Intramolecular Cation Exchange in Ion Pairs. Part II.[1] Isomeric Radical Ion Pairs of Dithiolactones

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The radical ion pairs of several dithiolactones have been studied by e.s.r. spectroscopy. The e.s.r. spectral shape is strongly temperature dependent owing to the intramolecular migration of the alkali counterion between the two carbonyl groups of the organic anion. In the case of asymmetric derivatives, two non-equivalent ion pairs have been unambiguously detected for the first time. The factors affecting their relative stability are described. The kinetics of the cation exchange has been investigated for some of the compounds examined, by analysing the line shape variations with temperature. It is emphasized that the activation parameters calculated on the usual assumption that the change of temperature influences only the rate of migration should be considered with some caution since parallel changes of the structure of the ion pairs may also occur. The effects of these variations on the measured parameters are discussed.

RADICAL anions generated by alkali metal reduction of carbonyl compounds usually form ion pairs in ethereal solvents. In the ion pair the cation tends to stay in positions of minimum potential energy, which are near the carbonyl oxygen because of its greater electronegativity. When the molecule contains two equivalent non-

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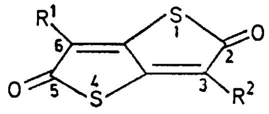
[1] Part I, M. Guerra, G. F. Pedulli, and M. Tiecco, *J.C.S. Perkin II*, 1973, 903.

adjacent carbonyl groups, the cation moves from one carbonyl to the other with rates depending on the temperature, the solvent, and the nature of the counterion. This effect becomes visible in the e.s.r. lines which alternate in width if the rate constant of migration has the same order of magnitude of the difference between the interchanging splittings. When the oscillation of the alkali ion is frozen in the e.s.r. time scale, the molecular symmetry is lost and spectra characteristic of a particular conformation of the ion pair are detected. If the two binding sites are equivalent both conformations give rise to the same spectrum and we observe only a single species.[1-4]

The situation is more complex when non-equivalent sites are involved. In general the effect of migration on the e.s.r. spectrum is not the simple line width alternation, as all the lines, including the central one if the two isomeric ion pairs have different *g* factors, are expected to broaden to a greater or lesser extent. On cooling, spectra of two different ion pairs should be resolved. The only example reported in the literature is that of 2,6-dimethyl-*p*-benzosemiquinone, where anyway only the isomer having the counterion on the unhindered oxygen was unambiguously detected.[5]

By examining the sodium ion pair of benzo[1,2-*b*; 5,4-*b*′]dithiophen-4,8-semidione, we have recently been able to observe a superposition of two distinct spectra which we attributed to the isomers of that complex.[6]

To obtain more information on the factors affecting the relative stability of isomeric ion pairs, we have undertaken an e.s.r. investigation on the alkali metal complexes of 3,6-substituted thieno[3,2-*b*]thiophen-2,5-diones (I)—(VII).



(I) $R^1 = R^2 = H$
(II) $R^1 = R^2 = Me$
(III) $R^1 = R^2 = Ph$
(IV) $R^1 = H, R^2 = Me$
(V) $R^1 = H, R^2 = Et$
(VI) $R^1 = H, R^2 = Bu^t$
(VII) $R^1 = H, R^2 = Ph$

In the case of the asymmetric dithiolactones (IV)—(VI) both isomers could be revealed and their structures assigned by considering the mesomeric systems available to the two species. The effect of temperature, solvent, size of the counterion, and steric crowding around the binding oxygen on the stability of these isomers is discussed.

Since the majority of the metal complexes of the above compounds show line broadening effects due to intramolecular transfer of the alkali cation, the kinetics of this process have also been studied. Activation parameters for cation exchange have been measured for a number of systems,[1-4] and the mechanism of this process is beginning to be clarified. In particular the important role of the solvent in determining the rate constant has been emphasised;[1,2] in fact the large negative activation entropies indicate that in the transition state solvation of the cation is considerably larger than in the ground state, thus suggesting that exchange between the equivalent contact type ion pairs occurs *via* a solvent shared ion pair. However it is worth pointing out that the kinetic data should be considered with some caution, since the structure of the ion pair may change with temperature as is often manifested by the dependence of the proton hyperfine splittings upon temperature. A greater number of experimental results is therefore required to understand fully the mechanism of intramolecular cation exchange.

EXPERIMENTAL

Thieno[3,2-*b*]thiophen-2,5-diones (I)—(VII) were obtained as by-products from the syntheses of the 2,5-dihydroxythieno[3,2-*b*]thiophens [7,8] carried out by hydrogen peroxide oxidation of the 2,5-thieno[3,2-*b*]thienylboronic acids.[9] They could also be easily obtained by the oxidation of the 2,5-dihydroxythieno[3,2-*b*]thiophens, which exist in the form of thiolactones;[8] for this purpose an alkaline solution of the dihydroxy-compounds was left open to the air for several hours and the mixture was acidified and extracted. Purification was carried out by column chromatography on silica gel and crystallization from ethanol.

Compounds (I)—(VII) have the following properties (n.m.r. spectra were recorded in CS_2 at 60 MHz): *thieno*[3,2-*b*]*thiophen*-2,5-*dione* (I), m.p. 155—156 °C, δ 6.42 (s) (Found: C, 43.15; H, 1.2; S, 37.5. $C_6H_2O_2S_2$ requires C, 42.35; H, 1.2; S, 37.65%); 3,6-*dimethylthieno*[3,2-b]*thiophen*-2,5-*dione* (II), m.p. 151—152 °C, δ 2.06 (s) (Found: C, 48.55; H, 3.1; S, 32.4. $C_8H_6O_2S_2$ requires C, 48.45; H, 3.05; S, 32.35%); 3,6-diphenylthieno[3,2-*b*]thiophen-2,5-dione (III), m.p. 224—225 °C (lit.,[10] 221—222.5 °C), δ ($CDCl_3$) 7.5 (m) (Found: C, 67.2; H, 3.3; S, 19.0. Calc. for $C_{18}H_{10}O_2S_2$: C, 67.05; H, 3.15; S, 18.9%); 3-*methylthieno*[3,2-b]*thiophen*-2,5-*dione* (IV), m.p. 91—93 °C, δ 6.29 (q) and 2.08 (d, *J* 0.3 Hz) (Found: C, 46.0; H, 2.15; S, 34.5. $C_7H_4O_2S_2$ requires C, 45.65; H, 2.2; S, 34.8%); 3-*ethylthieno*[3,2-b]-*thiophen*-2,5-*dione* (V), m.p. 50—52 °C, δ 6.18 (s), 1.25 (t, *J* 7.5 Hz), and 2.45 (q, *J* 7.5 Hz) (Found: C, 48.8; H, 3.15; S 35.0. $C_8H_6O_2S_2$ requires C 48.45; H 3.05; S 34.35%); 3-*t-butylthieno*[3,2-b]*thiophen*-2,5-*dione* (VI), m.p. 133—135 °C, δ 6.15 (s) and 1.38 (s) (Found: C, 52.95; H, 4.4; S, 28.6. $C_{10}H_{10}O_2S_2$ requires C, 53.05; H, 4.45; S, 28.35%); 3-*phenylthieno*[3,2-*b*]*thiophen*-2,5-*dione* (VII), m.p. 124—126 °C, δ 6.30 (s) and 7.4 (m) (Found: C, 58.3; H, 2.6; S, 26.4. $C_{12}H_6O_2S_2$ requires C, 58.5; H, 2.45; S, 26.05%).

Radicals.—The anion radicals were produced from compounds (I)—(VII) by treatment with potassium t-butoxide in dimethyl sulphoxide (DMSO) and by reduction with

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[2] K. S. Chen, T. Takeshita, K. Nakamura, and N. Hirota, *J. Phys. Chem.*, 1973, **77**, 708.

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

[4] T. E. Gough and P. R. Hindle, *Canad. J. Chem.*, 1971, **49**, 2412.

[5] J. Oakes and M. C. R. Symons, *Trans. Faraday Soc.*, 1970, **66**, 10.

[6] G. F. Pedulli, A. Alberti, L. Testaferri, and M. Tiecco, *J.C.S. Perkin II*, 1974, 1701.

[7] G. Martelli, L. Testaferri, M. Tiecco, and P. Zanirato, *J. Org. Chem.*, 1975, **40**, 3384.

[8] M. Tiecco, unpublished results.

[9] A. B. Hörnefeldt and S. Gronowitz, *Acta Chem. Scand.*, 1962, **16**, 789.

[10] J. Weinstock, J. E. Blank, and B. M. Sutton, *J. Org. Chem.*, 1974, **39**, 2454.

alkali metals in tetrahydrofuran (THF) or dimethoxyethane (DME). The temperature of the sample was controlled using standard variable temperature accessories and measured with a chromel–alumel thermocouple placed in the Dewar insert just above the sensitive part of the cavity.

MO Calculations.—Spin density calculations were carried out on the radical anions from (I), (II), and (IV) using the McLachlan method.[11] The necessary parameters for the methyl group (h_O 1.2, k_{CO} 1.56)[12] and for the hyperconjugative ($h_{C'}$ −0.05, h_X −0.5, $k_{CC'}$ 0.86, $k_{C'X}$ 2.5)[13] and inductive (h_O −0.13)[14] models of the methyl group were taken from the literature, while those for the sulphur atom (h_S 1.0, k_{CS} 0.86)[15] are the same we used for a number of thiophen derivatives.

RESULTS AND DISCUSSION

The radical anions of the compounds examined are present in solution as free ions or as ion pairs depending on whether the solvent is DMSO or an ether (DME or THF). Since in the latter solvents the e.s.r. spectra and the properties of the observed species are strikingly different with respect to DMSO, we will discuss separately the two cases.

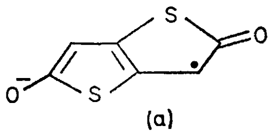
Free Ions.—The interpretation of the e.s.r. spectra of the dissociated anion radicals from (I)—(VII) is straightforward because of the reduced number of protons coupled with the unpaired electron. The measured hyperfine splitting constants together with their assignment are reported in Table 1. The relatively large values of the hydrogen splittings of (I) may be accounted for by simple resonance structures where the negative charge is located on the carbonyl oxygen, as the unpaired electron may be delocalized on the protonated position of one of the thiophen rings without destroying the aromaticity of the second [see structure (*a*)].

TABLE 1

Room temperature hyperfine splitting constants (G) of the radical anions produced by treatment of compounds (I)—(VII) with potassium t-butoxide in DMSO

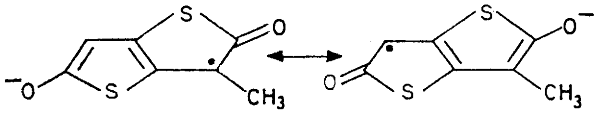
Compound	a_H	a_{CH_3}	a_o	a_m	a_p
(I)	3.94				
(II)		3.70			
(III)			0.70	0.29	0.75
(IV)	3.50	4.21			
(V)	3.52	2.69 *			
(VI)	3.49	0.15			
(VII)	3.81		0.75	0.31	0.82

* Methylene splitting.



(a)

When one of the aromatic protons is substituted by a methyl group the splitting constant of the other proton experiences a substantial decrease from 3.94 to 3.50 G. This suggests that in the radical from (IV) the resonance structure (b) is more important than (c), which is consistent with the known greater stability of tertiary with respect to secondary carbon radicals.



(b) (c)

Since the latter effect is usually explained in terms of hyperconjugation, we have performed McLachlan spin density calculations on the radicals from (I) and (IV) to test whether the observed reduction of the proton splitting could be justified by employing the hyperconjugative model for the methyl group. The computed decrease was however too small (0.13 G) with respect to the experimental reduction of 0.44 G. This is not unexpected considering that the value of the proton splitting in the monophenyl derivative (VII) is 3.81 G. Although partially rotated with respect to the molecular plane, the phenyl should certainly conjugate better than the methyl group. The calculations were therefore repeated by taking into account also the inductive effect of the methyl and the computed decrease was 0.52 G, in good agreement with experiment. The calculated charge distribution in the monomethyl derivative (IV) indicates that greater spin density is induced on the methylated position through the following mechanism: the repulsion of the σ-electrons from methyl makes the adjacent carbon partially negative in the neutral molecule, the π-charge is therefore preferentially localized on the protonated carbon. When producing the radical anion the extra electron finds the methylated carbon partially free of π-charge and then can be more easily localized on it.

The decrease of the proton splitting in the substituted ethyl (V) and t-butyl (VI) compounds may be explained in the same way. It is worth pointing out, mainly with regard to the following discussion on the ion pairs, that the coupling constant of the aromatic proton in the monosubstituted radicals is practically the same within experimental error; this indicates that the relative importance of the resonance structures (b) and (c) is the same whatever the aliphatic subsituent. The comparison of the hyperfine splitting at the methylene protons in (V) with the methyl splitting observed in (IV), may also give useful information on the conformational preference of the ethyl group. The determination of the conformation of protons attached to carbons β to π-system is usually made by assuming a relation between the hyperfine splitting and dihedral angle ϕ formed by the plane passing through C_α, C_β, and H and the plane defined by the C_α–C_β bond and the symmetry axis of the $2p_z$ orbital centred on C_α. This relation takes the form (1), where B_0 and B_2 are empirical constants and

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

[12] G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, 1961, **34**, 1333.

[13] D. Lazdins and M. Karplus, *J. Amer. Chem. Soc.*, 1965, **87**, 920.

[14] R. E. Moss, N. A. Ashford, R. G. Lawler, and G. K. Fraenkel, *J. Chem. Phys.*, 1969, **51**, 1765.

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

ρ_α is the spin density on the α carbon. For a freely

$$a^{\mathrm{H}} = \rho_\alpha(B_0 + B_2 \cos^2 \phi) \qquad (1)$$

rotating methyl group, where $\cos^2 \phi = 1/2$, the average coupling to each proton is given by (2). Being invariant

$$\bar{a} = \rho_\alpha(B_0 + B_2/2) \qquad (2)$$

the spin density distribution in (IV) and (V), ρ_α can be removed by dividing (1) by (2), thus obtaining expression (3), which can be written more conveniently as (4), where $[(2B_0 + B_2)/B_2] = 1.045$.[16]

$$\frac{a^{\mathrm{H}}}{\bar{a}} = \frac{B_0 + B_2 \cos^2 \phi}{B_0 + B_2/2} \qquad (3)$$

$$\cos 2\phi = \frac{a^{\mathrm{H}} - \bar{a}}{\bar{a}}\left(\frac{2B_0 + B_2}{B_2}\right) \qquad (4)$$

Since a^{H} and $\bar{a}$ are 2.69 and 4.21 G in the anion radicals from (V) and (IV) respectively, ϕ can be calculated as 124° at room temperature. This value represents the average on the torsional levels of the ethyl group; the temperature coefficient of the methylene splittings being positive, we may conclude that the equilibrium conformation for the ethyl group is that one placing the methyl on the plane perpendicular to the molecule and containing the symmetry axis of the $2p_z$ orbital of the adjacent carbon. This result is reasonable as any other conformations imply a greater steric repulsion between methyl and the neighbouring oxygen and sulphur atoms.

Ion Pairs.—The radicals we have examined are semiquinones, which, like the analogous benzene derivatives, exist in solution as contact ion pairs if they are produced by reduction with alkali metals in ethers. Also in this case the counterion is located close to one of the two oxygens since they are more electronegative than the other nuclei of the organic anion. In the symmetric derivatives (I) and (II) [the ion pair of the diphenyl substituted compound (III) has not been studied because of the complexity of its e.s.r. spectrum] the equivalence of the two oxygens causes the appearance of a unique type of ion pair. As an example Figure 1 shows the e.s.r. spectrum of the radical anion of the dimethyl derivative (II) in DMSO, which shows the expected septet due to the six methyl protons, and that of its lithium complex showing distinct couplings from the two unequivalent methyl groups. The difference Δa_{Me} of the observed methyl splittings may be taken as a measure of the strength of the perturbation induced by the cation, and therefore the variations of its magnitude when changing solvent, temperature, or the nature of the alkali metal may give information on the degree of interaction between anion and cation as function of these factors. Figure 2 shows that Δa_{Me}, or Δa_{H} in the case of (I), increases on going from the potassium to the lithium complex thus suggesting that the ion pair is more strongly bound the smaller the dimensions of the counterion. This observation is in agreement with previous results indicating that the covalent character of the metal–oxygen partial bond increases with decreasing size of the alkali cation.

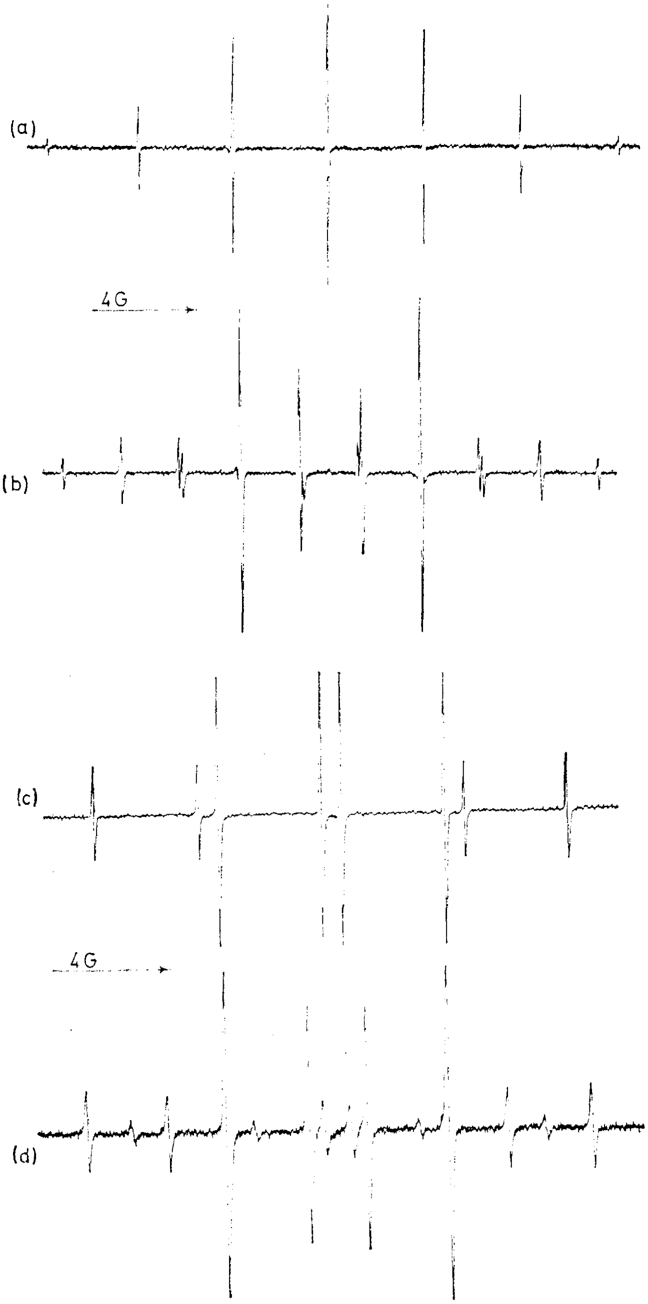

FIGURE 1 E.s.r. spectra of the radical anion from (II) in DMSO (a) and of its lithium complex in DME at −25 °C (b), and of the radical anion from (IV) in DMSO (c) and of its sodium complex in THF at −75 °C (d)

The reduction of Δa on going from THF to DME indicates that the interaction of the two ions is smaller in DME, and is in line with the known better solvating capability of the latter ether. The structure of the ion pair changes also with temperature as it results from the decrease in Δa observed on cooling. The reduced interaction between anion and cation is probably due

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[16] R. D. Allendoerfer, P. E. Gallagher, and P. T. Lansbury, *J. Amer. Chem. Soc.*, 1972, **94**, 7702.

to the fact that external solvation of the contact ion pair becomes more effective at lower temperatures. The reduction of Δa is accompanied by the appearance of a new species which can be identified as the free anion radical of (I) or (II) as its amount increases by dilution. The free ion is absent only in THF when using Li as the counterion. In the case of the potassium complex of (II) slow exchange spectra can be recorded only near the freezing point of the solvent, and therefore the temperature dependence of Δa_{Me} could not be measured. These spectra are also contaminated, mainly with DME, by large amounts of the free ion whose lines are practically superimposed on those of the ion pair in the fast exchange region.

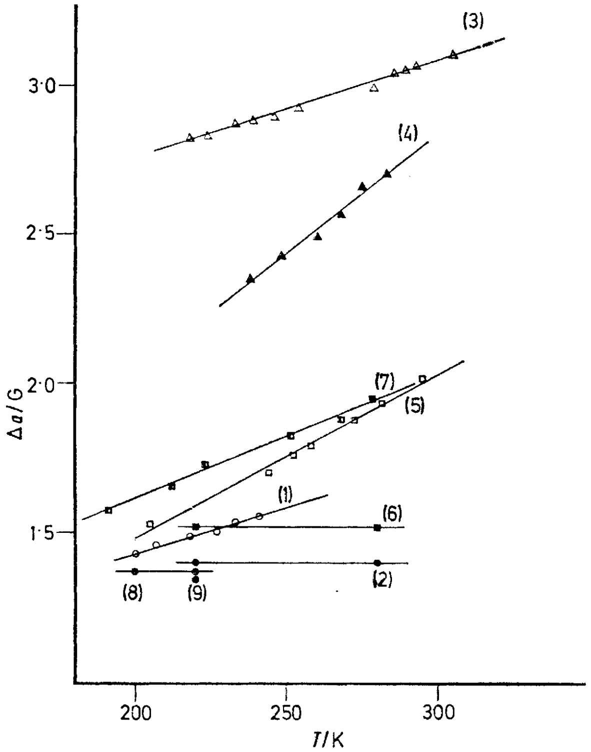


FIGURE 2 Temperature dependence of the difference Δa of the two hyperfine splitting constants in the radical ion pairs of (I) and (II). The mean value $\bar{a}$ (G) of these splittings for (I) is: 3.96 in THF-Na (1); 4.04 in DME-Na (2). For (II): 3.49 in THF-Li (3); 3.50 in DME-Li (4); 3.61 in THF-Na (5); 3.63 in DME-Na (6); 3.62 in DME-THF (1 : 1)-Na (7); 3.63 in THF-K (8); 3.64 in DME-K (9)

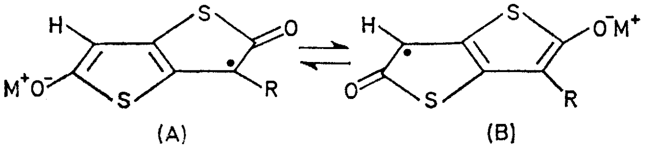
This is an unfortunate coincidence which represents the most serious source of error in determining the rate constants for the migration of the potassium cation.

The alkali metal splittings were in each case very small (<0.15 G) or undetectable and showed positive temperature dependence as in other semiquinone systems.[2]

While the radical anion of the dimethyldithiolactone (II) is stable for several hours even at room temperature, the radicals of the unsubstituted (I) and monosubstituted (IV)—(VI) derivatives decompose rapidly to give other radicals of unknown structure. The sample should then be renewed frequently to have e.s.r. spectra not contaminated by other signals. For this reason the latter compounds were not as thoroughly studied as those from (II). To have comparable data the sodium complexes were in each case more extensively investigated.

With regard to the asymmetric derivatives (IV)—(VI), a new important source of information is represented by the simultaneous presence of the two non-equivalent isomeric ion pairs. As a typical example Figure 1d shows the e.s.r. spectrum of the sodium complex of the monomethyl derivative (IV), which consists of the superposition of signals from two distinct species characterized by different proton splittings. The two isomers can be easily identified from the relative values of the couplings to the aromatic proton and to the methyl or methylene hydrogens. The resonance structures (A) and (B) give rise to electron spin density at the protonated or substituted position when the counterion is located on the same side (A) or on the opposite side (B) of the unsubstituted proton.

It is therefore straightforward to deduce that isomer (A) should be characterized by the smaller aromatic proton splitting and by the larger coupling to the hydrogens of the substituent, while the reverse should be true for isomer (B). As it can be seen from Figure 1d, the more stable isomer is (A) in the case of the monomethyl derivative (IV). This greater stability may partially depend on the inductive and hyperconjugative effects of the methyl group, since in the free anion radical of (IV) the resonance structure (b) was found to be more important than (c). However the electronic effects of the substituent are not sufficient to explain the variation of the isomer ratio observed by changing the methyl (IV) with an ethyl (V) or a t-butyl (VI) group. In fact the stability of the isomer with the alkali cation on the same side of the alkyl substituent (B), decreases along this series (see Table 2). The most obvious explanation of this behaviour may be found in the different steric hindrance of the alkyl groups, since the partial bond of the alkali cation to the negative oxygen in isomer (B) will become more difficult as the bulk of



(A) (B)

TABLE 2

Hyperfine splitting constants (G) and ratio between isomers (A) and (B) (see text) in the radical ion pairs of the monosubstituted dithiolactones

Compound	Solvent and counterion	t/°C	Isomer (A) a_{H}	Isomer (A) $a_{\mathrm{CH_3}}$	Isomer (B) a_{H}	Isomer (B) $a_{\mathrm{CH_3}}$	(A)/(B)
(IV)	THF,Na	−90	2.88	4.85	4.29	3.37	3.5
		−43	2.77	4.95	4.35	3.30	2.4
	DME,Na	−70	2.92	4.90	3.73	4.26	1.4
(V)	THF,Na	−60	2.86	2.90 *	4.33	1.94 *	3.3
(VI)	THF,Na	−60	2.90	0.19	3.75	0.18	5.0

* Methylene splitting.

the R substituent increases. The result will be a destabilization of the latter species in favour of the other ion pair where the metal is located on the same side of the aromatic proton (A).

External solvation of the contact ion pairs seems also to play an important role in stabilizing structure (A) with respect to (B), as indicated by the temperature dependence, reported in Table 2, of the isomer ratio in the case of the sodium complex of (IV) in THF. By measuring the equilibrium constant for the (B) $\rightleftharpoons$ (A) isomerization as function of temperature the thermodynamic quantities ΔH_0 and ΔS_0 were determined as 0.7 kcal mol^{-1} and -1.4 cal mol^{-1} K^{-1} respectively. The negative value of ΔS_0 suggests that solvation is slightly more efficient for species (A); this result may also be attributed to the larger steric crowding around the carbonyl oxygen adjacent to the aliphatic group, which makes more difficult the approach of the solvent molecules to the positive counterion.

Kinetics of Cation Transfer.—Quantitative information on the kinetics of the intramolecular cation exchange were obtained by analysing the line shape variations of the e.s.r. spectra taken at various temperatures using the density matrix theory.[17] The determination of the rate constants for the dynamic process was made by visually fitting to the experimental spectra those simulated by a computer program already described.[1] The results of the kinetic study are summarized in Figure 3, which report the Arrhenius diagrams for the radical ion pairs of (I) and (II). The activation parameters derived from these diagrams and the thermodynamic constants for the activated complex, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, have been calculated using the Eyring equation with a transmission coefficient of unity.

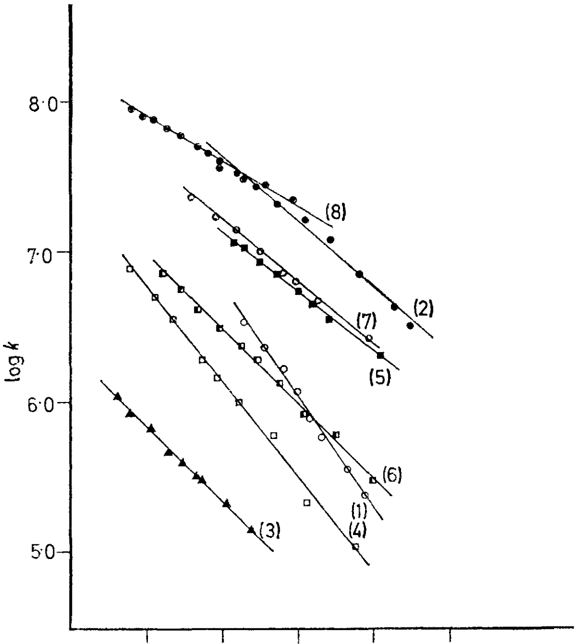


FIGURE 3 Arrhenius diagrams of the rate constants for the cation transfer in the alkali metal complexes of (I) in THF–Na (1), DME–Na (2); and of (II) in DME–Li (3), THF–Na (4), DME–Na (5), THF–DME(1 : 1)–Na (6), THF–K (7), and DME–K (8)

These results indicate, as in other ion pairs containing two binding sites,[1-4] that a considerable reorganisation of solvent molecules occurs during the exchange process. The negative activation entropies suggest that the transition state is much more solvated than the ground state, so that the picture representing the exchange as the passage between two equivalent externally solvated ion pairs through a solvent separated ion pair, seems to be appropriate in the present case. In fact the variations with solvent of the activation parameters are consistent with the stronger solvating power of DME, as larger entropy changes should be expected with this solvent with respect to THF. Moreover the better solvation of the transition state in DME should also induce a stabilisation of the activated complex and therefore a decrease of the activation energy as experimentally observed. Also the effect of changing the nature of the organic anion can be easily rationalized within that model; the smaller negative activation entropies measured for the sodium ion pair of (I) indicate that the solvation difference between ground and transition state is smaller than for the sodium complex of (II). Since it seems reasonable to admit that the solvent complexation of the transition state should not differ too much in the two derivatives, the difference may be explained in terms of a reduced solvation of the ground state in the case of the ion pair of (II) which originates from the greater steric crowding around the carbonyl oxygens arising from the presence of the bulky methyl groups.

Finally we have to consider the effect of changing the counterion on the activation parameters. We have seen in the previous section that on decreasing the size of the alkali cation, the perturbation induced on the organic anion (Δa) increases. This means that the degree of association and therefore the activation energy for the transfer of the cation should also increase, as it is experimentally observed. On the other hand closer association should also be accompanied by reduced solvation of the ground state, while the smaller size of the counterion should make the transition state more solvated. We may then expect the activation entropy to become less negative along the series Li, Na, and K. This sequence is followed when going from Li to Na, while with K the negative $\Delta S^{\ddagger}$ increases again. The breakdown of this sequence may result from the fact that the activation parameters have been calculated on the usual assumption that the change of temperature influences only the rate of migration. Actually in a number of cases the change of the proton splittings on cooling gives evidence of a parallel change in the structure of the ion pair; consequently the enthalpy and entropy contents of the ground state should be temperature dependent. Unfortunately it is not easy to visualize the effect of these variations on the measured kinetic parameters.

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

To this purpose we tried to calculate the rate constants by making the following assumption: the structure of the activated complex was considered temperature independent, while for the ground state the decrease of the perturbation when lowering the temperature was taken as an index of increased solvation. Larger values of $\Delta H^{\ddagger}$ and smaller negative values of $\Delta S^{\ddagger}$ were then assumed at lower temperatures. From Figure 4, which reports the results of these calculations, we notice that the resulting curves are not too far from being straight lines and also that some of the experimental plots of Figure 3 (particularly those referring to the sodium complex of the unsubstituted dithiolactone) show curvature similar to those calculated. Secondly it is worth emphasizing that the fictitious activation parameters which may be derived from a least square treatment of the data of Figure 4 differ significantly from their temperature averaged values (*i.e.* $\Delta H^{\ddagger}$ 5 kcal mol^{-1}, $\Delta S^{\ddagger}$ −12 cal mol^{-1} K^{-1}), being $\Delta H^{\ddagger}$ 4.04 or 7.54 kcal mol^{-1}, $\Delta S^{\ddagger}$ −16.0 or −2.0 cal mol^{-1} K^{-1} for curves (2) and (3) respectively. It is therefore obvious that, if the enthalpy and entropy content of the ground states are temperature dependent, it is not possible to make even an approximate estimate of the actual values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ unless we know their combined variation with temperature. This may therefore explain the apparent inconsistency with the model we have chosen for describing the intramolecular cation exchange, of the trend of the $\Delta S^{\ddagger}$ changes as a function of the counterion.

TABLE 3

Activation parameters for the intramolecular cation migration in the radical ion pairs of the dithiolactones (I) and (II)

Solvent and counterion	E_a/ kcal mol^{-1}	log A	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}
	Thieno[3,2-*b*]thiophen-2,5-dione (I)			
DME, Na	3.93 ±0.14	11.06 ±0.14	3.43 ±0.15	−9.59 ±0.67
THF, Na	6.84 ±0.17	12.77 ±0.17	6.40 ±0.18	−1.55 ±0.80
	3,6-Dimethylthieno[3,2-*b*]thiophen-2,5-dione (II)			
DME, Li	4.56 ±0.08	9.32 ±0.07	4.02 ±0.08	−17.68 ±0.32
DME, Na	3.63 ±0.07	10.31 ±0.06	3.19 ±0.07	−12.78 ±0.31
THF, Na	5.94 ±0.10	11.31 ±0.09	5.45 ±0.09	−8.40 ±0.37
DME, K	2.81 ±0.08	10.06 ±0.07	2.30 ±0.08	−14.23 ±0.32
THF, K	3.69 ±0.07	10.42 ±0.07	3.23 ±0.08	−12.35 ±0.33
DME–THF (1 : 1), Na	4.69 ±0.08	10.59 ±0.09	4.20 ±0.08	−11.74 ±0.37

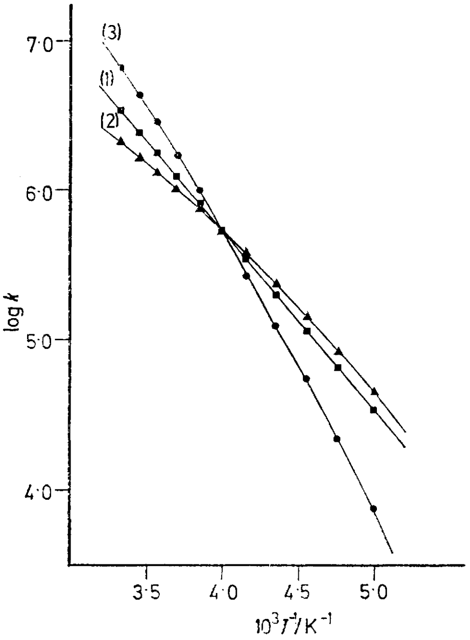

FIGURE 4 Plots of log k against $1/T$; log k was calculated from the Eyring equation assuming $\Delta H^{\ddagger}$ (kcal mol^{-1}) and $\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1}) to vary linearly with temperature between 200 and 300 K: (1); $\Delta H^{\ddagger}_{200} = \Delta H^{\ddagger}_{300} = 5$, $\Delta S^{\ddagger}_{200} = \Delta S^{\ddagger}_{300} = -12$; (2); $\Delta H^{\ddagger}_{200} = 5.3$, $\Delta H^{\ddagger}_{300} = 4.7$, $\Delta S^{\ddagger}_{200} = -10$, $\Delta S^{\ddagger}_{300} = -14$; (3); $\Delta H^{\ddagger}_{200} = 6$, $\Delta H^{\ddagger}_{300} = 4$, $\Delta S^{\ddagger}_{200} = -10$, $\Delta S^{\ddagger}_{300} = -14$

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