-*p*-benzosemiquinone and alkali metals in a number of ethereal solvents. Two possibilities were discussed by these authors. First, both the initial and transition states were assumed to have contact ion pair structures; the solvation of the cation was considered to be the same in the two states, while the anion would be more solvated in the transition state as a consequence of the reduced electrostatic interaction with the metal atom. Secondly, a solvent shared structure for the transition state was considered. Unfortunately the experimental data did not enable these authors to suggest ' which is the more plausible situation with regard to the solvation of the transition state '.

(I)



(II)



(III)

The present results for the alkali metal complexes of (I)—(III), can be better interpreted by assuming a contact ion pair structure for the ground state and a solvent shared configuration for the transition state. The different solvation of the cation in the two states is an extremely important factor in determining the rate of the process when using strongly solvating agents and large anions.

EXPERIMENTAL

The radical anions were obtained by reduction with sodium or potassium mirrors in carefully degassed 1,2-dimethoxyethane (DME) or tetrahydrofuran (THF) solutions.

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[1] L. Lunazzi, G. F. Pedulli, M. Tiecco, C. Vincenzi, and C. A. Veracini, *J.C.S. Perkin II*, 1972, 751, and references therein.

[2] L. Lunazzi, G. F. Pedulli, M. Tiecco, and C. A. Veracini, *J.C.S. Perkin II*, 1971, 755.

[3] K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, 1971, **93**, 6004.

[4] T. Takeshita and N. Hirota, *J. Amer. Chem. Soc.*, 1971, **93**, 6421.

[5] A. Hudson and G. R. Luckhurst, *Chem. Rev.*, 1969, **69**, 191.

[6] P. D. Sullivan and J. R. Bolton, *Adv. Mag. Resonance*, 1970, **4**, 39.

[7] T. E. Gough and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 269.

[8] M. P. Khakhar, B. S. Prabhananda, and M. R. Das, *J. Amer. Chem. Soc.*, 1967, **89**, 3100.

[9] P. S. Gill and T. E. Gough, *Trans. Faraday Soc.*, 1968, **64**, 1997.

[10] I. C. Chippendale and E. Warhurst, *Trans. Faraday Soc.*, 1968, **64**, 2332.

[11] E. Warhurst and A. M. Wilde, *Trans. Faraday Soc.*, 1971, **67**, 605.

Thiophen-2,5-dicarbaldehyde,[12] thieno[3,2-*b*]thiophen-2,5-dicarbaldehyde,[1] and dithieno[3,2-*b*:2′,3′-*d*]thiophen-2,6-dicarbaldehyde[13] were prepared as described in the literature.

The e.s.r. spectra were recorded on a Varian 4502 spectrometer with 100 KHz field modulation. The temperature of the sample was controlled using a Varian V-4540 variable temperature accessory, and measured with a chromel–alumel thermocouple placed in the Dewar inset just above the sensitive part of the cavity.

RESULTS

Thiophen-2,5-dicarbaldehyde (I).—The room temperature e.s.r. spectrum of the radical from (I) produced by means of potassium in THF is shown in Figure 1(a). The spectrum can be straightforwardly interpreted on the basis of the coupling of the unpaired electron with two pairs of protons whose hyperfine splitting constants are reported in Table 1. There is also a small coupling with the potassium atom indicating that the radical is present as a strongly associated ion pair.

Even at high amplification, no other signal due to the possible conformational isomers could be detected. It can therefore be argued that in this case the formation of ion pairs stabilizes one of the two symmetric conformations, presumably the *O-cis-cis*, which in polar solvents, where the radical exists as a free ion, was also found to be the more stable.

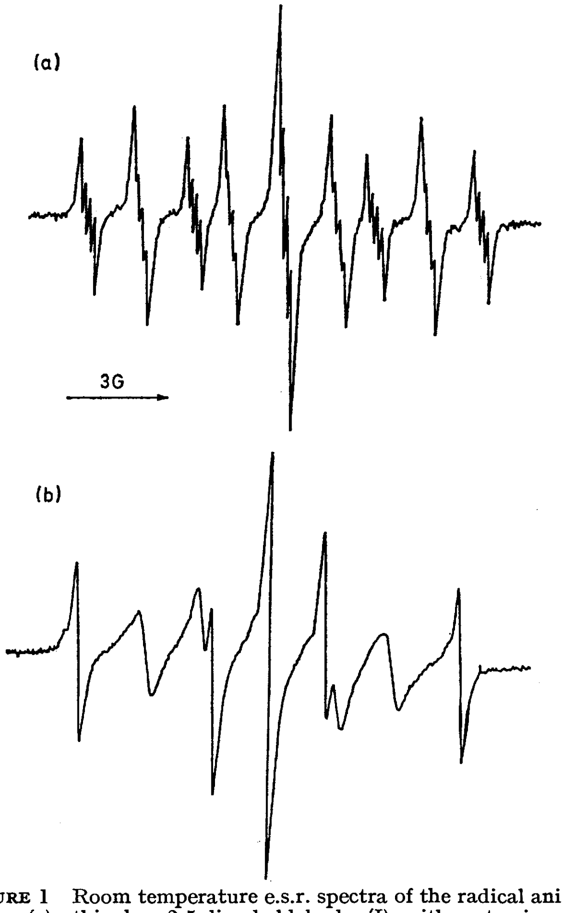

FIGURE 1 Room temperature e.s.r. spectra of the radical anions of: (a), thiophen-2,5-dicarbaldehyde (I) with potassium as counterion in THF; (b), thieno[3,2-*b*]thiophen-2,5-dicarbaldehyde (II) with potassium in DME

Moreover there is a marked linewidth alternation which becomes more apparent when the temperature is lowered.

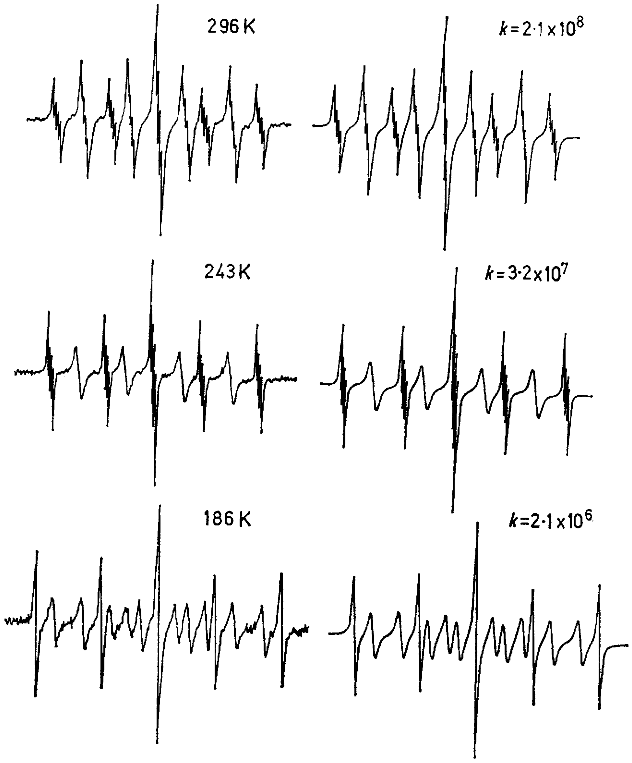

FIGURE 2 Experimental and simulated e.s.r. spectra of the radical anion of (I) in THF with potassium as counterion at various temperatures; k in s^{-1}

This behaviour can be explained as due to a rapid isomerisation between two equivalent ion pairs. The cation will tend to stay in positions corresponding to a minimum of potential energy which should be near the carbonyl groups because of their greater electronegativity. The movement of the cation from one carbonyl group to the other modulates the proton isotropic hyperfine splitting constants and gives rise to the alternating linewidth effect. By decreasing the temperature the rate constant of this process is reduced and changes of the spectral shape are noticed. While the odd lines remain sharp the even ones gradually broaden and finally disappear as shown in Figure 2; when the temperature is further decreased, new broad lines appear in the e.s.r. spectrum and become progressively sharper. The last spectrum of Figure 2, which shows that all four protons are nonequivalent, indicates that the interconversion frequency is much less than the differences between the frequencies of interchanging lines. The rate constant for the exchange process can be determined at each temperature by analysing the spectral line shape as described in the next section. The results of these measurements are graphically summarized in Figure 3(a), where log K is plotted against $1/T$; the activation parameters which can be derived from this plot and the thermodynamic constants for the activated complex $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are collected in Table 2. Measure-

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[12] M. Robba, R. C. Moreau, and B. Roques, *Compt. rend.*, 1964, **259**, 3568.

[13] G. F. Pedulli, M. Tiecco, and co-workers, to be published.

ments have been also carried out using DME as solvent and Na as counterion and the relative value are shown together with those of the experiment discussed above.

When reducing (I) with potassium in DME, even at very low temperature (−80 °C) the slow exchange region could never be reached. Further, new lines, due to a second paramagnetic species having a g factor somewhat larger than that of the ion pair, appear at about −20 °C; their intensity increases by decreasing the temperature and the initial concentration of radical. The new spectrum consists of a triplet of triplets where the two coupling constants have slightly smaller values (Table 1) than those of the main spectrum. This species, which arises from the dissociation of the ion pair,[14] can be identified as the free anion radical of (I). When using THF as solvent or Na as counterion the free ion is absent.

TABLE 1

Experimental and calculated (in parentheses) hyperfine splitting constants of the radical anions of derivatives (I)—(III) relative to the ion pairs in the fast (f.e.r.) and slow (s.e.r.) exchange regions and to the free ions (f.i.)

Metal	Solvent		a_{A}/G *	$a_{\mathrm{A'}}$/G	a_{T}/G	$a_{\mathrm{T'}}$/G
Thiophen-2,5-dicarbaldehyde (I)						
K	THF	S.e.r.	4·83 (5·39)	3·49 (3·60)	2·10 (1·19)	0·85 (0·14)
		F.e.r.	4·10		1·51	
K	DME	S.e.r.				
		F.e.r.	4·12		1·53	
		F.i.	3·92 (4·06)		1·51 (0·63)	
Na	THF	S.e.r.	5·00	3·33	2·32	0·69
		F.e.r.	4·25		1·54	
Na	DME	S.e.r.	5·00	3·35	2·34	0·70
		F.e.r.	4·24		1·55	
Thieno[3,2-*b*]thiophen-2,5-dicarbaldehyde (II)						
K	THF	S.e.r.	4·44 (4·99)	2·75 (3·15)	2·92 (3·11)	1·04 (1·85)
		F.e.r.	3·55		1·95	
K	DME	S.e.r.	4·43	2·75	2·91	1·06
		F.e.r.	3·54		1·98	
		F.i.	3·37 (3·64)		1·92 (2·38)	
Dithieno[3,2-*b*:2′-3′-*d*]thiophen-2,6-dicarbaldehyde (III)						
K	THF	S.e.r.	3·96 (5·09)	2·16 (2·87)	2·84 (2·81)	0·80 (1·36)
		F.e.r.	3·10		1·82	
K	DME	S.e.r.				
		F.e.r.	3·08		1·83	
		F.i.	2·85 (3·54)		1·70 (1·98)	

* The indexes A,A′ and T,T′ refer to the aldehydic and aromatic protons respectively. The primes denote positions on the opposite side of the counterion.

TABLE 2

Summary of the activation parameters for the intramolecular exchange process in the radical anions of (I)—(III)

Solvent	Metal	E_a/kcal mol^{-1}	log A	ΔH‡/kcal mol^{-1}	ΔS‡/cal mol^{-1} K^{-1}
Thiophen-2,5-dicarbaldehyde					
THF	K	4·74 ± 0·11	11·76 ± 0·10	4·28 ± 0·13	−6·23 ± 0·50
THF	Na	4·79 ± 0·26	10·89 ± 0·25	4·40 ± 0·26	−10·04 ± 1·13
DME	K	3·50 ± 0·09	10·91 ± 0·08	3·00 ± 0·09	−10·30 ± 0·32
DME	Na	3·57 ± 0·09	10·04 ± 0·08	3·03 ± 0·09	−14·45 ± 0·36
Thieno[3,2-*b*]thiophen-2,5-dicarbaldehyde					
THF	K	3·74 ± 0·13	10·23 ± 0·12	3·27 ± 0·14	−13·31 ± 0·63
DME	K	2·34 ± 0·11	9·27 ± 0·10	1·86 ± 0·12	−17·71 ± 0·47
Dithieno[3,2-*b*:2′,3′-*d*]thiophen-2,5-dicarbaldehyde					
THF	K	2·82 ± 0·06	9·47 ± 0·06	2·30 ± 0·07	−16·95 ± 0·29
DME	K	1·86 ± 0·09	8·92 ± 0·07	1·32 ± 0·09	−19·54 ± 0·34

The lowering of the temperature also produces a reduction of the hyperfine splitting due to the alkali metal, as shown in Figure 2. The temperature dependence of the metal coupling constants for the cases examined, is depicted in Figure 4.

Thieno[3,2-b]*thiophen*-2,5-*dicarbaldehyde* (II) *and Dithieno*[3,2-b:2′,3′-d]*thiophen*-2,6-*dicarbaldehyde* (III).—The radicals of these compounds were produced in THF and DME using potassium as the reducing agent. The room temperature spectrum of the radical from (II) in DME is shown in Figure 1(b) and the relative hyperfine splitting constants are collected in Table 1, together with those of the radical from (III). In the spectrum of Figure 1(b) other less intense lines can be observed; we assign this second spectrum to the *O-cis-trans* conformer by analogy with the results obtained for the same molecule when using polar solvents.[1]

For both radicals from (II) and (III) no coupling with the counterion could be observed in either solvent. This suggests that the metal atom is not as strongly associated

[14] T. A. Claxton, J. Oakes, and M. C. R. Symons, *J. Amer. Chem. Soc.*, 1971, **93**, 3779.

with the anion as in the case of the thiophen-2,5-dicarbaldehyde. However we are still dealing with ion pairs as indicated by the linewidth alternating effect which is evident even at room temperature and by the remarkably large intrinsic linewidth which presumably hides unresolved metal hyperfine structure.

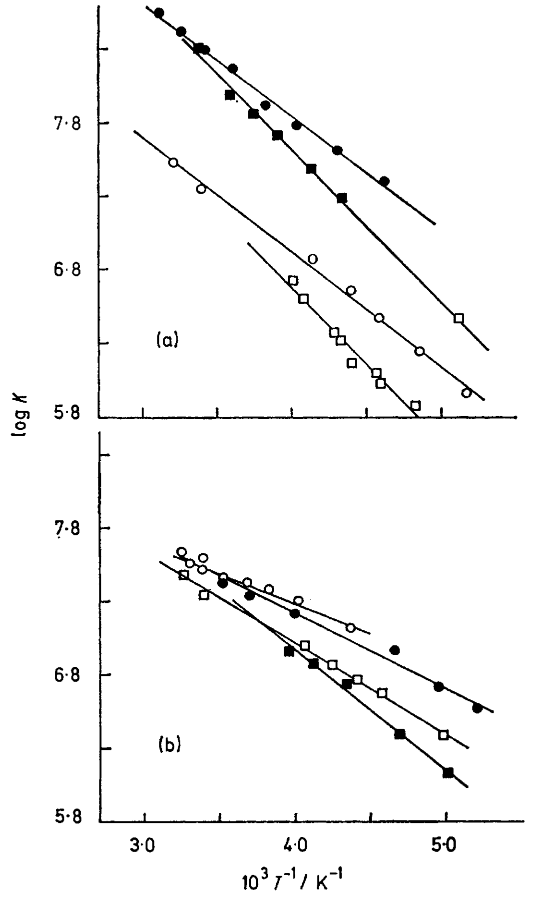


FIGURE 3 Arrhenius diagrams of the rate constants for the exchange process in the metal complexes of: (a), thiophen-2,5-dicarbaldehyde (I) (■, THF–K; ●, DME–K; □, THF–Na; ○, DME–Na); (b), thieno[3,2-*b*]thiophen-2,5-dicarbaldehyde (II) (■, THF–K; ●, DME–K) and dithieno[3,2-*b*:2′,3′-*d*]-thiophen-2,6-dicarbaldehyde (III) (□, THF–K; ○, DME–K)

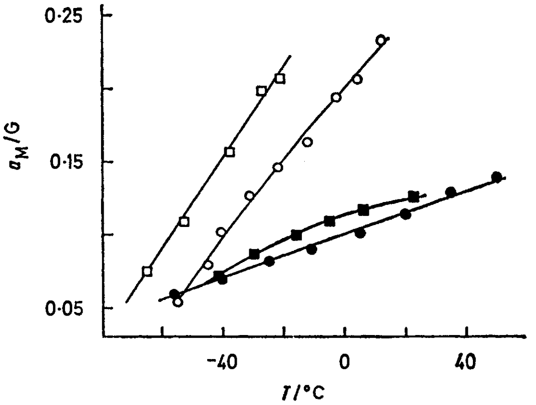


FIGURE 4 Temperature dependence of the alkali metal splittings in the anion radical of (I): ○, DME–Na; □, THF–Na; ■, THF–K; ●, DME–K

From a determination of the rate constants for the exchange process at various temperatures [see Figure 3(b)], the activation parameters reported in Table 2 were derived. Owing to the presence of a considerable amount of the free ion and of some other paramagnetic impurity, whose concentration increases with time, the values determined for the radical from (III) are believed to be less accurate than in the other two cases. The relative amount of the free ion was found to increase progressively with the molecular dimensions of the anion, even if no quantitative estimation has been made.

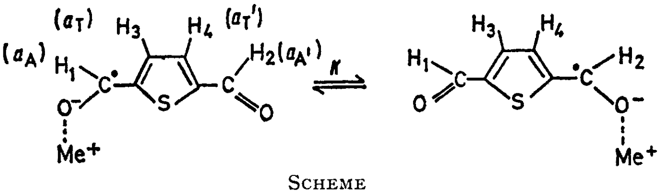
THEORY

The linewidth changes have been analysed using the Redfield relaxation theory [15] for the fast exchange region and the density matrix theory in the Liouville representation [16] for the slow exchange region. The Redfield theory has been employed, when possible, since it allows a considerable amount of computer time to be saved, relative to the density matrix theory, when simulating the e.s.r. spectra.

Redfield Theory.—The line-broadening effects of modulating an isotropic hyperfine coupling constant may be investigated using the time-dependent spin Hamiltonian (1), where the nonsecular terms have been neglected.

$$\mathscr{H}(t) = \gamma_e \sum_i [a_i(t) - \bar{a}_i] I_z^{(i)} S_z \qquad (1)$$

The present situation where the two aldehydic and the two aromatic protons interchange their coupling constants can be described by assuming a two-jump model as exemplified for the radical from (I) (Scheme). In the Redfield limit the linewidth of each hyperfine line depends on the proton magnetic quantum numbers and may be written as (2) [17] where the term $T_{2,0}^{-1}$ is the intrinsic linewidth in



SCHEME

$$T_2^{-1}(m_1, m_2, m_3, m_4) = T_{2,0}^{-1} + \sum_{i,j} m_i m_j j_{ij}(0) \qquad (2)$$

the absence of a contribution due to exchange and the spectral densities $j_{ij}(0)$ are given by equation (3) where τ is

$$j_{ij}(0) = \gamma_e^2 (a_i - a'_i)(a_j - a'_j)\tau/8 \qquad (3)$$

the mean lifetime of the metal nucleus in each site.

It is easy to show that $j_{11} = j_{22}$; $j_{33} = j_{44}$; $j_{12} = j_{21} = -j_{11}$; $j_{34} = j_{43} = -j_{33}$; and $j_{13} = j_{24} = -j_{14} = -j_{23}$. Then the linewidth can be given more explicitly as equation (4) where $M_A = m_1 - m_2$; $M_T = m_3 - m_4$; and $j'(0) = (\Delta a_A)^2\tau/4$, $j''(0) = (\Delta a_T)^2\tau/4$, and $j'''(0) = \Delta a_A \Delta a_T \tau/4$.

$$T_2^{-1} = T_{2,0}^{-1} + M_A^2 j'(0) + M_T^2 j''(0) + 2M_A M_T j'''(0) \qquad (4)$$

This expression requires that only the even lines are broadened and that the central line is a superposition of two Lorentzians having different widths.

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[15] A. G. Redfield, *IBM J. Res. Dev.*, 1957, **1**, 19.

[16] G. Binsch, *Mol. Phys.*, 1968, **15**, 469.

[17] J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 326.

The rate constants $k = \tau^{-1}$ can be determined by comparing the experimental spectra with those computed using τ as a variable parameter.

Density Matrix Theory.—The shape of the absorption spectrum $L(\omega)$ in a low power electron resonance experiment is given by expression (5),[16,18] where $\boldsymbol{S}^-$ is a row vector

$$L(\omega) \propto Re(\boldsymbol{S}^-\boldsymbol{M}_0^{-1}\boldsymbol{\sigma}) \qquad (5)$$

composed of the matrix elements of the lowering operator and the column vector $\boldsymbol{\sigma}$ contains the populations of the sites. The matrix $\boldsymbol{M}_0$ is given by (6) where $\mathbf{L}_0$ is the

$$\boldsymbol{M}_0 = -i\mathbf{L}_0 + \mathbf{R} + \mathbf{X} \qquad (6)$$

Liouville superoperator arising from the electron Zeeman and isotropic hyperfine coupling Hamiltonians and $\mathbf{R}$ and $\mathbf{X}$ are respectively the relaxation and exchange superoperators. The relaxation superoperator is assumed to be diagonal with all the elements identical to T_2^{-1}.

Since the nonsecular terms are negligible and because of the absence of pseudosecular terms in the hyperfine Hamiltonian the $\boldsymbol{M}_0$ matrix can be factorized into submatrices $\boldsymbol{M}_{0j}$ of dimensions equal to the number of sites. The shape function $L(\omega)$ then can be written as (7),[19] N being $\Pi_i(n_i + 1)$

$$L(\omega) \propto Re \sum_{j=1}^{N} D_j(\boldsymbol{S}^-\boldsymbol{M}_{0j}^{-1}\boldsymbol{\sigma}) \qquad (7)$$

where n_i is the number of completely equivalent protons of the ith group and D_j the degeneracy of the transition. Since in e.s.r. spectroscopy the derivative of the absorption curve is usually measured, it is more convenient to obtain the derivative $L'(\omega)$ of the shape function [equation (8)].[20]

$$L'(\omega) \propto -I_m \sum_{j=1}^{N} Dj(\boldsymbol{S}^-\boldsymbol{M}_{0j}^{-2}\boldsymbol{\sigma}) \qquad (8)$$

The only problem in the practical applications is the inversion of the $\boldsymbol{M}_{0j}$ matrices at each point of the spectrum. For a two equivalent sites problem the inversion can be performed analytically, so that $L'(\omega)$ is given by equation (9) where $X_{\lambda j} = i(\omega - \omega_{\lambda j}) - T_2^{-1} - k$, and $\omega_{\lambda j}$ are the interchanging frequencies.

$$L'(\omega) \propto -I_m \sum_{j=1}^{N} D_j \frac{(X_{1j}^2 + X_{2j}^2)/2 - k(X_{1j} + X_{2j}) + k^2}{(X_{1j}X_{2j} - k^2)^2} \qquad (9)$$

Calculations.—The determination of the rate constants for the exchange process was made by visual fitting of the spectra simulated by one of the two computer programs based on the theories outlined above, to the experimental ones. The Redfield or the density matrix theory was employed when dealing with spectra in the fast exchange or in the slow exchange region respectively. The input data for the two programs were the number of nonequivalent protons, the hyperfine splitting constants in the slow exchange limit, the intrinsic linewidth in absence of exchange, and the rate constants. The coupling constants employed are those reported in Table 1. When a significant temperature dependence of the proton couplings was encountered, only the sum of the interchanging constants was allowed to vary, keeping the difference unchanged. In the case of the radicals from (I) and (III) produced by means of potassium in DME, where the slow exchange region could never be reached, we used the splitting constants measured from the spectrum of the potassium complex in THF; this seems reasonable since no solvent dependence of the coupling constants was observed when using sodium as counterion nor in the radical from (II).

The activation parameters were obtained from the rate constants by standard least-squares procedures. The thermodynamic constants for the activated complex result from application of the Eyring equation with a path degeneracy factor of 1.

DISCUSSION

Before discussing the dynamics of the intramolecular cation exchange we will examine some details concerning the assignment of the proton coupling constants in the free ions and in the asymmetric ion pairs, their dependence on the nature of the counterion, and the temperature variations of the alkali metal splittings.

The assignment of the hyperfine splitting constants in the free ion may be made by analogy with the results obtained in polar solvents by using methyl substituted derivatives;[1] the larger splittings come from the aldehydic hydrogen atom and the smaller from the aromatic protons in each radical. The same attribution is also predicted by theoretical calculations made using the McLachlan MO method.[21] The parameters which have been employed are: for the carbonyl group those used by Takeshita and Hirota[4] for the anion radical of anthraquinone ($h_0 = 1{\cdot}15$, $h_{c'} = 0{\cdot}11$, $k_{c'0} = 1{\cdot}55$) and for the sulphur atom the same as used for a number of thiophen derivatives[22] ($h_s = 1{\cdot}0$, $k_{cs} = 0{\cdot}86$). The theoretical splitting constants given in Table 1 have been calculated from the spin densities using a Q value of $-26{\cdot}5$.

In the asymmetric ion pair (slow exchange region) the perturbation induced by the metal atom was accounted for by changing the coulomb parameter of the oxygen linked to the cation by $0{\cdot}26\beta$. The same value was used by Hirota[4] for similar calculations on several ketyl–potassium complexes dissolved in DME. Our calculations predict larger splitting constants for the hydrogens on the same side of the metal atom (Table 1), in agreement with the qualitative assignment which can be made by considering simple resonance structures where the negative charge is localized on one oxygen of the ketyl radical.[23]

An examination of the coupling constants of the radical from (I) shows that the proton splittings depend on the nature of the counterion both in the fast and in the slow exchange regions. At low temperatures the differences $a_{\mathrm{A}} - a_{\mathrm{A'}}$ and $a_{\mathrm{T}} - a_{\mathrm{T'}}$, between the couplings of similar protons on the same side and on the opposite side of the metal atom, are larger for sodium than for potassium. The increased perturbation induced by the cation by

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[18] G. Binsch, *J. Amer. Chem. Soc.*, 1969, **91**, 1304.

[19] J. Heinzer, *Mol. Phys.*, 1971, **22**, 167.

[20] G. R. Luckhurst and G. F. Pedulli, *Mol. Phys.*, 1971, **22**, 931.

[21] A. D. McLachlan, *Mol. Phys.*, 1960, **3**, 233.

[22] L. Lunazzi, A. Mangini, G. F. Pedulli, and M. Tiecco, *Gazzetta*, 1971, **101**, 10.

[23] T. A. Claxton, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, 1966, **62**, 279.

decreasing its atomic number, indicates that sodium is more strongly associated with the anion as expected;[4,24] the same trend can also be observed by looking at the room temperature values, where the aldehydic constants of the sodium and potassium complexes in DME are 4·24 and 4·12 respectively to be compared with the value 3·92 measured for the free ion.

By lowering the temperature, the metal splitting constants in the ion pairs derived from (I) gradually decrease (Figure 4). This behaviour which has been already observed in other carbonyl derivatives[4,24] is due to a better solvation of the counterion which produces an increase of the interionic distance.

Kinetics of the Cation Transfer.—The study of the intramolecular exchange of the alkali metal between the two equivalent electronegative sites has been carried out by examining the effects produced on the rate constants when changing the solvating power of the medium, the size of the cation, and the molecular dimensions of the organic anion. The activation parameters and the thermodynamic constants determined as previously described are given in Table 2.

When, in ion pairs, the cation is rapidly moving between two positions of the negative ion a more or less pronounced reorganisation of solvent molecules has to be expected; a quantitative measure of the solvent involvement during the process is given by the experimental value of the activation entropy. In the present cases the large negative $\Delta S^{\ddagger}$ values which have been found indicate that the solvent plays a very important role during the interconversion. The negative activation entropies reflect a larger degree of order and greater solvation for the transition state than for the ground state.

Although solvent reorganisation could occur, in principle, around both cation and anion, for reasons that will be discussed below and because of the nature of the solvents employed, which should solvate positive ions more easily, we believe that greater changes should be experienced by the solvent shell of the counterion.

When we consider the effects produced by changing the solvent, it is reasonable to expect that the greatest entropy variations should be encountered with solvents having the strongest solvating power. This has been experimentally confirmed for all the cases examined; as shown in Table 2, in fact, the activation entropies have been found to be more negative for DME than for THF.

Also the enthalpy variations with solvent can be rationalized in the light of the considerations reported above by writing the total $\Delta H^{\ddagger}$ as a sum of two terms, one due to the ion–ion and the other due to the ion–solvent interaction: $\Delta H^{\ddagger} = \Delta H^{\ddagger}_{\text{ion-ion}} + \Delta H^{\ddagger}_{\text{ion-solvent}}$: A third contribution due to the solvent–solvent interaction can probably be neglected. In the two solvents $\Delta H^{\ddagger}_{\text{ion-ion}}$ should be about the same since in the ground state the solvent invariance of the proton splitting constants suggest a similar degree of interaction between the two ions, and in the transition state the metal–oxygen distances are presumably large enough to make the electrostatic energy negligible. Then, the differences in the activation enthalpy should be mainly attributable to the ion–solvent interaction; because of its better solvating capability, the transition state should be more stabilized in DME, and a lower value of $\Delta H^{\ddagger}$ is expected in this solvent.

The change on the counterion mainly reflects on the activation entropy, the greater negative values being found with sodium, while the activation enthalpy remains almost unaltered. As said before, the degree of association in the ground state should be greater in the sodium than in the potassium complex as a consequence of the different size of the cation; for the same reason, the sodium ion should be more solvated in the transition state and this will obviously lead to a greater negative activation entropy in the case of the smaller ion. The invariance of the activation enthalpy is probably due to a compensation of the two terms which contribute to the $\Delta H^{\ddagger}$. The $\Delta H^{\ddagger}_{\text{ion-ion}}$ value should be greater for sodium, but its better solvation in the transition state will result in a change in energy in the opposite direction.

The final point to be considered is the effect of changing the molecular dimensions of the anion. As reported in Table 2 the negative activation entropy increases regularly going from the dialdehyde of thiophen to those of thienothiophen and dithienothiophen. This behaviour can be easily understood by assuming a solvent-shared configuration for the transition state. In fact, when the distance between the two oxygen atoms increases, more space is available for the solvent molecules to solvate the positive ion in the transition state making the activation entropy progressively more negative. The decrease of the activation enthalpy may be explained as due to two effects acting in the same direction: the greater solvation of the transition state and the reduced electrostatic interaction between oxygen and metal in the initial state.

The observed trend of the activation parameters when the dimensions of the anion are increased cannot be satisfactorily interpreted by assuming a contact ion pair structure for the activated complex.[11] According to this model the most important factor is the change in the solvation of the oxygen atom of the vacant site, which is related to the difference of charge density on it, in the initial and transition states. In the asymmetric ground state the cation will attract negative charge away from the vacant site oxygen which will thus be poorly solvated, and in the transition state, where this effect will be absent, the increased charge on it will favour its solvation. In the three cases examined here the electrostatic interaction between oxygen and metal seems to decrease when going to larger anions, as indicated by the disappearence of the alkali metal splitting and by the increase of the relative amount of free ions. This implies a reduced difference in the charge density and then in the solvation of the vacant site oxygen, so that the activation entropy should follow an opposite trend to that

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[24] M. Brustolon, C. Corvaja, and L. Pasimeni, *J.C.S. Faraday II*, 1972, 223.

experimentally observed. Moreover, simple Hückel calculations performed on the free ion and on the asymmetric ion pair, show that in each radical the difference of charge density on the vacant site oxygen is only *ca.* 0·01 charge units, which seems too small to justify the very large negative activation entropies determined experimentally.

[2/2350 *Received, 16th October, 1972*]