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Relaxation processes of some aromatic sulfides, sulfoxides, and sulfones in a polystyrene matrix

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Dielectric absorption studies have been made of a number of aromatic sulfides, sulfoxides, and sulfones in a polystyrene matrix at a variety of temperatures in the frequency range of 10^2–10^5 Hz, and in three cases between 10^4–10^7 Hz. One compound, bis (4-pyridyl) sulfide, was also examined as a pure compressed solid in the frequency range of 10^4–10^7 Hz. The Eyring parameters have been determined and used to characterize the relaxation processes. Low enthalpies of activation (~ 15 kJ mol^{-1}) have been estimated for an intramolecular relaxation process of diphenyl, bis (4-tolyl) and bis (4-pyridyl) sulfide, and rotation about the C–S bond in these symmetrical aromatic sulfides would, thus, be expected to occur quite readily. These low barriers are to be contrasted with those for the molecular relaxation values of 60–78 kJ mol^{-1} for diphenyl, bis(4-tolyl) and bis(4-chlorophenyl) sulfoxides and sulfones. The enthalpies of activation (~ 39 kJ mol^{-1}) for the molecular relaxation of the disklike molecules, dibenzothiophene and its oxides, are also lower than those for the corresponding nonplanar diphenyl sulfur oxides.

INTRODUCTION

Dielectric studies by Cumper and Rossiter[1] in the microwave region have demonstrated that for diphenyl sulfide, sulfoxide, and sulfone in benzene solution the diphenyl sulfide has a significantly shorter relaxation time (~8 ps) than the latter two molecules (~14.7 and ~22 ps, respectively). In the case of diphenyl sulfide the relaxation was attributed to a rapid intramolecular process of the type observed in diphenyl ether.[2] They also concluded that the relaxation times for diphenyl sulfoxide and sulfone are low for molecules of their size and shape so that a contribution from an internal relaxation process is likely to be present. The existence of a mesomeric moment from the sulfur atom to the aromatic rings, and its variation with direction as the rings rotate, was suggested as a possible cause for the intramolecular process.

Cumper, Read, and Vogel[3,4] provided evidence for mesomerism in diaryl sulfoxides and sulfones from dipole moment measurements and ultraviolet spectra.

Craig *et al.*[5] have indicated for the sulfones that the highly difuse 3d orbitals are unlikely to enter into effective conjugation with the π-electrons of the aromatic rings. In sulfones, however, the presence of two electronegative oxygen atoms could so reduce the size of the 3d orbitals that conjugation would be possible.[4]

Besides electronic considerations the shape of the molecules also affects the relaxation parameters. X-ray studies by Toussaint[6] have shown that in crystalline bis(4-bromophenyl) sulfone each ring is twisted 90° out of the C-S-C plane, while for diphenyl sulfoxide Abrahams[7] provided evidence that each ring is twisted 82° out of the C-S-C plane.

It has been shown by Davies and Swain[8] that the use of a solute dispersed in a polystyrene matrix may enable the complete separation of relaxation processes in a molecule which can relax both internally and as a whole. A number of such studies has been made[8-10], and the corresponding Eyring activation energies and relaxation parameters have been determined.

The work now described is an extension of the research into the relaxation processes of aromatic sulfur compounds and of the behavior of polar solutes in a polystyrene matrix. In view of the controversies regarding the structural and rotational properties of diaryl sulfides, sulfoxides, and sulfones a study was undertaken of eleven such compounds in a polystyrene matrix. Information was sought on the relative magnitude of ΔH_E and ΔG_E values and their correlation with the mean volume swept out during molecular relaxation.

One of the major aims of this work was to attempt to detect any intramolecular process exhibited by symmetrically ring-substituted molecules of the type $(X\text{-}C_6H_4)_2Y$ where Y = S, SO, and SO_2 in the polystyrene matrix and to determine its energy barrier. An intramolecular process has long been recognized for the case where Y = O and S and X = H for such molecules in nonpolar solvents.

EXPERIMENTAL

Dielectric measurements of the polystyrene matrices were made on a General Radio 1615-A capacitance bridge in the frequency range 10^2–10^5 Hz. The measuring cell consisted of a three-terminal, circular, parallel-plate capacitor mounted in a temperature-controlled chamber flushed with dry nitrogen gas. The cell is operational from about 77 to 400 K. In a few cases, including a pure compressed solid, additional measurements have been made in the range 2.2×10^4–3.0×10^7 Hz on a Hewlett–Packard HP4342A Q meter with a temperature-controlled, two-terminal cell. The apparatus and measurement techniques have been described previously.[9,10]

Atactic polystyrene with a weight average molecular weight of 2.3×10^5 was used in the matrices. The procedure followed in the preparation of the matrices was essentially that of Davies and Swain.[8]

In the case of bis(4-pyridyl)sulfide a disk of the pure polycrystalline solid was prepared. This was accomplished by grinding with a mortar and pestle about 5 g

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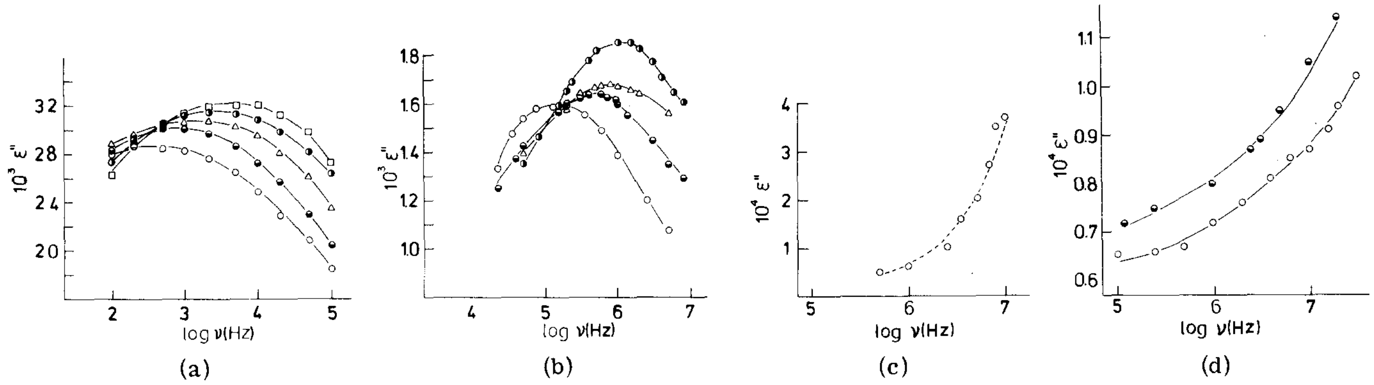

FIG. 1. (a) Dielectric absorptions of 0.643 M diphenyl sulfoxide in polystyrene ○, 250.8 K; ◒, 256.0 K; △, 263.0 K; ◑, 269.0 K; □, 274.1 K; (b) Dielectric absorptions of 0.855 M diphenyl sulfide in polystyrene ○, 89.0 K; ◒, 94.1 K; △, 96.7 K; ◑, 98.9 K; (c) Dielectric absorption of bis(4-pyridyl) sulfide as a pure compressed solid at 88 K calculated loss from Fuoss–Kirkwood equation; (d) Dielectric absorption of 0.572 M bis(4-pyridyl) sulfide in polystyrene; ○, 98.3 K; ◒, 109.4 K.

of the solid. A disk was prepared by placing the powder in a stainless steel die with the application of a pressure of $\simeq 660$ kg cm^{-2}.

The disks were wrapped in aluminum foil and stored in a desiccator over calcium chloride prior to use. All compounds were purchased from either the Aldrich Chemical Company or the K&K Laboratory, except for bis(4-tolyl) sulfide and bis(4-pyridyl) sulfide which were synthesized.

MATERIALS

Bis(4-*tolyl*) sulfide was prepared by a new technique utilizing the reducing agent di-isobutylaluminum hydride,[11] whereby the sulfone was reduced directly to the sulfide. Bis(4-pyridyl) sulfide was prepared by a modification of a published method.[12]

Bis(4-*tolyl*) *sulfide*: To a solution of bis(4-tolyl) sulfone {1.0 g (4 mmol)} in toluene (60 ml.) was added 50 ml of a 20% solution of di-isobutylaluminum hydride in *n*-hexane. The solution was stirred at reflux for 52 h in dry nitrogen. After the solution had been cooled to room temperature, methanol (60 ml.) was added, the mixture filtered, and the solvents were removed from the filtrate *in vacuo*. The residue was chromatographed on a column (silica gel/benzene) to give a white solid, which was recrystallized several times from methanol to yield bis(4-tolyl) sulfide, mp 54° (Ref. 3, 56°) (56%).

Bis(4-*pyridyl*) *sulfide*: The preparation was according to the method of Jerchel *et al.*,[12] with the modification that the 4-mercaptopyridine and *N*-(4-pyridyl) pyridinium dichloride were allowed to react in dry nitrogen for 10 min at 150°. The product was recrystallized several times from benzene to yield bis(4-pyridyl)sulfide, mp 67° (Ref. 12, 67°) (97%).

RESULTS

Representative dielectric absorption curves are shown in Figs. 1(a) and (b) for a polystyrene matrix [$\epsilon'' = \epsilon''$(obs) $-\epsilon''$ (polystyrene)], and in Fig. 1(c) for bis(4-pyridyl) sulfide as a pure compressed solid and in Fig. 1(d) in a polystyrene matrix. The experimental loss data as a function of frequency were analyzed by computer for a best linear fit to the Fuoss–Kirkwood equation:

$$\cosh^{-1}(\epsilon''_{\max}/\epsilon'') = \beta\,(\ln\nu_{\max} - \ln\nu)\ .$$

The solid line in the ϵ'' vs $\log\nu$ plot in Figs. 1(a), (b), and (d), is the best fit to the experimental points. As a result of the analysis three parameters were generated: $\epsilon''_{\max}$, the maximum loss factor of the absorption; $\tau = 1/2\pi\nu_{\max}$, the mean relaxation time characterizing the dipolar motion giving rise to the absorption, and β, the Fuoss–Kirkwood distribution parameter which ranges between 0 and 1, with $\beta = 1$ corresponding to a simple relaxation process involving a single relaxation time and $\beta \ll 1$ to a broad distribution of relaxation times. Table I lists the Fuoss–Kirkwood analysis parameters for the solutes in polystyrene at various temperatures.

Once the relaxation time was evaluated at a given temperature, the free energy of activation was determined from the Eyring rate equation:

$$\tau = (h/kT)\exp(\Delta G_E/RT)$$
$$= (h/kT)\exp(\Delta H_E/RT)\exp(-\Delta S_E/R)\ .$$

Computer extrapolation of partial loss curves for bis(4-pyridyl) sulfide led to an estimation of $\nu_{\max}$ and subsequently the τ and ΔG_E values. Figure 2 shows a typical plot of $\log T\tau$ vs T^{-1}, from which the ΔH_E and ΔS_E values were evaluated.

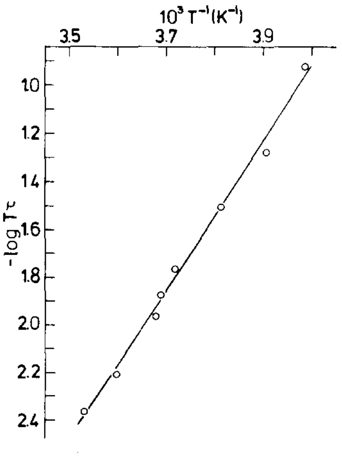

FIG. 2. Eyring plot for 0.643*M* diphenyl sulfoxide in polystyrene.

TABLE I. Fuoss–Kirkwood analysis parameters of some symmetric diaryl compounds in polystyrene matrices at a variety of temperatures.

T(K)	$10^6\tau(s)$	β	$10^3\epsilon''_{max}$
	0.840 M dibenzothiophene		
201.3	167	0.21	3.40
207.2	85.1	0.20	3.55
213.7	41.9	0.20	3.67
219	24.9	0.20	3.80
226.2	13.8	0.24	3.95
230.6	7.0	0.21	4.02
	0.359 M dibenzothiophene sulfone		
204.4	163	0.22	3.24
209.9	90.1	0.21	3.30
213.9	64.0	0.22	3.50
218.4	38.5	0.28	3.88
221.3	27.0	0.22	3.66
230.8	10.0	0.22	3.85
	0.124 M dibenzothiophene sulfoxide		
264.6	125	0.10	6.1
269.4	96.8	0.11	6.2
275.2	63.4	0.10	6.4
281.9	47.4	0.10	7.1
288.1	27.7	0.13	7.9
	0.643 M diphenyl sulfoxide		
250.8	478	0.17	28.8
256	205	0.18	30.1
263	119	0.16	30.8
269	63.3	0.17	31.6
271.2	49.4	0.18	31.8
274.1	39.9	0.18	32.3
278	22.2	0.18	33.4
283.3	15.1	0.18	33.8
	0.423 M diphenyl sulfone		
205.4	530	0.22	9.6
211	248	0.26	11.6
213	175	0.27	12.2
225	16.5	0.32	13.2
231.6	8.3	0.34	15.0
240	2.8	0.28	15.4
	0.190 M bis(4-chlorophenyl) sulfone		
306.2	798	0.12	3.40
311	459	0.15	3.64
316.1	303	0.14	3.61
321.1	192	0.11	3.67
325.5	105	0.11	4.00
	0.462 M bis(4-tolyl) sulfoxide		
294.7	641	0.17	20.6
303.3	285	0.17	22.3
318.7	69.6	0.10	25.9
323.6	46.9	0.11	28.0
	0.417 M bis(4-tolyl) sulfone		
279.8	89.8	0.20	19.4
283.8	68.9	0.20	20.8
288.2	43.3	0.21	22.2
291.8	30.3	0.20	23.1
297.2	17.1	0.19	24.9
299.8	15.2	0.18	25.3
	0.855 M diphenyl sulfide		
89.0	0.99	0.28	1.59
91.6	0.67	0.28	1.59
94.1	0.34	0.26	1.64
96.7	0.19	0.23	1.68
98.9	0.15	0.26	1.85
	0.362 M bis(4-tolyl) sulfide		
92.5	1.00	0.58	0.81
97.5	0.40	0.47	1.07
99.4	0.32	0.61	1.00
101.2	0.20	0.47	1.14
103.1	0.12	0.63	0.78

The errors involved in the determination of the activation parameters were as described previously.[8,10,13,14] In all cases the error in ΔH_E is of the order of ±10%. Tay, Walker, and Wyn-Jones[15] compared intramolecular energy barriers determined by the dielectric matrix technique with those from the ultrasonic and NMR approaches.

DISCUSSION

The diaryl molecules containing C_6H_4X systems (molecules I–III, V, VI, VIII, IX, and XII in Fig. 3) all exhibit absorption maxima at temperatures from 201 to 326 K within the frequency range 10^2–10^5 Hz. In the case of dibenzothiophene, its sulfoxide and sulfone (structures I, II, and III in Fig. 3) ΔH_E values of 39, 39, and 40 kJ mol^{-1} respectively were observed, which within error limits (Table II) are identical. These molecules have the two benzene rings linked at the ortho positions so that the structures are essentially disk-shaped and rigid. Furthermore, there are large dipole moment components perpendicular to the X and Z molecular axes. The molecular axes have lengths in the order $X > Y > Z$ and are oriented orthogonally. The Y-axis was taken to bisect the $C\text{-}\hat{S}\text{-}C$ valency angle (see Fig. 4). The rotational volumes swept out during relaxation were taken to be about the center of volume. Extension of the molecular system by the addition of one or two oxygen atoms to the sulfur atoms does not significantly alter the ΔH_E value of ~40 kJ mol^{-1} within the absolute

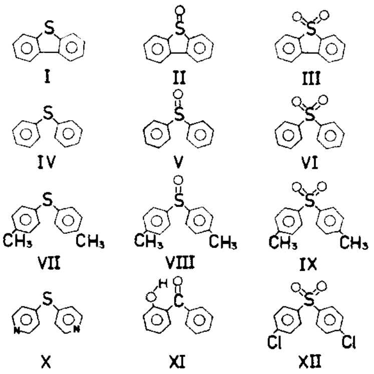

FIG. 3. Structures of molecules discussed in text.

TABLE II. Dielectric relaxation and activation parameters for some symmetric diaryl molecules in polystyrene.

Molecule	Temperature range (K)	$\tau(s)$ 100 K	200 K	300 K	ΔG_E (kJ mol^{-1}) 100 K	200 K	300 K	ΔH_E[a] (kJ mol^{-1})	ΔS_E[a] (J K^{-1} mol^{-1})
Dibenzothiophene sulfone	204–231		3.0×10^{-4}	7.0×10^{-8}		35	32	40 ± 3	24 ± 12
Dibenzothiophene sulfoxide	265–288		5.2×10^{-2}	1.4×10^{-5}		43	46	39 ± 3	23 ± 9
Dibenzothiophene	201–231		2.0×10^{-4}	5.9×10^{-8}		34	32	39 ± 3	22 ± 15
Diphenyl sulfone	205–240		1.7×10^{-3}	4.6×10^{-9}		38	26	62 ± 2	121 ± 11
Diphenyl sulfoxide	251–283			3.3×10^{-6}		48	42	60 ± 4	60 ± 15
Bis(4-tolyl) sulfone	280–300			1.3×10^{-5}		54	45	71 ± 4	84 ± 15
Bis(4-tolyl) sulfoxide	295–324			3.7×10^{-4}		58	54	68 ± 3	49 ± 10
Bis(4-chlorophenyl) sulfone	306–326			1.5×10^{-3}		64	57	78 ± 6	70 ± 16
Diphenyl sulfide	89–99	1.1×10^{-7}			10.3			14 ± 2	33 ± 20
Bis(4-tolyl) sulfide	93–103	2.2×10^{-7}			10.8			16 ± 3	53 ± 26

[a] Error estimates for ΔH_E and ΔS_E are for 90% confidence intervals and these are distinct from the absolute error which for ΔH_E is ± 10%.

error limits of ± 4 kJ mol^{-1}. Davies and Swain[8] observed for fluorenone, a rigid molecule of similar size and shape to the dibenzothiophenes, a ΔH_E value of 40 kJ mol^{-1}. This value therefore appears to be typical for disk-shaped, rigid molecules, the size of dibenzothiophene. The ΔG_E value for dibenzothiophene sulfoxide is at least 8 kJ mol^{-1} greater than that for the dibenzothiophene and dibenzothiophene sulfone. This difference, in the main, is likely to be attributed to the fact that the sulfoxide—unlike the other two molecules—can relax about the Y-axis as well as the X- and Z-axes, and the volume swept out about this axis is of the order of 50% greater than that about the other two axes (see Table III).

From the straight line $\log T\tau$ vs T^{-1} plots for diphenyl sulfoxide, bis(4-tolyl) sulfoxide, diphenyl sulfone, bis(4-tolyl) sulfone, and bis(4-chlorophenyl) sulfone the corresponding ΔH_E values are 60, 68, 62, 71, and 78 kJ mol^{-1}, respectively. The range of β values (0.11–0.34) compares well with those for the dibenzothiophenes at similar temperatures (Table I). 2-Hydroxybenzophenone (structure XI in Fig. 3), which has one ring chelated to the carbonyl group by a strong hydrogen bond, may be regarded as a rigid molecule[16] of similar size to that of diphenyl sulfoxide and sulfone. On the basis of steric and energetic considerations it is probable that the aromatic rings are not planar in these molecules. This has been noted already for bis(4-bromophenyl) sulfone[6] and diphenyl sulfoxide[7] where each ring is twisted out of the C–S–C plane by 90° and 82°, respectively. As a consequence of the nonplanar structure the higher ΔH_E value[16] of 58 kJ mol^{-1} for 2-hydroxybenzophenone as compared to the essentially flat dibenzothiophene molecule is to be related to the larger volume swept out by the nonplanar molecule.

The ΔH_E values for diphenyl sulfoxide and diphenyl sulfone (structures V and VI respectively, in Fig. 3) suggest that they are of similar size and shape not only to each other but also to 2-hydroxybenzophenone, and this nonplanarity is borne out by earlier studies.[3]

No internal relaxation process was apparent in diphenyl sulfoxide and sulfone, and this is in contrast to the observations of Cumper and Rossiter[1] where a contribution from an internal relaxation process was suggested to account for the apparently short mean relaxation times for diphenyl sulfoxide ($\tau_{298}\sim 14.7$ ps) and diphenyl sulfone ($\tau_{298}\sim 22$ ps) in benzene; no such motion was detected in polystyrene. The molecular dipole moments of both the sulfoxides and sulfones are large, and if overlap of an intramolecular and molecular process occurred, then it would seem likely that the latter process would tend to outweigh the former. For example, diphenyl sulfone has a dipole moment (5.05 D at 298 K in benzene[3]) along the Y axis (Fig. 4) and perpendicular to both the X and Z axes. Consequently, molecular rotation is possible about the latter two axes. It is to be noted that the weight factor governing rotation about a particular axis is directly proportional to the square of the dipole moment component perpendicular to that axis. A similar dielectric behavior occurs for diphenyl sulfoxide, except that the direction of the net dipole moment (4.07 D at 298 K in benzene[3]) is out of the C–S–C plane, so that molecular rotation is feasible about all three axes.

As was the case with dibenzothiophene sulfoxide and

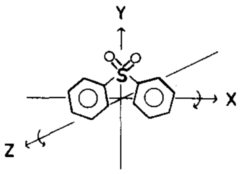

FIG. 4. Axes of rotation for diphenyl sulfone.

TABLE III. Length (Å) along principal molecular axes and swept volumes (Å^3 per molecule) about these axes during the molecular relaxation of some symmetrically substituted diaryl molecules. V_m is the mean volume swept about by molecular relaxation about the appropriate axes.

Molecule	l_x	l_y	l_z	V_x	V_y	V_z	V_m
Dibenzothiophene	11.0	7.10	3.70	436		352	394
Dibenzothiophene sulfoxide	11.0	7.40	4.25	473	703	404	527
Dibenzothiophene sulfone	11.0	7.40	5.10	473		485	479
Diphenyl sulfoxide[a]	11.10	7.00	6.00	427	677	580	561
Diphenyl sulfone[b]	11.10	6.80	6.30	403		609	506
Bis(4-tolyl) sulfoxide[a]	13.00	7.90	6.00	637	1049	796	827
Bis(4-tolyl) sulfone[b]	13.00	7.70	6.30	605		836	721
Bis(4-chlorophenyl) sulfone[b]	13.65	7.72	6.30	639		921	780

[a] Calculations based on the assumption that the aromatic rings are each 82° out of the C–S–C plane. (7).

[b] Calculations based on the assumption that the aromatic rings are each 90° out of the C–S–C plane. (6).

sulfone the ΔG_E of the sulfoxide is about 10 kJ mol^{-1} larger than the sulfone and is to be related to the largest volume swept out about the Y-axis for the sulfoxide.

With the symmetrical addition of substituents such as methyl groups and chlorine atoms in each of the para positions the net dipole moment still lies along the Y-axis in the sulfones. Bis(4-tolyl) sulfone has a dipole moment of 5.54 D at 298 K in benzene[3] since the methyl groups exert positive mesomeric(+M) and inductive(+I) effects; these two effects direct charge into the aromatic rings. Bis(4-chlorophenyl) sulfone, however, has a lower net dipole moment of 3.30 D at 298 K in benzene[3] than diphenyl sulfone since the C–Cl bond moments oppose the sulfone group moment.

As the size of the diaryl sulfones increases, so does the ΔH_E for molecular relaxation. This is evident from Table II, where the ΔH_E values are 40, 62, 71, and 78 kJ mol^{-1}, respectively, for dibenzothiophene sulfone, diphenyl sulfone, bis(4-tolyl) sulfone and bis(4-chlorophenyl) sulfone (structures III, VI, IX, and XII in Fig. 3). ΔG_E values (Table II) show a similar trend with increasing molecular size.

The enthalpy of activation for the sulfoxides follows the same pattern with respect to size as do the sulfones. The ΔH_E values for the series dibenzothiophene sulfoxide, diphenyl sulfoxide and bis(4-tolyl) sulfoxide are 39, 60, and 68 kJ mol^{-1}, respectively.

It would seem likely that a correlation exists between ΔH_E, ΔG_E, and rotational volume[9] for all the rigid diaryl sulfur compounds examined. For the nonplanar molecules when the molecule has it dipole moment along the Y-axis then molecular relaxation may give rise to two extreme types of swept volume: one involves a large displacement of the surrounding medium corresponding to rotation about the Z-axis, while for the other, rotation about the X-axis involves less displacement of adjacent molecules. If the volumes of revolution are treated as cylindrical then with the aid of known radii and lengths of the cylinders the rotational volumes about various axes can be determined. The rotational volumes were calculated about the center of volume from Courtauld models. This approach has been employed previously by Tay and Walker.[9] The volumes V_x, V_y, and V_z swept out by rotation about the X, Y, and Z axes, as well as the mean volume (V_{mean}) given by

$$V_{\text{mean}} = \frac{V_x + V_y + V_z}{3} \quad ,$$

[if the molecule, for example, does not relax about the Y-axis then $V_{\text{mean}} = (V_x + V_z)/2$] are presented in Table III. When the mean volume swept out by rotation about the axes is plotted against ΔG_E or ΔH_E and the errors are taken into account a rough linear dependence results. These plots are given in the subsequent paper where rigid molecules therein are also included.

In view of the ΔH_E value for dibenzothiophene (ΔH_E = 40 kJ mol^{-1}), diphenyl sulfide (structure IV in Fig. 3) would be expected to have a similar value if the rings are coplanar and the molecule rigid. If each ring is out of plane, then the ΔH_E should be similar to that for diphenyl sulfoxide and diphenyl sulfone ($\Delta H_E \sim 60$ kJ mol^{-1}). Diphenyl sulfide, in fact, has a ΔH_E value of 14 kJ mol^{-1}, which is much too low for molecular relaxation, and thus must originate from an internal relaxation process. The dielectric loss curves were observed in the frequency range 10^4–10^7 Hz at temperatures of 89–99 K. This temperature range is much lower than that for a molecular process. One would expect the molecular process to appear at temperatures of about 205–240 K in the frequency range 10^2–10^5 Hz, as is the case with diphenyl sulfone.

A study by Di Carlo and Smyth[17] showed diphenyl sulfide to have a mean relaxation time of 10 ps in benzene solution at 293 K which was interpreted as being too short to be completely due to overall molecular rotation. The estimated relaxation time (16 ps at 200 K) in polystyrene is also far too short to originate from a molecular process (e.g., 2.0×10^{-4} and 1.7×10^{-3} s at 200 K for dibenzothiophene and diphenyl sulfone, respectively, in polystyrene). The ΔG_E values also reflect this pattern: for example, $\Delta G_{E200} = 3.6$ kJ mol^{-1} for diphenyl sulfide, while $\Delta G_{E200} = 34$ and 38 kJ mol^{-1} for dibenzothiophene and diphenyl sulfone respectively.

The internal relaxation process which occurs in diphenyl sulfide in the liquid state is expected to be similar to that in diphenyl ether. A number of intramolecular mechanisms has been postulated to account for the process in the liquid state.[18–22]

Bis(4-tolyl) sulfide (structure VII in Fig. 3) in polystyrene shows similar dielectric relaxation behavior to diphenyl sulfide. A low enthalpy process of 16 $\mathrm{kJ\,mol^{-1}}$ (Table II) (which is slightly greater than that for diphenyl sulfide) was observed in the frequency range 10^4–10^7 Hz at temperatures 93–103 K. The difference in ΔH_E could well be attributed to experimental error. However, an increase is to be expected because of the electron-donating properties of the para-methyl groups which direct a small fraction of charge into the aromatic rings by $+M$ and $+I$ effects, thereby stiffening to a small extent the C-S bonds as compared to diphenyl sulfide. Tay *et al.*[23] have reported similar findings for hydroxyl group relaxation, and Silver and Wood[24] for aldehyde group relaxation, in that the addition of a para-methyl group marginally increases the barrier for group relaxation. Further, the addition of such groups can substantially increase the enthalpy of activation for molecular rotation, as for example in the case of diphenyl sulfone and bis(4-tolyl) sulfone, where $\Delta H_E = 62$ and 71 $\mathrm{kJ\,mol^{-1}}$, respectively. The ΔG_E value for bis(4-tolyl) sulfide of 10.8 $\mathrm{kJ\,mol^{-1}}$ at 100 K compares well with that of 10.3 $\mathrm{kJ\,mol^{-1}}$ for diphenyl sulfide at the same temperature, as do also the respective relaxation times of 2.2×10^{-7} and 1.1×10^{-7} at 100 K. That these values are for intramolecular processes and not molecular ones becomes apparent when the ΔG_{E100} are compared with those for rigid molecules of similar size and shape, namely, diphenyl sulfone ($\Delta G_{E100} = 44\ \mathrm{kJ\,mol^{-1}}$) and bis(4-tolyl) sulfone ($\Delta G_{E100} = 62\ \mathrm{kJ\,mol^{-1}}$) which are extrapolated values.

Bis(4-pyridyl) sulfide in polystyrene showed absorption curves [Fig. 1(d)] in the range 10^4–10^7 Hz, at temperatures from 98–120 K, although the peak values were out of the range of the apparatus. The ΔG_E values were clearly low, and these were estimated by extrapolation with the use of a computer and the Fuoss–Kirkwood equation. The estimated ΔG_E value of 7.8 $\mathrm{kJ\,mol^{-1}}$ at 119 K compares well with those for diphenyl and bis(4-tolyl) sulfide at similar temperatures (see Table II). From the frequency range of the absorption at these low temperatures there can be no doubt that the barrier is low although its value could be in serious error.

Bis(4-pyridyl) sulfide as a pure compressed solid shows partial absorption curves [Fig. 1(c)] at similar frequencies and temperatures as in the matrix. In the pure solid state the crystal lattice, in most cases, imposes a hindrance to molecular reorientation so that only intramolecular relaxation would seem likely, and this has been found to be so in aromatic–acetyl compounds where only the group relaxation was observed.[10] Computer extrapolation and analysis of the loss curve for bis(4-pyridyl) sulfide at 88 K gave the ΔG_E value as 5.5 $\mathrm{kJ\,mol^{-1}}$, which is similar in magnitude to those for the other nonrigid sulfides. The short relaxation time of 9.4×10^{-10} s which was estimated for 88 K further suggests that the observed relaxation is to be attributed to internal rotation.

CONCLUSIONS

The results of dielectric relaxation studies of a series of symmetric aromatic sulfides, sulfoxides, and sulfones in a polystyrene matrix suggest that within the limitations of the technique all the molecules examined dielectrically behave as rigid molecules, except for diphenyl, bis(4-tolyl) and bis(4-pyridyl) sulfides. Dibenzothiophene, dibenzothiophene sulfoxide, and dibenzothiophene sulfone all have a ΔH_E value of about 39 $\mathrm{kJ\,mol^{-1}}$, which may be considered typical for the molecular relaxation of disklike molecules of this size. Once the aromatic rings become appreciably orientated out of the plane of the C–S–C group, as in diaryl sulfoxides and sulfones, then the ΔH_E and ΔS_E values increase considerably in comparison to the flat analogue.

Diaryl sulfoxides and sulfones relax predominantly by overall molecular reorientation in a polystyrene matrix. From other physical evidence[3,4] these molecules appear to possess significant electron density in the sulfinyl-ring and sulfonyl-ring bonds which leads to a high energy barrier to rotation about the C–S bonds, and this could oppose the occurrence and detection of the intramolecular motion. That the process is molecular is borne out by ΔH_E values, such as 60 and 62 $\mathrm{kJ\,mol^{-1}}$ for diphenyl sulfoxide and diphenyl sulfone respectively and by their values being of a suitable magnitude for their shape and size when compared to a known rigid molecule such as 2-hydroxybenzophenone ($\Delta H_E = 58\ \mathrm{kJ\,mol^{-1}}$).[16] Further, as the size of the diaryl sulfoxides and sulfones increases, so does the enthalpy of activation. On passing from 4, 4′-H to 4, 4′-CH_3 to 4, 4′-Cl diphenyl sulfone the respective ΔH_E values vary from 62 to 71 to 78 $\mathrm{kJ\,mol^{-1}}$. A similar pattern with slightly lower ΔH_E values was observed for the corresponding sulfoxides. The diaryl sulfones and dibenzothiophene have a net dipole moment along the Y-axis, so that rotation can occur only about the X and Z axes. The sulfoxides, however, possess a net dipole moment which lies out the C–S–C plane; consequently rotation is possible about all three molecular axes.

Within the error limits of the Eyring parameters and V_{mean} values the plots of ΔH_E or ΔG_E against the mean volume swept out during molecular relaxation are linear; this applies to the molecules in this and the succeeding paper when they are placed on the same plot.

Diphenyl sulfide, bis(4-tolyl) sulfide and bis(4-pyridyl) sulfide exhibit a rapid, low energy internal relaxation process in polystyrene, and for the latter compound also in the pure solid state. The enthalpy of activation for the process has been characterized [$\Delta H_E = 14\ \mathrm{kJ\,mol^{-1}}$ for diphenyl sulfide and $\Delta H_E = 16\ \mathrm{kJ\,mol^{-1}}$ for bis(4-tolyl) sulfide]. ΔG_E values are typically $\sim 8\ \mathrm{kJ\,mol^{-1}}$ for the process in polystyrene and of a similar magnitude in the pure solid state [$\Delta G_E = 5.5\ \mathrm{kJ\,mol^{-1}}$ for bis(4-dipyridyl) sulfide at 88 K].

The present work establishes that the energy barrier for the rotation about the C–S bond in symmetrically substituted aromatic sulfides is fairly low and not appreciably greater than that for either hydroxyl group rotation in phenol (13.6 $\mathrm{kJ\,mol^{-1}}$)[25] or methoxy group relaxation in aromatic ethers (~ 10 to 14 kJ mol^{-1}).[13] Thus, it would be anticipated that in the symmetrically substituted aromatic sulfides an intramolecular motion involving rotation about the C–S bonds would readily take place.

Previous studies have shown that the enthalpy of activation for an intramolecular process is the same (within experimental error) whether determined by the dielectric absorption approach using the matrix technique or by the NMR or ultrasonic approaches in liquid state studies. In particular, a study by Tay, Wyn-Jones, and Walker[15] demonstrated that results from all three techniques yielded similar energy barriers for a number of intramolecular processes. Thus, despite there being a variety of environments which molecules experience in the polystyrene matrix it does not appear to influence significantly the energy barrier for group relaxation or switching from one chair form to another in a monocyclohexyl derivative. However, the intramolecular process occurring in molecules such as diphenyl ether and diphenyl sulfide in the liquid phase is not fully understood and could even involve more than one process. Gaither and Vaughan[26] have recently given theoretical consideration to two models and from their quantitative treatment prefer a fluctuating mesomeric moment model associated with rotation of the rings about their C–O axes. However, from the present work in a polystyrene matrix we are able to conclude only that the mechanism responsible for the low temperature absorption in diphenyl sulfide and bis(4-tolyl) sulfide is of an "internal" nature and that the precise physical model which satisfies our data must await study by other physical or chemical techniques.

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