

779. The Infrared Absorption of Diphenyl [¹⁸O]Sulphone and Diphenyl [¹⁸O]Sulphoxide.

By S. PINCHAS, DAVID SAMUEL, and MARTA WEISS-BRODAY.

The infrared absorption spectra of normal and labelled diphenyl sulphone and sulphoxide have been measured in the 3700—670 cm.⁻¹ region in solution or as a mull. The origin of the triplet observed with a carbon tetrachloride solution of the normal sulphone at about 1310 cm.⁻¹ is discussed.

The intensities of the various S=¹⁸O and S=¹⁶O stretching bands are compared for carbon tetrachloride and chloroform solutions. It is concluded that there seems to be some correlation between the high polarity of an X=O group and the increase of the intensity of the X=¹⁸O band over that of the respective X=¹⁶O band. However, the exact form of the individual stretching is also of importance.

THE integrated absorption intensity of the X=O (X = C or P) stretching bands is markedly changed when oxygen-18 is substituted for oxygen-16 in a number of compounds.¹ This is usually observed as a decrease of about 15% in the relative integrated absorption of the X=¹⁸O band, as compared with that of the X=¹⁶O band.^{1a,b,d} Benzamides,^{1c,e,f} however, showed a 20% increase in the absorption of the C=¹⁸O relative to that of the C=¹⁶O band, a difference possibly connected with the high polarity of the amidic C=O group. The effect of such an isotopic change on the intensity of the S=O bands was therefore studied.

Table I gives the absorption bands observed in the 3700—670 cm.⁻¹ region, for solutions and mulls of normal diphenyl sulphone and when labelled approximately with 80 atom-% oxygen-18. The corresponding optical densities are in parentheses.

¹ Halmann and Pinchas, *J.*, 1958, (a) 1703; (b) 3264; (c) Pinchas, Samuel, and Weiss-Brodav, *ibid.*, 1961, 1688; (d) *idem, ibid.*, p. 2382; (e) *idem, ibid.*, p. 2666; (f) *idem, ibid.*, p. 3063.

TABLE 1.

The infrared absorption bands (cm.⁻¹) of normal (*N*) and diphenyl [¹⁸O]sulphone (*L*).

Species	Soln. or Mull	Concn.*	Solv.	Thick-ness (mm.)	Bands
<i>N</i>	Soln.	0.040	CHCl ₃	0.1	1592(0.04), 1474(0.05), 1450(0.15), ^a 1181(0.12), 1158(0.74), 1108(0.31), 1070(0.13), 1023(0.07), 999(0.05) ^b
<i>L</i>	Soln.	0.083	CHCl ₃	0.1	1592(0.06), 1475, 1450(0.27), ^a 1136(1.13), 1109(0.78), 1052(0.54), 1022(0.29), 1000(0.23) ^b
<i>N</i> ^c	Soln.	0.014	CHCl ₃	0.2	1320(0.33), 1309(0.37), 1296(0.17)
<i>L</i> ^c	Soln.	0.014	CHCl ₃	0.2	1274(0.40)
<i>N</i> ^d	Nujol	—	—	Capill.	844w, 796w, 757s, 727s, 698m, 686s, 678m
<i>L</i> ^d	Nujol	—	—	Capill.	844w, 797w, 757s, 726s, 696m, 686s, 677m
<i>N</i> ^e	Perfluoro-kerosene	—	—	Capill.	3090, 2180, 1985, 1889, 1768, 1723, ~1685, 1645, 1620, 1575 ^f
<i>L</i> ^e	Perfluoro-kerosene	—	—	Capill.	3090, 2210, 1985, 1910, 1768, 1724, ~1685, 1645, 1611, 1576 ^f
<i>N</i> ^g	Soln.	0.006	CCl ₄	1	1327(0.83), 1309(0.39), 1295(0.18), 1162 ^h (0.8)
<i>L</i>	Soln.	0.004	CCl ₄	1	1297(0.30), 1282(0.75), 1138(0.98)

w = weak, m = medium, s = strong.

* Concentration in g. per ml. of solvent.

^a The 1350—1250 cm.⁻¹ region was measured separately under higher precision. ^b Measured only down to 830 cm.⁻¹. ^c Measured precisely and only near the 1300 cm.⁻¹ bands. ^d Measured only in the 860—670 cm.⁻¹ region. ^e Measured only in the 3700—1540 cm.⁻¹ region. ^f All these bands are very diffuse. ^g The measurements in carbon tetrachloride were only in the region of the SO₂ stretching bands. ^h Found for a different concentration and calculated for a 0.006 g./ml. solution.

The data for the ordinary compound are in good agreement with those in the literature,^{2d,e,f} although a number of minor discrepancies were observed.

The origin of the asymmetrical S=O stretching^{2a} band triplet^{2d} which appears in the spectrum of the normal sulphone at about 1310 cm.⁻¹ is not clear, especially since it is shown also by the solid^{2c} and by other sulphones.^{2a,2d,3} That the 1160 cm.⁻¹ symmetrical stretching band^{2a} remains a singlet is also noteworthy. This splitting may be the result of the motion of the carbon atoms during the S=O stretching of the C₂SO₂ group, which is probably tetrahedral.⁴ The fact that the highest branch is the strongest^{2d} for a carbon tetrachloride solution while the middle branch is the strongest for a chloroform solution cannot be taken as an indication that these branches are due to various rotational isomers in equilibrium since the molecular extinction coefficient of the 1327—1320 cm.⁻¹ branch in carbon tetrachloride was about the same as in chloroform (~320 and ~260 units, respectively) while that of the 1309 cm.⁻¹ branch was different by a factor of about 2 (~150 and ~290). Thus, it is obvious that the hydrogen-bonding solvent affects the intensity of the various branches very differently, and this effect is the reason for the change in the relative intensity of the two branches.

The various spectra of the labelled sulphones differ mainly in the -SO₂ frequencies. However, minor other differences also appear, e.g., in the spectra of perfluorokerosene mulls. The disappearance of the 1181 cm.⁻¹ normal band (which seems to be due to in-plane C_{ar}-H bending of monosubstituted benzenes)⁵ in the spectrum of the labelled compound appears to be connected with the shift in the symmetrical -SO₂ stretching (in chloroform) from 1158 to 1136 cm.⁻¹. Thus, for the normal sulphone this stretching is sufficiently near the original frequency of the 1181 cm.⁻¹ band for Fermi resonance to intensify the latter, a

² (a) Barnard, Fabian, and Koch, *J.*, 1949, 2442; (b) Schreiber, *Analyt. Chem.*, 1949, 21, 1169, (c) Cymerman and Willis, *J.*, 1951, 1334; (d) Bavin, Gray, and Stephenson, *Spectrochim. Acta*, 1960, 16, 1312; (e) Haszeldine and Kidd, *J.*, 1955, 2901; Documentation of Molecular Spectroscopy Catalogue, compound card No. 5; (f) Waight, *J.*, 1952, 2440.

³ Jerchel, Dippelhofer, and Renner, *Ber.*, 1954, 947 (DMS Catalogue No. 412).

⁴ This was actually found for di-*p*-bromophenyl sulphone (see Toussaint, *Bull. Soc. Roy. Sci. Liège*, 1944, 4, 163).

⁵ Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1958, pp. 65, 81.

situation no longer occurring in the labelled compound, which therefore cannot show this band clearly.

The shift of the 1070 cm^{-1} normal absorption to 1052 cm^{-1} might be the result of its being due, at least in part, to the first overtone of the $-\text{SO}_2$ bending vibration. This fundamental appears in sulphur dioxide⁶ at 519 cm^{-1} and can give an overtone, at about 1050 cm^{-1} , sensitive to labelling with oxygen-18.

The antisymmetrical band due to the $-\text{S}^{18}\text{O}_2$ group is clearly at 1274 cm^{-1} in chloroform and at 1297—1282 cm^{-1} (a doublet) in carbon tetrachloride. The 1274 cm^{-1} frequency corresponds to the (main) 1309 cm^{-1} branch of the normal band since the isotopic-substitution difference is then 35 cm^{-1} . This value agrees with a difference of 39 cm^{-1} calculated for the antisymmetrical stretching of the $-\text{SO}_2$ group (the rest of the molecule being neglected) on the basis of the equation given in ref. 7. That the band due to the labelled compound does not show a triplet structure similarly to that of the normal $-\text{SO}_2$ absorption seems to be the result of a different effect of the hydrogen-bonding solvent on the relative absorption intensity of the various branches of the $-\text{S}^{18}\text{O}_2$ bands. A further factor in this respect is the presence of small amounts of $\text{R}\cdot\text{S}^{16}\text{O}_2$ and $\text{R}\cdot\text{S}^{16}\text{O}^{18}\text{O}$ modifications in the labelled sample which add to the "smearing out" of the side branches of the $\text{R}\cdot\text{S}^{18}\text{O}_2$ band.

The 1297 and 1282 cm^{-1} branches of the S^{18}O_2 band in the spectra of carbon tetrachloride solutions correspond, respectively, to the normal frequencies at 1327 and 1309 cm^{-1} . The isotopic shifts here are thus equal to 30 and 27 cm^{-1} . The third branch, being the weakest of all, is still masked in the spectrum of the labelled compound. It is noteworthy that the absorption intensity of the 1309—1282 cm^{-1} branch for the labelled sulphone in carbon tetrachloride is higher than that of the 1327—1297 cm^{-1} branch (as in the chloroform solution of the normal material) unlike the situation in the carbon tetrachloride solution of the "light" compound and many other sulphones.^{2f} Here again,¹ therefore, an X^{18}O group shows behaviour markedly different from that of a corresponding X^{16}O group.

The isotopic shift for the symmetrical $-\text{SO}_2$ stretching is 22 cm^{-1} for chloroform solutions and 24 cm^{-1} for carbon tetrachloride solutions. If it is assumed that this stretching is similar to that of an $\text{S}-(\text{O}_2)$ oscillator one can estimate this shift on basis of Hooke's equation. This gives $\nu^1/\nu = 0.972$ and $\Delta\nu = 32 \text{ cm}^{-1}$.

The intensities of the $-\text{SO}_2$ stretching bands of normal and labelled diphenyl sulphone are summarised in Table 2. Comparison of the integrated intensity of the antisymmetrical $-\text{SO}_2$ band of the labelled compound with that of the normal substance is made very difficult by its splitting in most of the measured spectra, and the estimation of the integrated area of this band is therefore omitted (Table 2).

TABLE 2.

The intensity of the SO_2 bands of normal (*N*) and diphenyl [^{18}O]sulphone (*L*).

Species	Solv.	Asymmetrical band						Symmetrical Band			
		Fr.*	<i>E</i> *	Fr.*	<i>E</i> *	Fr.*	<i>E</i> *	Fr.*	<i>E</i> *	<i>W</i> *	R*
<i>N</i>	CCl_4	1327	329	1309	151	1295	66	1162	576	11	6300 \pm 300
<i>L</i>	CCl_4	1297	189 ^b	1282	470	—	—	1138	618	10	6200 \pm 300
<i>N</i>	CHCl_3	1320	262	1309	291	1296	135	1158	609	11	6700 \pm 300
<i>L</i>	CHCl_3	—	—	1274	408	—	—	1136	683	10	6800 \pm 300

* Fr, frequency (cm^{-1}). *E*, molecular extinction coefficient ($\text{l. mole}^{-1} \text{ cm}^{-1}$). *W*, half-width (cm^{-1}). R, relative integrated absorption ($\text{l. mole}^{-1} \text{ cm}^{-2}$).^a

^a Estimated by multiplying the apparent molecular extinction coefficient by the apparent half-width. ^b All the values for the extinction coefficients of the labelled compound were corrected for its lower effective concentration but not for the absorption of the neighbouring bands, or the oxygen-16 modifications, at the absorption maxima of the labelled compound.

⁶ Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co. Inc., Princeton, N.J., 1945, p. 285.

⁷ Ref. 6, p. 228.

Table 2 shows that, as expected for the highly polar diphenyl sulphone (its electrical moment being ⁸ 5.1 D), the sum of the molecular extinction coefficients of the antisymmetrical S¹⁸O₂ stretching branches, in carbon tetrachloride solution (659), is considerably higher than that of the S¹⁶O₂ absorptions (480). In spite of the approximate nature of this estimation, based on molecular coefficients rather than integrated absorptions and neglecting tail absorption, it still seems to show that the intensity of the antisymmetrical band as a whole is considerably greater in a spectrum of a carbon tetrachloride solution of the labelled sulphone.

In chloroform solutions the sum of the extinction coefficient of the -S¹⁸O₂ middle branch and the coefficient at the point where the first branch of the labelled compound could be expected (on basis of the 1274 cm.⁻¹ value for the middle branch of the S¹⁸O₂ band and the difference of 11 cm.⁻¹ between the normal branches), *i.e.*, at 1285 cm.⁻¹, is almost equal to the sum of the two maximum coefficients of the normal sulphone, the figures being: 408 + 156 = 564 and 262 + 291 = 553 l. mole⁻¹ cm.⁻¹, respectively.

These facts compare with the results for the intensity of the CO bands of normal and [¹⁸O]benzamide^{1c} and *N*-methylbenzamide^{1c} where the integrated absorption is practically independent of the isotopic content in spectra for chloroform solutions although quite variable for carbon tetrachloride solutions.

Data for the symmetrical SO₂ band show, for the first time in the case of carbon tetrachloride solutions of isotopic modifications of X=O compounds,¹ a practically equal integrated absorption intensity for the normal and ¹⁸O-compound. The intensity remains equal also for chloroform solutions although, as usual, it rises somewhat, relative to its value for carbon tetrachloride solution (6250—6750 units). It is however possible that this constancy of the relative integrated absorption is brought about by the coincidence of two opposite effects which cancel: (*a*) a decrease in the intensity of the normal band at about 1160 cm.⁻¹ as a result of resonance between the symmetrical SO₂ stretching and the C_{ar}-H in-plane bending (which is responsible for the 1181 cm.⁻¹ band); such resonance was assumed on the basis of the disappearance of the 1181 cm.⁻¹ band from the [¹⁸O]-sulphone spectrum and can be expected to increase the 1181 cm.⁻¹ absorption on account of the SO₂ band; (*b*) a decrease of the symmetrical S¹⁸O₂ band, relative to the corresponding original S¹⁶O₂ band, as in the case of the stretching bands of a number of C=O compounds.^{1a,b,d}

The much lower isotopic shift for the symmetrical band (22—24 cm.⁻¹), as compared with the shift for the antisymmetrical band (27—35 cm.⁻¹), can also be due, at least in part, to this Fermi resonance of the symmetrical band in the normal compound which must move it to a frequency lower than the original and hence decrease the expected isotopic shift.

The bands observed in the 3700—670 cm.⁻¹ region in the spectrum of a normal sulphone and when labelled with approximately 81 atom % oxygen-18, in carbon tetrachloride or chloroform solutions or as Nujol mulls, are reported in Table 3.

The band at 3080 cm.⁻¹ is the C_{ar}-H stretching band⁹ which absorbs at a frequency somewhat higher than usual⁹ (near 3030 cm.⁻¹) probably because of the electronegative SO substituent which, it seems, strengthens (at least part of) the C_{ar}-H bonds. Benzoyl chloride,^{1d} methyl benzoate,^{1d} and nitrobenzene⁹ also show C-H bands near 3080 cm.⁻¹.

The absorptions at about 1090, 1075, 1025, and 999 cm.⁻¹ seem to be due to a splitting of each of the usual monosubstituted benzene bands⁹ of this region, as a result of the interaction of the neighbouring aromatic rings.

The strongest band of the normal sulphoxide in carbon tetrachloride solution, at 1051 cm.⁻¹, loses most of its intensity in the labelled compound and is clearly the S=O stretching band.^{2c} In the spectrum of the [¹⁸O]sulphoxide it appears at 1021 cm.⁻¹. The

⁸ Wesson, "Tables of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948, p. 51.

⁹ Ref. 5, pp. 65, 66.

TABLE 3.

The infrared absorption bands (cm.^{-1}) of normal (*N*) and diphenyl [^{18}O]sulphoxide (*L*).^a

Material	Solv. or mull	Concn. (g./l.)	Thick-ness (mm.)	
<i>N</i>	CCl_4	48	0.2	3080(0.13), 1575(0.04), 1476(0.22), 1442(0.35), 1385(0.03), 1304(0.09), 1177(0.06), ^b 912(0.05), 872(0.07)
<i>N</i>	CCl_4	30 ^c	0.2	1094(0.64), 1073(0.20), 1051(0.77), 1024(0.20), 999(0.10)
<i>L</i>	CCl_4	40	0.2	3080(0.13), 1576(0.1), 1474(0.15), 1443(0.24), 1389(0.03), 1303(0.05), 1177(0.06), ^b 912(0.03)
<i>L</i>	CCl_4	29 ^c	0.2	1088(0.37), 1075(0.15), 1051(0.11), 1032(0.56), 1021(0.75), 999(0.31)
<i>N</i>	CHCl_3	31.7 ^c	0.2	1090(0.53), 1076(0.20), 1041(0.63), 1023(0.40), 999(0.21)
<i>L</i>	CHCl_3	30.1 ^c	0.2	1088(0.34), 1076(0.20), 1043(0.07), 1023(0.28), 1009(0.53), 995(0.59)
<i>N</i>	Nujol	—	Capill. ^d	820(0.65), 755(1.5), 736(1.2), 698(1.5), 688(>1.5), 680(1.5)
<i>L</i>	Nujol	—	Capill. ^d	821(0.62), 752(>1.5), 735(1.5), 696(1.0), 685(>1.5), 680(>1.5)

^a The optical densities are added in parentheses. ^b The 1100—990 cm.^{-1} region was measured separately and more precisely. ^c Measured precisely and only in the 1100—990 cm.^{-1} region. ^d Measured only in the 830—670 cm.^{-1} region.

difference between the values of 1094 and 1088 cm.^{-1} for the ~ 1090 cm.^{-1} aromatic band of the two isotopic sulphoxides, as well as the appreciably higher intensity of this band in the normal spectrum, relative to its intensity in the labelled compound, seem to be due to some Fermi resonance between this aromatic vibration and the $\text{S}=\text{O}$ stretching, which is destroyed by the isotopic shift to lower frequencies. The $\text{S}=\text{O}$ stretching is probably also in Fermi resonance but now with the ~ 1025 cm.^{-1} aromatic band. This resonance is shown by the appearance of a new strong band at 1032 cm.^{-1} in the spectrum of the [^{18}O]sulphoxide. This band, which is still not as strong as that at 1021 cm.^{-1} , seems to be the aromatic absorption, originally at ~ 1025 cm.^{-1} after its interaction with the $\text{S}=\text{O}$ stretching which, as a result, moves to 1021 cm.^{-1} . The isotopic shift of the $\text{S}=\text{O}$ band appears thus to be entangled in resonance effects (which operate, however, in the same direction).

The hydrogen-bonding solvent, chloroform, decreases ^{2a} the $\text{X}=\text{O}$ stretching frequencies. As a result neither of the isotopic $\text{S}=\text{O}$ stretching vibrations is still coupled with the aromatic vibrations which are not affected by the solvent. The $\text{S}=\text{O}$ stretching frequency at 1041 cm.^{-1} therefore undergoes a purely isotopic shift and moves to 1009 cm.^{-1} while the aromatic bands remain practically at the same frequency in the labelled compound (the values being 1090—1088 and 1023—1023 cm.^{-1}). The shift thus amounts to 32 cm.^{-1} , in good agreement with a shift of 39 cm.^{-1} calculated for the diatomic $\text{S}=\text{O}$ model according to Hooke's law.

The data in Table 3 are generally in good agreement with the partial curve for normal diphenyl sulphoxide given by Cymerman and Willis ^{2c} except for a band they observed at 1163 cm.^{-1} which is missing from our results. Since this band is shown very strongly by diphenyl sulphone (at 1162 cm.^{-1} ; Table 1) and since sulphoxides often contain the corresponding sulphones as impurities (see Experimental) it seems that its presence in their curve is due to such an impurity.

The results for the absorption intensities of the isotopic $\text{S}=\text{O}$ bands are compared in Table 4.

It is evident from Table 4 that the integrated absorption of the $\text{S}=\text{O}$ band in carbon tetrachloride solution is much larger than that of the corresponding $\text{S}=\text{O}$ band. Even when account is taken of the difference between the integrated absorption of the (normal) 1094 cm.^{-1} frequency and that of the (labelled compound) 1088 cm.^{-1} frequency, probably due to resonance of the first with the $\text{S}=\text{O}$ vibration, the $\text{S}=\text{O}$ absorption still remains considerably higher than can be expected on theoretical grounds. Thus, the relative integrated absorption at 1094 cm.^{-1} is estimated at 2650 units while the corresponding one at 1088 cm.^{-1} is found to be 1600 units. If this difference is considered as "borrowed"

TABLE 4.

The absorption intensity of the diphenyl sulphoxide isotopic S=O bands.

Species	Solv.	Fr *	E *	W *	R *
N	CCl ₄	1051	256 ± 8	10.5	2700 ± 100
L	CCl ₄	1021	303 ± 7 ^a	14 ^b	4250 ± 300
N	CHCl ₃	1041	200 ± 10	9.5	1900 ± 100
L	CHCl ₃	1009	214 ± 5 ^a	^c	

* See footnote to Table 2.

^a Corrected for the absorption of the normal sulphoxide at this point and for the lower concentration of the labelled compound. ^b Graphically corrected for the effect of the nearby 1032 cm.⁻¹ band.^c The half-width cannot be evaluated because of the strong 999 cm.⁻¹ band nearby.

from the absorption of the S=¹⁶O band one arrives at a value of 3700 units for the S=¹⁶O band as compared with 4250 units for the S=¹⁸O band. The last value should also be corrected, this time for the intensity "borrowed" by the 1032 cm.⁻¹ band; the true value is therefore even higher than 4250 units. Theoretically, however, one would expect some decrease in the intensity of the S=¹⁸O band relative to that of the corresponding S=¹⁶O band.^{1b} The X=O absorption of the highly polar diphenyl sulphoxide in carbon tetrachloride solution is thus analogous to the antisymmetrical S=O stretching band of the very polar diphenyl sulphone (Table 2) and the strongly polar benzamides.^{1c, e, f}

The integrated absorption intensity for chloroform solutions of the labelled sulphoxide cannot be evaluated (because of the strong 999 cm.⁻¹ band which makes it impossible to estimate the half-width of the nearby S=¹⁸O band) but, judged from the molecular extinction coefficients, the increase of the S=¹⁸O band intensity over that of S=¹⁶O is here again appreciably less than in carbon tetrachloride solution.

The results for the isotopically substituted sulphone and sulphoxide thus show that the correlation between higher X=¹⁸O band intensities and high polarity of the X=O group seems to be valid generally but the relative intensity of the isotopic vibration band is also much dependent upon the exact form of the stretching motion. In the case of the symmetrical S=O stretching band of diphenyl sulphone this last factor possibly suppresses the anomalous isotopic effect of highly polar X=O compounds.

EXPERIMENTAL

Diphenyl [¹⁸O_s]Sulphone.—Dry chlorine was passed through an 0.2% solution of sodium hydroxide in water enriched with oxygen-18 (50 ml.; made by dissolving the calculated amount of sodium amalgam in the water). The temperature was kept below 25° and diphenyl sulphide (0.3 g.) added with shaking.¹⁰ After 1 hr., the white precipitate was filtered off and recrystallised from light petrol or ethanol. Traces of sulphoxide also formed were oxidised to sulphone by hydrogen peroxide. After a second recrystallisation the sulphone had m. p. 120—123°. Isotopic analysis was carried out by Anbar and Guttman's method¹¹ as described for organic compounds by Samuel.¹²

In order to obtain consistent results it was, however, necessary to heat the [¹⁸O]sulphone to 500° with the mercuric salts used and to purify the carbon dioxide formed, carefully.

The sulphone, prepared as above, contained approximately 80 atom % of oxygen-18.

Diphenyl [¹⁸O]Sulphoxide.—Dry chlorine was passed through a cooled solution of diphenyl sulphide (1 g.) in dry benzene–light petrol (10 ml.; 3 : 1 by volume). It was continued for 5 min. only, from the first appearance of yellow diphenyl sulphide dichloride, to prevent chlorination of the aromatic rings. The dichloride was hydrolysed¹³ by water (1 ml.) enriched with oxygen-18 which was added to its solution with shaking. After 1 hr. at room temperature the organic layer was decanted, the solvent removed, and the residue recrystallised from light petrol; it had m. p. 70—71°. At no stage of the synthesis should the temperature rise above

¹⁰ Wood and Travis, *J. Amer. Chem. Soc.*, 1928, **50**, 1226.¹¹ Anbar and Guttman, *Internat. J. Radiation and Isotopes*, 1959, **4**, 234.¹² Samuel, *J.*, 1960, 1318.¹³ Fries and Vogt, *Annalen*, 1911, **381**, 341.

40° since this causes formation of oily decomposition products. The sulphoxide contained 81 atom % of oxygen-18.

Direct oxidation of diphenyl sulphide by use of various reagents gives mixtures of sulphone and sulphoxide which are extremely difficult to separate.

The normal diphenyl sulphone and sulphoxide were prepared similarly.

The infrared absorptions were measured as described earlier.^{1d} The slit-width in the quantitative measurements was 0.14—0.17 mm.

THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL.

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