Pergamon

Tetrahedron, Vol. 53, No. 29, pp. 10103-10112, 1997
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0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00351-7

Equilibrium Acidities of Some Sulfones and Sulfoxides in Tetrahydrofuran[1]

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Abstract: Ion pair acidities are reported in tetrahydrofuran (THF) solution for the lithium and cesium salts of several sulfones and one sulfoxide. These salts are shown to be monomeric in the THF solutions studied. Thermodynamic constants are reported for several salts. The results and some conductivity studies show that both the lithium and cesium salts are contact ion pairs in THF. Because of ion association the relative p*K*s are slightly lower for cesium salts and much lower for lithium salts than for the free ions in DMSO solution. © 1997 Elsevier Science Ltd.

The sulfonyl group has long been known to stabilize an adjacent carbanion. In a seminal experiment Doering and Levy showed that the mechanism of this stabilization differs significantly from that of the carbonyl group because the sulfonyl group stabilizes bridgehead carbanions as well as acyclic carbanions.[2] Carbanions stabilized by α-sulfonyl and α-sulfinyl groups are now used extensively as reaction intermediates in organic synthesis.[3] Equilibrium acidities for a number of sulfur functions have been determined by the Bordwell group in dimethyl sulfoxide (DMSO) solution.[4-9] These results pertain generally to the free ions in the polar solvent. Many synthetic procedures make use of lithium salts in ethers such as tetrahydrofuran (THF) in which the carbanions are present as ion pairs and aggregates. Crystal structures of a number of lithium salts containing sulfonyl[10-15] and sulfinyl[16] groups have recently been determined. These crystals consist generally of dimers linked by Li-O bonds. The Cα-S bond is shortened considerably but the S-O bond is only slightly lengthened. No bond is formed between the Li atom and the carbanion carbon, Cα. All of these structural features agree well with ab initio calculations.[17] However, these solid-state or computed gas phase structures are not necessarily relevant to structures and reactions in solution.

In the present paper relative ion pair acidities are presented for some lithium and cesium salts of sulfones and a sulfoxide in THF solution. Some preliminary results were published earlier for benzyl phenyl sulfone, **1**.[18] Ion pair acidities are defined as the transmetallation equilibrium (1). Such equilibria give only the acidity differences of the two compounds but it is more convenient to deal with absolute numbers; hence, the resulting Δp*K*s are converted to absolute acidities[19] by setting the p*K* of fluorene equal to its ionic Δp*K* of 22.9 (per hydrogen) measured by the Bordwell group in DMSO.[4]

$$\text{Ind}^{-}\text{M}^{+} + \text{AH} \rightleftharpoons \text{IndH} + \text{A}^{-}\text{M}^{+} \qquad \text{eq. (1)}$$

$$\Delta pK = -\log K, \quad pK(\text{AH}) = pK(\text{IndH}) + \Delta pK \qquad \text{eq. (2)}$$

The carbanions derived from **1** do not have useful absorbance in the accessible UV-vis spectrum and measurement of their equilibria made use of the "single indicator technique".[20] In this method a known amount of substrate is added to the indicator and the decrease in the absorbance of the indicator measures the amount of indicator anion converted to substrate anion. The more extended conjugation of the p-biphenylylmethyl group provides a better chromophore and useful absorption; thus, this study included p-biphenylylmethyl phenyl sulfoxide, **2**, and sulfone, **3**, which could therefore be studied by the more accurate "double indicator technique". These compounds were prepared by oxidation of the corresponding sulfide with hydrogen peroxide at different temperatures. The p*K*s of two other sulfones, methyl phenyl sulfone, **4**, and dimethyl sulfone, **5**, were also studied. The carbanions of these sulfones also do not have absorbance in a useful region and were studied by the single indicator technique. The present work also includes aggregation, thermodynamic studies, and conductivity measurements of the lithium and cesium salts of **2** and **3**.

RESULTS AND DISCUSSION

Ion Pair Acidities

The alkali salts of **2** and **3** exhibit strong visible absorbance. The spectral data are listed in Table 1. The accuracy of the extinction coefficient values is estimated as ± 5%. The cesium salt of p-methylbiphenyl has λ_{max} = 471 nm; addition of a phenylsulfinyl group on the carbanion shifts the λ_{max} to 414 nm, and a further addition of one more oxygen to the sulfur shortens the λ_{max} to 393 nm. This effect can be interpreted as a simple electrostatic effect resulting from decreased charge delocalization in the p-biphenylylmethyl system by the strong electron-withdrawing groups.

The λ_{max}'s of the two cesium salts, **2C** and **3C**, undoubtedly are those of the contact ion pairs. The λ_{max}'s of the two lithium salts, **2L**, 404 nm, and **3L**, 384 nm, are about 10 nm shorter than those of the corresponding cesium salts and therefore also are those of the contact ion pairs. This conclusion will be confirmed by other observations discussed below.

Table 1. Spectral Data for the Salts of **2** and **3** in THF at 25 °C.

Compound	λ_{max} (nm)	ε
2L	404	24 600
3L	384	21 200
2C	414	36 700
3C	393	26 500

The relative ion pair acidities were measured spectroscopically according to equation (1) in which IndH is a suitable indicator with an acidity designated as $pK_{Li/THF}$ or $pK_{Cs/THF}$.[21,22] For each compound, two or three indicators were used. The acidity differences, K, were converted to the corresponding pK values. The experimental results given in Table 2 show that the pK assignments are independent of the indicator used. The results are summarized in Table 3. The accuracy of the average pK values listed in Table 3 is about ± 0.1 unit, but the precision of these measurements is much better. Table 3 also includes the pK_a values in DMSO determined by Bordwell.[4]

Table 2 Ion Pair Equilibria[a] with Indicators[b] in THF at 25 °C

RH	M^+	InH[b]	$\Delta pK_{M/THF}$	$pK_{M/THF}$
2	Li^+	1,2-BF	0.38± 0.02	20.08
		BA	0.02± 0.01	20.15
		BnFl	-1.24± 0.02	20.12
	Cs^+	9-t-BuFl	0.83± 0.01	25.22
		TPP	-1.52± 0.02	25.24
3	Li^+	9-PhFl	1.31± 0.01	18.91
		1,2-BF	-0.94± 0.01	18.76
		BA	-1.29± 0.04	18.84
	Cs^+	BnFl	0.90± 0.01	22.20
		Fl	-0.59± 0.01	22.31
1	Li^+	1,2-BF	-0.18± 0.02	19.52
		BA	-0.57± 0.03	19.56
	Cs^+	4,5-MP	0.09± 0.05	23.00
		2,3-BF	-0.64± 0.03	22.99
4	Cs^+	TPP	0.52± 0.02	27.28
		PDDA	-0.88± 0.04	27.23
5	Cs^+	9-PX	0.05± 0.12	28.78
		BDPM	-1.30± 0.03	28.77

[a] On per hydrogen basis. [b] Abbreviations and pKs of indicators: Lithium salts:[19] 9-PhFl, 9-phenylfluorene, 17.60; 1,2-BF, benzo[a]fluorene, 19.70; BA, benzanthrene, 20.13; BnFl, 9-benzylfluorene, 21.36. Cesium salts:[22] 9-BnFl, 9-benzylfluorene, 21.30; Fl, fluorene, 22.90; 4,5-MP, 4,5-methylenephenanthrene, 22.91; 2,3-BF, benzo[c]fluorene, 23.63; 9-t-BuFl, 9-tert-butylfluorene, 24.39; TPP, 1,3,3-triphenylpropene, 26.76; PDDA, 9-phenyl-10,10-dimethyldihydroanthracene, 28.11; 9-PX, 9-phenylxanthene, 28.73; BDPM, biphenylyldiphenylmethane, 30.07.

Table 3. Summary of Equilibrium Acidities.

Compound	$pK_{Li/THF}$	$pK_{Cs/THF}$	DMSO[a]
1, benzyl phenyl sulfone	19.5	23.0	23.4
2, p-biphenylylmethyl phenyl sulfoxide	20.1	25.2	
3, p-biphenylylmethyl phenyl sulfone	18.8	22.3	
4, phenyl methyl sulfone		27.3	29.0
5, dimethyl sulfone		28.8	31.1

(a). Reference 4.

The α-sulfonyl and α-sufinyl stabilization of carbanions is quite dramatic. p-Methylbiphenyl has $pK_{Cs/THF} = 38.9$, while the $pK_{Cs/THF}$'s of **2** and **3** are 25.2and 22.3, respectively, indicating that the sulfinyl and sulfonyl group stabilizes the biphenylmethyl anion by 13 and 16 p*K* units, respectively. For the benzylic carbanion, the stabilization is even larger. Toluene has $pK_{Cs/THF} = 41$,[22] while benzyl phenyl sulfoxide has $pK_{Cs/THF} = 23.0$, leading to 18 p*K* units stabilization. The difference of acidity of sulfoxide **2** and sulfone **3** is about 3 p*K* units on the cesium scale. On the other hand, the additional conjugation of a p-phenyl group has a much smaller effect on a sulfone (the $pK_{Cs/THF}$ difference between **1** and **3** is only 0.7 units) than on toluene ($pK_{Cs/THF}$ difference of 2.1 units) indicative of electrostatic inhibition of delocalization of charge away from the sulfone group.

One striking point from these measurements is the cation dependence of p*K*s of these compounds. Cesium ion pair p*K*s are generally quite similar to the corresponding ionic p*K*s in DMSO.[19] In accord with this generalization, $pK_{Cs/THF}$ of **1** is similar to the DMSO value, but the $pK_{Cs/THF}$ values of **4** and **5** are substantially lower than the values determined in DMSO indicative of tighter ion pair bonding in these localized carbanions. The $pK_{Li/THF}$s of **1**, **2**, and **3** are 3-4 p*K* units lower than $pK_{Cs/THF}$s. These results demonstrate that the carbanions are stabilized by association with cesium or lithium cation and that the lithium ion pair as a contact ion pair is even more stable than the cesium contact ion pair.

Concentration Measurements

All of the crystal structures of α-sulfonyl and α-sulfinyl carbanions determined by X-ray are dimers.[10-16] To determine the average degree of aggregation of these carbanion salts in solution we used the technique of coupled equilibria. We showed previously that an aggregation equilibrium together with a transmetallation equilibrium causes the apparent p*K* value to change with concentration.[23,24] The slope of a plot of apparent p*K* vs the formal M^+R^- concentration equals (1-n)/n where n is the average aggregation number. Examples of such plots are shown in Figure 1 in which the lithium salt of **3** is shown with three different indicators. All three indicators give straight line functions whose slopes give aggregation numbers of 1.08 - 1.39. Similar plots with the other salts give the aggregation numbers summarized in Table 4. The results show that the sulfone salts are mostly monomeric at these concentrations.

Table 4. Average Aggregation Constants of Sulfone Salts in THF.

Compound	Cation	Aggregation no., n	Concn range, M
1, benzyl phenyl sulfone	Cesium	1.0	(3-8) x 10^{-4}
3, p-biphenylylmethyl phenyl sulfone	Lithium	1.1 - 1.4	(0.9-9) x 10^{-5}
	Cesium	1.1 - 1.3	(0.4-9) x 10^{-4}
4, phenyl methyl sulfone	Cesium	1.1	(4-25) x 10^{-5}
5, dimethyl sulfone	Cesium	1.0	(1-5) x 10^{-4}

Thermodynamic Measurements

The equilibrium constants of equilibrium (1) were determined at several temperatures from 25 °C to -20 °C. Standard enthalpies and entropies of reactions were then determined via Van't Hoff plots. Each determination involved at least three runs. The results are summarized in Table 5. The errors assigned are the average deviations from the Van't Hoff plots of two or more runs. The values are probably accurate to about ±0.5 kcal mol^{-1} for $\Delta H°$ and ±1.0 eu for $\Delta S°$. Note that for both $\Delta H°$ and $\Delta S°$ the summation of the results with two indicators overlap well with the direct measurements between the indicators. This further confirms the accuracy of our p*K* assignments.

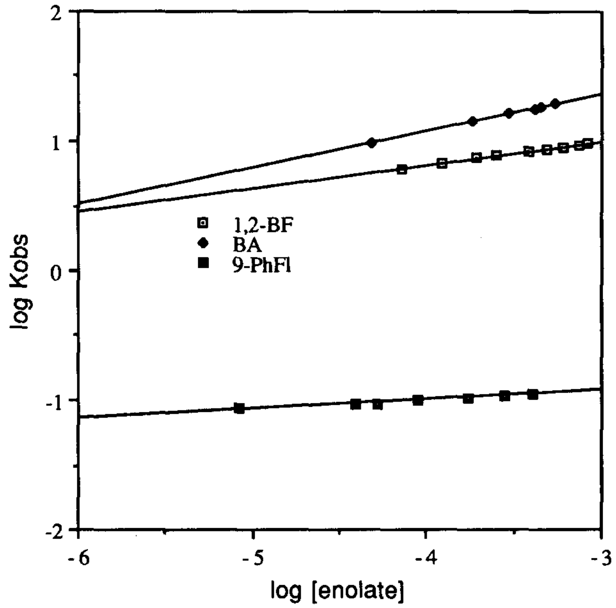

Fig. 1. Aggregation effects of **3** vs indicators with lithium as counterion. See Table 2 for abbreviations.

Table 5. Overlapping Thermodynamic Measurements for $RH + R'^{-}M^{+} \rightarrow R^{-}M^{+} + R'H$.

M^+	RH[a]	R'H[a]	$\Delta H^{\circ b,c}$	$\Delta S^{\circ c,d}$
Cs	45MP	**1**	-3.0 ± 0.5	-9.5 ± 0.5
	1	23BF	1.9 ± 0.5	8.3 ± 0.7
	45MP	23BF	-1.1 (-1.2)	-1.2 (-0.7)
Li^+	**3**	1,2-BF	4.8± 0.1	20.8 ± 0.4
	3	BA	5.9± 0.3	26.0 ± 0.5
	BA	1,2-BF	-0.9 (-0.7)	-5.2 (-4.3)
Cs^+	**3**	9-BnFl	0.7 ± 0.1	2.0 ± 0.3
	3	Fl	-0.4 ± 0.3	4.6 ± 1.1
	Fl	9-BnFl	1.1 (1.7)	-6.6 (-6.2)
Cs	TPP	**4**	-7.6 ± 0.4	-21.4 ± 1.1
	4	PDDA	1.8 ± 0.3	8.9 ± 1.0
	TPP	PDDA	-5.8 (-5.4)	-12.5 (-10.6)
Cs	9PX	**5**	-3.9 ± 0.2	-12.7 ± 5.3
	5	BDPM	3.7 ± 0.1	18.5 ± 1.0
	9PX	BDPM	-0.2 (0.2)	5.8 (6.6)

[a]See Table 2 for abbreviations. [b]In kcal mol^{-1}. [c]Direct measurement in parentheses. [d]In eu corrected for the symmetry component (per hydrogen).

Analysis of the thermodynamic values gives additional insight. The entropy changes for **3** with the cesium salts of indicators are small (less than 5 eu). This result indicates further that the cesium salt of **3**, like the indicator salts, exists as contact ion pairs, and that solvation is comparable for both salts. The changes are somewhat greater for the more localized carbanion salts. Previously, changes in ΔS° have been associated with the restriction of rotations within carbanions.[25] In the present cases, however, it seems more likely that the effects are those of solvation. The oxygens of the sulfone anions probably solvate cesium better than the solvent THF and solvent is effectively released when the indicator salt forms the sulfone salt. In contrast, the equilibrium (1) of the lithium salt of **3** involves large positive entropy changes (20-26 eu). The solvation changes are much larger and are in the direction expected for conversion of the solvent-separated indicator salt to a localized or contact ion lithium salt. This result is also consistent with the difference between $pK_{Li/THF}$ and $pK_{Cs/THF}$ for **3** and with the coordination of the sulfone oxygens with lithium cation shown by X-ray structures[10-15] and ab initio calculations.[17]

Conductivity Measurements

Conductivity measurements are exceedingly important generally[26] in studies of ion pairing and we have found such studies to be useful for interrelating the lithium and cesium scales of ion pair acidities.[19] We found to our surprise, however, that solutions of the cesium and lithium salts of **3** have extremely low conductivities. At the same salt concentration, the lithium salt is much less conductive than the cesium salt . A similar study by Biellman and Vicens agrees with this result.[27] They found that the lithium salt of benzyl methyl sulfoxide is not conductive in THF, THF-TMEDA and THF-DME at -78 °C. By contrast, under the same conditions they found a solution of the lithium salt of benzyl phenyl sulfide to be conductive.

The conductivities of the lithium and cesium salts of **3** were measured and the dissociation of **3L** and **3C** to the free ions was calculated from the Fuoss equation (eq. 3),[28]

$$F/\Lambda = 1/\Lambda_o + f^2 c\Lambda / F K_d \Lambda_o^2 \qquad \text{eq. 3}$$

where F is the Fuoss term, Λ is the equivalent conductance, f is the mean activity coefficient, and Λ_o is the equivalent conductance at infinite dilution. For consistency with our previous work,[19] Λ_o was assigned as 85 $cm^2\ \Omega^{-1}\ M^{-1}$ for **3L** and 120 $cm^2\ \Omega^{-1}\ M^{-1}$ for **3C**; F was assigned as 0.94 for **3L** and 1.0 for **3C**; f was set equal to 0.85 for **3L** and 1.0 for **3C**. From the conductivity data, plots of F/Λ versus $f^2c\Lambda/F$ are shown in Fig. 2. There is a small curvature in these plots for both compounds when $f^2c\Lambda/F$ is close to zero. From the linear parts of these plots, K_d was estimated for **3L** and **3C** according to equation (3). The curvature reduces the accuracy of the results but the accuracy is sufficient for the present purpose. The results are summarized in Table 6.

The free ion (FI) acidity of **3** was calculated from the corresponding ion pair (IP) by equation 4,

$$pK(FI) = pK(IP) - \log K_d/K_d^\circ \qquad \text{eq. 4}$$

where K_d° is the dissociation constant of the acidity standard, fluorene ($K_d[Li] = 0.69 \times 10^{-5}$ M, $K_d[Cs] = 1.49 \times 10^{-8}$ M).[19] The dissociation constants of solvent separated ion pair lithium salts of carbanions is generally about 10^{-5} M.[19] In sharp contrast, K_d of **3L** is 7×10^{-9} M and clearly means that the lithium salt of **3** is present as contact ion pairs in THF solution. The K_d of **3C** is 1.3×10^{-8} M and is somewhat smaller but of comparable magnitude to the K_d values of the cesium salts of delocalized indicators.[19] The free ion pK values derived from the lithium and cesium salts of **3** should, of course, be equal; the difference of 0.5 pK units reflects the limited accuracy of the conductivity experiments, primarily probably of the lithium salt. The low conductivity of the lithium salt is nevertheless consistent with its lower pK value in Table 2; both numbers indicate a dissociation of **3L** about 10^{-3} that of the indicator salts.

Conclusion

Ion pair acidities of four sulfones and one sulfoxide have been determined in THF solution. The $pK_{Cs/THF}$ values of these compounds are somewhat lower than the ionic pK_a's determined in DMSO and indicate a stronger association of the cesium cation with the sulfone anion than with the delocalized indicator carbanions; the $pK_{Li/THF}$'s are 4-5 units lower than the $pK_{Cs/THF}$'s indicating still strong association of lithium cation with the sulfone anion. Both the cesium and lithium salts of delocalized sulfones and sulfoxides are monomeric in dilute THF solution, and they are both present as contact ion pairs. The contact ion pairs with lithium cation are less dissociating than those with the larger cesium cation.

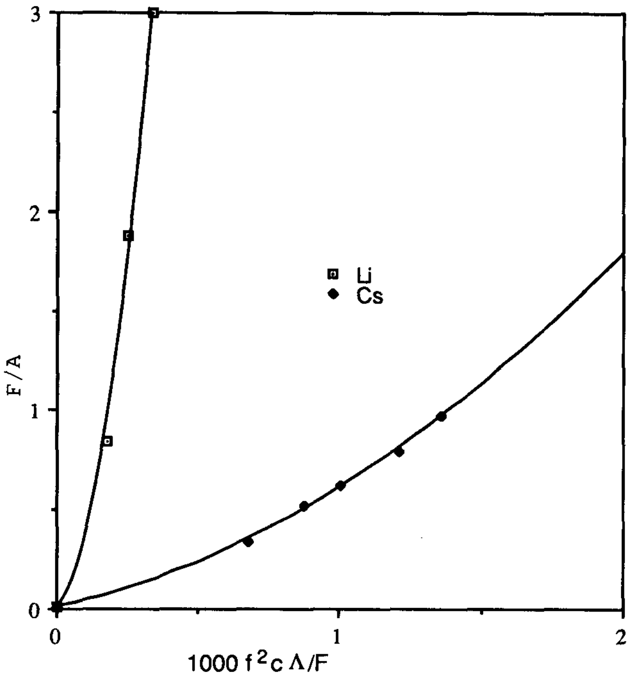

Fig. 2. Fuoss plot for the lithium and cesium salts of **3** at 25 °C.

Table 6. Conductimetric Dissociation Constants and Free Ion Acidity of **3**.

M	K_d (M)	pK(FI)
Li^+	7×10^{-9}	21.8
Cs^+	1.3×10^{-8}	22.3

EXPERIMENTAL

Starting materials for syntheses were obtained from commercial suppliers and purified by recrystallization or distillation prior to use. The hydrocarbon acids used in this work as indicators were available from our previous studies. The purification of THF and preparation of cesium and lithium bases were reported previously.[29] Elemental analyses were performed by the Microanalytical Laboratory, operated by the College of Chemistry.

p-Biphenylylmethyl phenyl sulfoxide, (**2**)

To a 250 mL flask containing 5.0 g (0.027 mol) of 4-biphenylylmethanol and 140 mL of methylene chloride was added 4.2 g (0.041 mol) of triethylamine. To this solution at 0 °C was added 3.5 g 0.030 mol) of methanesulfonyl chloride over a period of 10 min. The reaction was stirred for an additional 15 min; then the reaction mixture was transferred to a separatory funnel with the aid of methylene chloride. The mixture was first extracted with water, followed by cold 20% hydrochloric acid, saturated sodium bicarbonate solution and brine. The methylene chloride layer was dried over anhydrous magnesium sulfate overnight. After removal of the solvent under reduced pressure, 5.8 g of p-biphenylylmethyl methanesulfonate was obtained as a white solid (82%); m.p. 60-62 °C. ^{1}H NMR (CD_3Cl, δ) 2.94 (s, 3 H), 5.29 (s, 2 H), 7.25-7.61 (m, 9 H).

To a round bottom flask equipped with magnetic stirrer, a reflux condenser and a pressure equalizing addition funnel was added 25 mL of 95% aqueous ethanol, 1.4 g (0.024 mol) of potassium hydroxide and 2.68 (0.024 mol) of thiophenol. The solution was stirred and heated to 40 °C in a water bath. When all of the potassium hydroxide had disappeared, 5.8 g (0.022 mol) of p-biphenylylmethyl methanesulfonate was added through the addition funnel over 10 min. The reaction was stirred for 1 h at room temperature. About 200 mL of distilled water was then poured into the reaction mixture to dissolve the salts. The organic layer was extracted with diethyl ether. The ethereal extract was washed with 1 M potassium hydroxide to remove residual thiophenol and then with water. The organic layer was dried over anhydrous magnesium sulfate overnight. The ether was removed *in vacuo* to give 6.0 g (97%) of white p-biphenylylmethyl phenyl sulfide; m.p. 125-127 °C. ^{1}H NMR (CD_3Cl, δ) 4.16 (s, 2 H), 7.25-7.55 (m, 14 H).

To a solution of 5.0 g (0.018 mol) of p-biphenylylmethyl phenyl sulfide in 25 mL of glacial acetic acid was added 5.0 mL (0.055 mol) of 30% hydrogen peroxide. The reaction stirred for 4 h at room temperature. The solvent was removed *in vacuo* to afford 5.2 g of p-biphenylylmethyl phenyl sulfoxide (**2**) as a white solid (98%). Sublimation *in vacuo* produced white crystals; m.p. 197-198 °C. Anal. Calcd. for $C_{19}H_{16}OS$: C, 78.07; H, 5.48. Found: C, 78.25; H, 5.52. ^{1}H NMR (CD_3Cl, δ) 4.07 (dd, J = 15, 12 Hz, 2 H), 7.05-7.57 (m, 14 H).

p-Biphenylylmethyl phenyl sulfone (**3**)

To a solution of 2.0 g (6.85 mmol) of p-biphenylylmethyl phenyl sulfoxide in 25 mL of glacial acetic acid was added 5.0 mL (0.055 mol) of hydrogen peroxide. The reaction was stirred for 5 h at 85 °C. The solvent was removed under vacuum to give 2.05 g of white solid with a yield of 98%. Sublimation under high vacuum produced white crystals; m.p. 203-204 °C. Anal. Calcd. for $C_{19}H_{16}O_2S$: C, 74.01; H, 5.19; Found: C, 74.16; H, 5.30. ^{1}H NMR (CD_3Cl, δ) 4.35 (s, 2 H), 7.15-7.69 (m, 14 H).

Equilibrium acidity measurements

Details of the single and double indicator methods used have been published previously.[20,30] Thermodynamic constants were obtained from the p*K*'s at 5 to 10 °C intervals over a temperature range of 25 to -20 °C. Linear least-squares plots of log*K* vs. 1/T gave ΔH° and ΔS°.

Conductance measurements.

The measurements were also done within the glovebox with an ESI Model 2110 Video Bridge operating in the parallel equivalent circuit mode. The procedure was that of our previous work.[19]

ACKNOWLEDGMENTS

This work was supported in part by NIH grant no. GM-30369.

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(*Received* 4 *November* 1996)