

STUDIES IN THE THERMOCHEMISTRY OF SULPHONES

PART 6.—HEATS OF COMBUSTION, FUSION, VAPORIZATION AND ATOMIZATION OF SIX AROMATIC AND TWO ALLYLIC SULPHONES

BY H. MACKLE AND P. A. G. O'HARE

Dept. of Chemistry, Queen's University, Belfast

Received 31st January, 1961

The gas-phase heats of formation of the following unsaturated sulphones are reported: phenyl methyl, p-tolyl methyl, allyl ethyl, dibenzyl, diphenyl, di-p-tolyl sulphones. The above quantities have been evaluated via the combustion, fusion and vaporization heats. The experimental atomization heats have been derived. A comprehensive scheme of bond-energy and group-energy terms which gives reliable predictions of the atomization heats of olefines, unconjugated dienes, aromatic hydrocarbons and aromatic sulphones has been established. Some tentative conclusions are drawn concerning the transmission of conjugation effects via the sulphone group. The bond dissociation energies $D(R-SO_2CH_3)$, where $R = Ph, p\text{-tolyl}$ are also reported.

In part 5,¹ a detailed scheme for the reliable prediction of the heats of atomization and thence the gas-phase heats of formation of saturated aliphatic sulphones is presented. It contains new group-energy and bond-energy terms. Once these are known for saturated systems, or more generally, for systems where there is no likelihood of resonance or conjugation effects, the method may be applied to diagnose such effects when they do exist. The work reported in the present paper was planned to try to find out among other things, whether, and if so, in what manner, conjugation effects are transmitted via the $(C-SO_2-C)$ group. There has been a good deal of discussion about this but comparatively little relevant experimental information.

EXPERIMENTAL

MATERIALS

Phenyl methyl sulphone (m.p. 87-88°C), benzyl methyl sulphone (m.p. 126-127°C) and allyl ethyl sulphone (b.p. 70°C/0.05 mm) were kindly supplied by Dr. D. Barnard, Natural Rubber Producers' Research Association, Welwyn Garden City, and were used without further purification.

DIPHENYL SULPHONE (B.D.H. Laboratory Reagent) was purified several times by zone melting. Another sample was recrystallized eight times from pure ether. The melting point of both materials was 124°C (lit. 125°C), and had boiling point 378°C at 760 mm Hg, with appreciable decomposition. (Analysis: found C, 66.3 %; H, 4.66 %; theoretical C, 66.0 %; H, 4.62 %.)

DI-p-TOLYL SULPHONE (Eastman Kodak Ltd.) was zone melted four times. Another batch was recrystallized eight times from A.R. di-ethyl ether and fused several times. Both batches had an identical melting point at 158-159°C (lit. 158°C); the boiling point at 760 mm Hg is 403°C \pm 1°C (lit. 405°C). (Analysis: found C, 68.4 %; H, 5.71 %; theoretical C, 68.3 %; H, 5.73 %.)

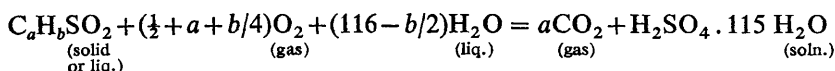
DI-BENZYL SULPHONE.—Di-benzyl sulphide (B.D.H.) was dissolved in acetic acid. An excess of 30 % hydrogen peroxide (Laporte Chemicals Ltd.) was dropped into the solution and the temperature was maintained at about 30°C, by frequent immersion in ice. When the reaction appeared to be complete, heating was continued under reflux for 2 h to ensure complete conversion of sulphoxide to sulphone. The reaction mixture

was carefully evaporated to dryness under high vacuum and the crude sulphone obtained in 90 % yield. It was vacuum (0.5 mm Hg) sublimed three times; the purified product had m.p. 150°C (lit. 151°C). (Analysis: found C, 68.4 %; H, 5.81 %; theoretical C, 68.3 %; H, 5.73 %).

p-TOLYL-METHYL SULPHONE.—The method of synthesis was essentially that of Field and Clark.² 60 g anhydrous sodium sulphite, 42 g sodium bicarbonate and 240 ml of water were stirred together under reflux at 70–80°C. This temperature was maintained during the addition of 48.4 g of p-toluene sulphonyl chloride over a period of 3 h. When the addition was complete stirring was continued for a further hour at the same temperature. The mixture was allowed to stand for 10 h. The separated solid was mixed with 40 g of sodium bicarbonate, and 49 g of di-methyl sulphate and 25 ml of water were added to make the mixture fluid enough for stirring. A further 70 ml of water was added dropwise, with stirring, under reflux, over a period of 3 h. The mixture was then heated under reflux for 20 h. On cooling to around 75°C, 20 ml of benzene was added. The aqueous layer was separated and extracted again with 20 ml benzene. The solid was then taken up in benzene, the total extracts combined, and the benzene distilled off under reduced pressure. Crude p-tolyl-methyl sulphone was obtained in 70 % yield. Purification was effected by zone-melting and the sulphone had a m.p. 83.6–84.1°C (lit. 83.87–5°C). It had boiling point 316°±1°C at normal atmospheric pressure. (Analysis: found C, 56.6 %; H, 5.90 %; theoretical C, 56.4 %; H, 5.92 %).

COMBUSTION CALORIMETRY.—The heats of combustion of the sulphones at 298°K were determined in the fluidless rotating bomb calorimeter previously described.³ All the aromatic sulphones are solids and were combusted using 4 mg of filter paper (Whatman no. 1) as fuse. The initial total bomb pressure in all cases was 35 atm (3 atm N₂, 32 atm O₂). The amount of water added to the bomb before combustions was 5 ml. The general calorimetric procedure was exactly as described in part 2.⁴

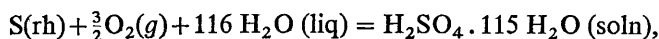
The heats of combustion at constant volume, $-\Delta U$, which refer to the following reaction are listed in table 1:



The scheme of symbols is the same as that used in part 2.

In table 1, A = di-phenyl sulphone (218.266), B = di-benzyl sulphone (246.318), C = phenyl methyl sulphone (156.200), D = di-p-tolyl sulphone (246.318), E = p-tolyl methyl sulphone (170.226) and F = allyl-ethyl sulphone (134.196). The figures in brackets are the molecular weights used in calculating $-\Delta U$.

Standard heats of formation, $-\Delta H_f^\circ$, have been derived by correcting to constant pressure and combining with the following thermochemical data at 25°C (all in kcal mole⁻¹):



$$\Delta H = -143.85 \pm 0.06,^5 \quad \Delta H_f(\text{CO}_2)(g) = -94.05 \pm 0.01,^6$$

$$\Delta H_f(\text{H}_2\text{O})(l) = -68.32 \pm 0.01.^6$$

The $-\Delta H_f^\circ$ values are listed in table 2 (column 1), and the uncertainties have been calculated in the usual way.

LATENT HEATS OF FUSION AND VAPORIZATION

The melting-point depression method described in part 3⁷ has been used to determine the heats of fusion. The values are recorded in table 2 (column 2).

The Watson-Kistiakowsky equation⁸ has been used to evaluate the vaporization heats of the sulphones at their boiling points and these have been adjusted to refer to 25°C using specific heat terms estimated as set out in part 3. Although no experimental values are available for direct comparison we consider the results to be quite reliable in view of the validity of the method as demonstrated in part 3. They are recorded in table 2 (column 3). The consequent gas-phase heats of formation are listed in column 4. In table 2 are included the values obtained previously⁹ for allyl methyl and benzyl methyl sulphones.

TABLE 1.—HEATS OF COMBUSTION

sample and run no.		weight, g (vac)	heat quantities (cal)					$-\Delta U$ (kcal mole ⁻¹)	Δ
			total	-f.p.	-iso corr	<i>N</i> (dec)	Σ corr		
A	3	0.423891	3112.23	18.23	35.30	7.29	2.34	1558.96	0.06
A	5*	0.435478	3172.16	17.54	35.52	6.51	2.32	1558.91	0.11
A	6	0.418829	3956.65	20.12	35.02	7.28	2.49	1559.10	0.08
A	9*	0.426637	3107.88	17.32	35.39	5.36	2.51	1558.98	0.04
A	10	0.411234	2999.89	16.87	35.61	7.81	2.48	1559.15	0.13
A	12*	0.458427	3336.47	17.21	35.72	6.52	2.38	1559.12	0.10
A	13*	0.416039	3029.35	14.32	35.21	5.98	2.41	1558.89	0.13
A	14	0.424351	3092.99	16.41	35.36	7.64	2.48	1559.05	0.03
average								1559.02	± 0.07
B	1	0.485319	3672.71	12.31	36.29	3.21	2.53	1873.30	0.12
B	3	0.491342	3720.09	13.47	36.87	4.26	2.67	1873.15	0.03
B	7	0.487671	3691.54	12.89	38.23	5.83	2.51	1873.18	0.00
B	9	0.457382	3459.39	10.47	37.47	5.76	2.51	1873.08	0.10
B	12	0.478482	3620.55	11.31	36.77	4.27	2.60	1873.40	0.22
B	13*	0.477321	3615.09	15.47	37.53	4.31	2.34	1873.15	0.03
B	14*	0.499322	3779.25	13.21	38.07	4.15	2.72	1873.22	0.04
B	15*	0.447738	3390.53	14.78	36.93	5.06	2.48	1873.27	0.09
B	16*	0.491002	3718.83	15.53	36.64	3.97	2.59	1872.90	0.28
average								1873.18	± 0.05
C	3	0.499987	3158.42	13.51	33.64	2.47	2.61	991.42	0.09
C	4	0.578424	3658.75	17.32	34.72	2.56	2.68	991.30	0.21
C	6	0.581132	3680.26	21.46	34.74	2.31	2.44	991.50	0.01
C	7	0.572426	3625.44	20.22	34.70	2.58	2.66	991.80	0.29
C	8	0.565334	3576.62	17.42	34.50	2.52	2.61	991.52	0.01
C	11	0.578475	3660.37	17.89	34.72	2.61	2.78	991.46	0.05
C	12	0.562243	3558.73	19.38	34.69	2.62	2.80	991.45	0.06
C	14	0.581273	3676.51	15.88	34.74	2.49	2.55	991.67	0.16
C	15	0.499342	3157.32	16.03	33.64	2.51	2.60	991.55	0.04
C	17	0.571003	3611.23	16.54	34.76	2.54	2.57	991.48	0.03
average								991.51	± 0.09
D	3	0.430381	3252.13	21.42	33.27	7.50	2.84	1862.13	0.10
D	4	0.411253	3104.50	17.36	32.81	8.16	3.09	1861.95	0.08
D	5	0.388192	2941.32	25.90	32.46	10.77	2.30	1862.22	0.19
D	6	0.406511	3076.94	22.36	32.63	11.72	2.55	1861.99	0.04
D	7*	0.399427	3015.96	16.96	32.51	9.37	2.51	1862.13	0.10
D	8*	0.387419	2916.53	16.95	32.19	10.79	2.36	1862.00	0.03
D	10*	0.427416	3235.33	23.13	32.97	11.87	2.68	1861.80	0.23
average								1862.03	± 0.12
E	1	0.512344	3463.33	15.78	31.79	2.88	2.36	1143.68	0.01
E	2	0.520731	3519.04	14.32	31.83	3.41	2.47	1143.76	0.07
E	3	0.516643	3496.69	19.68	31.80	3.22	2.57	1143.72	0.03
E	5	0.522418	3528.39	13.44	31.86	2.79	2.61	1143.57	0.12
E	6*	0.517634	3500.74	17.32	31.85	2.89	2.48	1143.76	0.07
E	7*	0.507032	3429.01	16.49	31.54	3.10	2.47	1143.82	0.13
E	8*	0.547413	3700.64	17.31	31.71	3.00	2.32	1143.74	0.05
E	9*	0.531176	3592.11	18.43	31.62	2.74	2.61	1143.55	0.14
E	11*	0.517745	3503.29	19.18	31.84	2.91	2.89	1143.62	0.07
average								1143.69	± 0.06
F	2	0.174879	3532.29	33.30	2501.22	4.21	2.07	856.77	0.29
F	5	0.235593	3282.11	32.47	1894.93	5.17	2.31	856.22	0.26
F	6	0.176621	3365.79	33.41	2324.64	4.38	2.09	856.51	0.03
F	7	0.152038	3525.33	32.97	2627.79	4.92	2.21	856.25	0.23
F	9	0.248396	3314.26	32.42	1852.19	5.01	2.15	856.43	0.05
F	10	0.329709	3484.03	32.82	1545.04	4.73	2.26	856.72	0.24
average								856.48	± 0.20

* these are samples purified by zone-melting.

TABLE 2.—HEATS OF FORMATION, FUSION, VAPORIZATION
(kcal mole⁻¹)

compound	$-\Delta H_f^\bullet$	L_f^{25}	L_v^{25}	$-\Delta H_f$ (gas)
A	54.1 ± 0.2	3.7 ± 0.3	21.7 ± 0.5	28.7 ± 0.6
B	64.1 ± 0.2	3.3 ± 0.3	24.0 ± 0.5	36.8 ± 0.6
C	83.3 ± 0.2	1.6 ± 0.2	18.3 ± 0.5	63.4 ± 0.6
D	75.2 ± 0.2	2.4 ± 0.3	23.8 ± 0.5	49.0 ± 0.7
E	93.2 ± 0.2	2.0 ± 0.3	19.6 ± 0.5	71.6 ± 0.6
F	98.3 ± 0.3	—	19.9 ± 0.5	78.4 ± 0.6
A.M.S.	92.3 ± 0.3	—	18.8 ± 0.3	73.5 ± 0.4
B.M.S.	89.5 ± 0.3	2.0 ± 0.9	19.5 ± 0.4	68.0 ± 1.0

When the gas-phase heats of formation are combined with the currently accepted values for the atomization heats of C, H, O, S (see part 5), the atomization heats Q_a of the sulphones are obtained. They are set out in table 3 (bottom section).

TABLE 3

compound	Q_a (obs.)	Q_a (calc.)	compound	Q_a (obs.)	Q_a (calc.)
ethylene	537.7	536.6	1-hexene	1660.5	1660.5
propylene	820.4	820.5	2-methyl-1-pentene	1664.1	1664.4
1-butene	1100.4	1100.5	2-methyl-2-pentene	1665.5	1664.0
2-methylpropene	1104.3	1104.4	2-ethyl-1-butene	1663.4	1664.4
1-pentene	1380.4	1380.5	3,3-dimethyl-1-butene	1664.8	1665.3
2-methyl-1-butene	1384.1	1384.4	2,3-dimethyl-1-butene	1665.3	1665.9
2-methyl-2-butene	1386.6	1388.3	1,4-pentadiene	1246.0	1246.2
ethylbenzene	1881.0	1881.2	1,3,5-trimethylbenzene	2167.0	2167.2
m-xylene	1884.0	1884.2	isopropylbenzene	2162.3	2162.7
1-methyl-3-ethylbenzene	2163.7	2164.2	1,3-butadiene	969.8	971.8
benzyl methyl sulphone	2140.9	2139.8	di-phenyl sulphone	2787.2	2787.2
phenyl methyl sulphone	1862.2	1860.8	di-p-tolyl sulphone	3356.7	3353.2
p-tolyl methyl sulphone	2145.8	2143.8	allyl methyl sulphone	1359.6	1360.1
di-benzyl sulphone	3344.5	3347.2	allyl ethyl sulphone	1639.6	1640.1

DISCUSSION

To calculate reliable and meaningful atomization heat values for unsaturated and aromatic compounds, it is necessary to establish a scheme of bond-energy and group-energy terms which gives results in conformity with experimental observation and is, at the same time, acceptable on theoretical grounds. The following is an attempt to achieve these ends. It is based on the assumption that the cumulative effect of neglecting second-nearest neighbour interactions is no larger than the uncertainties (~ 2 kcal) in the experimental atomization heat data. Only nearest neighbour interactions are considered. We therefore retain the energy terms quoted in part 5 for the following bonds:

$$E(\text{C}_{sp^3}-\text{C}_{sp^3}) = 85.0; \quad E(\text{C}-\text{H})_p = 98.3;$$

$$E(\text{C}-\text{H})_s = 97.5; \quad E(\text{C}-\text{H})_t = 96.6.$$

The figures, and all future ones, are in kcal. The subscripts p , s , t indicate that the C—H bonds are primary, secondary or tertiary as defined by Laidler.¹⁰ The symbol $\text{C}_{sp^3}-\text{C}_{sp^3}$ means that the bond is one between two sp^3 hybridized carbon atoms; it is, in other words, a pure single bond. For our present purpose we have to establish values for the following additional bond energy terms: $E(\text{C}_{sp^2}-\text{H})$, $E(\text{C}_{sp^2}-\text{C}_{sp^3})$, $E(\text{C}_{sp^2}-\text{C}_{sp^2})$, $E(\text{C}=\text{C})$, $E(\text{C}-\text{H})_{\text{ar}}$, $E(\text{C}-\text{C})_{\text{ar}}$. For $E(\text{C}_{sp^2}-\text{H})$, $E(\text{C}_{sp^2}-\text{C}_{sp^3})$ and $E(\text{C}_{sp^2}-\text{C}_{sp^2})$, we accept the values 100.9, 89.9 and 100.4

derived by Dewar.¹¹ The above values, in conjunction with the known atomization heats of a large variety of olefines and dienes, lead to a value of 133 for $E(\text{C}=\text{C})$. This differs significantly from Dewar's value of 129.1 but it has the pragmatic advantage that it gives results in conformity with experimental observation whereas his does not. Furthermore, Dewar's value leads to a conjugation energy of 5.8 kcal for butadiene in direct conflict with his own conclusions. Ours indicates that the conjugation energy is zero. The atomization heats of a number of olefines and one unconjugated diene, calculated on the basis of all the bond energy values previously quoted, are compared with the corresponding observed values in table 3 (top section). The agreement is remarkably good. It is better than that which results from Laidler's scheme,¹⁰ which must be rejected in any case because it is based on the erroneous assumption that a carbon-carbon single bond next to a double bond is the same as a carbon-carbon single bond which is not next to a double bond. In other words, it takes no account of the effect of the hybridization change on one of the carbon atoms.

We now come to aromatic compounds and to a consideration of $E(\text{C}-\text{H})_{\text{ar}}$ and $E(\text{C}-\text{C})_{\text{ar}}$, where these quantities refer respectively to the energy terms for the C-H and C-C bonds in benzene. We derive $E(\text{C}-\text{H})_{\text{ar}}$ and $E(\text{C}-\text{C})_{\text{ar}}$ in the following way:

$$Q_a(\text{C}_6\text{H}_6) = 6E(\text{C}-\text{H})_{\text{ar}} + 6E(\text{C}-\text{C})_{\text{ar}} = 1318.1, \quad (1)$$

$$Q_a(\text{CH}_3\text{C}_6\text{H}_5) = 5E(\text{C}-\text{H})_{\text{ar}} + 6E(\text{C}-\text{C})_{\text{ar}} + E(\text{C}_{sp^2}-\text{C}_{sp^3}) + 3E(\text{C}-\text{H})_p = 1601.1. \quad (2)$$

Subtracting (1) from (2) we have

$$E(\text{C}-\text{H})_{\text{ar}} = E(\text{C}_{sp^2}-\text{C}_{sp^3}) + 3E(\text{C}-\text{H})_p - 283 = 89.9 + 3(98.3) - 283 = 101.8.$$

Hence

$$E(\text{C}-\text{C})_{\text{ar}} = 117.9.$$

When these two energy terms are combined with the relevant ones already set out we can calculate atomization heats for a wide variety of aromatic hydrocarbons. Some typical results, along with the observed values, are shown in table 3 (middle section). The agreement is once again remarkable. It may be noted in passing that $E(\text{C}-\text{H})_{\text{ar}}$ is somewhat greater than $E(\text{C}-\text{H})$ in general.

Finally, with respect to the present work on aromatic and unsaturated sulphones, we have to try to assign energy values to the groups $\text{C}_{sp^2}-\text{SO}_2-\text{C}_{sp^2}$ and $\text{C}_{sp^2}-\text{SO}_2-\text{C}_{sp^3}$. In part 5, we have already assigned a value of 344.6 to $E(\text{C}_{sp^3}-\text{SO}_2-\text{C}_{sp^3})$. If we assume that a change of hybridization of the carbon atom from sp^3 to sp^2 has the same strengthening effect on the C-S bond that it has on the C-C bond then we arrive at the following group-energy values:

$$E(\text{C}_{sp^2}-\text{SO}_2-\text{C}_{sp^3}) = 349.5,$$

$$E(\text{C}_{sp^2}-\text{SO}_2-\text{C}_{sp^2}) = 354.4.$$

In conjunction with the relevant bond-energy terms already quoted, these may be used to calculate the atomization heats of the sulphones. These calculated values are compared with our observed ones in table 3 (bottom section). The agreement between the two sets of values is very good for benzyl methyl, allyl ethyl sulphones. These and dibenzyl sulphone are all molecules in which we would not expect any conjugation effects. For dibenzyl sulphone the agreement is not so good. Our observed atomization heat appears a little low. We intend to repeat our measurements on this compound. If there are any conjugation effects involving the d -orbitals of the sulphur in phenyl methyl, p -tolyl methyl, di-phenyl and di- p -tolyl sulphones, they appear to involve quite small (1-3 kcal) conjugation energies.

BOND DISSOCIATION ENERGIES

The values reported in the present paper for the gas-phase heats of formation of phenyl methyl and p-tolyl methyl sulphones may be used to derive values for $D(R-SO_2CH_3)$, where $R = Ph, p\text{-tolyl}$. The appropriate equation is

$$D(R-SO_2CH_3) = \Delta H_f(R)_g + \Delta H_f(SO_2CH_3)_g - \Delta H_f(RSO_2CH_3)_g;$$

$$\Delta H_f(SO_2CH_3)_g = -61.8 \pm 1.8;^9 \quad \Delta H_f(Ph)_g = 70 \pm 3;^{12}$$

$$\Delta H_f(p\text{-tolyl}) = 61 \pm 2.^{13}$$

These, in conjunction with the appropriate $\Delta H_f(RSO_2CH_3)_g$ values give

$$D(Ph-SO_2CH_3) = 71.6 \pm 2.6; \quad D(p\text{-tolyl}-SO_2CH_3) = 70.8 \pm 2.$$

NOTE.—All the observed atomization heat values quoted for hydrocarbons in table 3 are based on data available in *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons* (A.P.I. Research Project 44, Carnegie Press, 1952).

We thank the Royal Society for a grant towards the cost of the apparatus. P. A. G. O'H. is grateful to the Courtauld's Education Trust for the award of a maintenance grant.

¹ Mackle and O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1070.

² Field and Clarke, *J. Org. Chem.*, 1957, **22**, 1129.

³ Keith and Mackle, *Trans. Faraday Soc.*, 1958, **54**, 353.

⁴ Busfield, Mackle and O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1054.

⁵ Good, Lacina and McCullough, *J. Amer. Chem. Soc.*, 1960, **82**, 5589.

⁶ Wagman *et al.*, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143.

⁷ Busfield, Ivin, Mackle and O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1058.

⁸ Watson, *Ind. Eng. Chem.*, 1931, **23**, 360. Kistiakowsky, *Z. phys. Chem.*, 1923, **107**, 65.

⁹ Busfield, Ivin, Mackle and O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1064.

¹⁰ Laidler, *Can. J. Chem.*, 1956, **34**, 626.

¹¹ Dewar, *Conference on Hyperconjugation* (Bloomington, 1958; Pergamon Press, 1959, London), p. 83.

¹² Skinner, *Royal Inst. Chem. Monograph*, 1958, no. 3.

¹³ Mackle and O'Hare, unpublished.