Ammonolysis of Aryl Toluenesulphonate Esters: Evidence for the Concerted Displacement of the Aryl Oxide Group

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Rate constants have been measured for the ammonolysis of aryl toluenesulphonate esters in aqueous solution. The Brønsted-type β value of -1.08 coupled with the β_{eq} for the overall reaction indicates a large increase in negative effective charge on the leaving oxygen in the transition state of the rate-limiting step. Data for β_{nuc} for attack of amines on sulphonates taken from the literature indicate a large increase in positive effective charge on the attacking nitrogen; this coupled with the present data excludes a stepwise mechanism for the displacement of the aryl oxide group. The large changes in effective charge on attacking and leaving atoms are consistent with a concerted S_N2(S) displacement mechanism in this case.

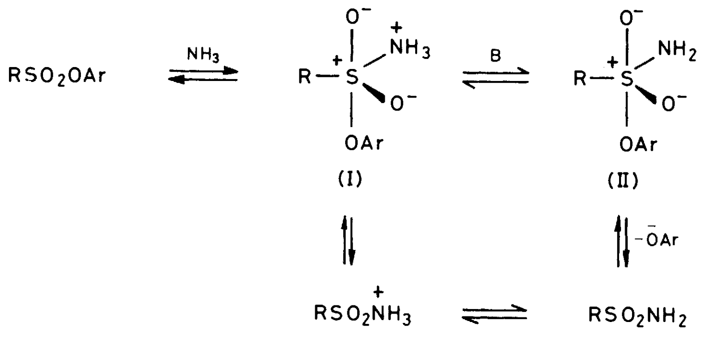
The transfer of the sulphonyl group (RSO_2^-) from donor to acceptor in aqueous solution can proceed by a variety of mechanisms[1,2] including a stepwise or a concerted addition–elimination process exemplified respectively in equations (1) and (2) for the ammonolysis of aryl sulphonate esters. Recent work from this laboratory has provided the β_{eq} value (-1.83) for the variation of the equilibrium constant for sulphonyl group transfer from a phenol donor to an acceptor.[3] This selectivity arises from an effective charge of $+0.83$ on the ether oxygen in the sulphonate ester relative to a change in charge of unity in the ionisation of phenols. We are therefore in a position to determine the effective charge on the ether oxygen in the controlling transition state of any sulphonyl group transfer reaction and compare this with the charge change expected from possible mechanisms. We have shown that the alkaline hydrolysis of aryl sulphonates[4] and ring fission by phenolate ions of the 2-hydroxyphenylmethanesulphonic acid sultone system[3] involve charge changes on the aryl oxygen consistent with concerted processes as shown respectively in transition states (III) and (IV).

The present investigation is simply to determine the β_{lg} for ammonolysis of aryl sulphonates to estimate charge changes on the aryl oxygen in the transition state. We show that β_{lg} compared with the known β_{eq} for the reaction is consistent with a concerted mechanism.

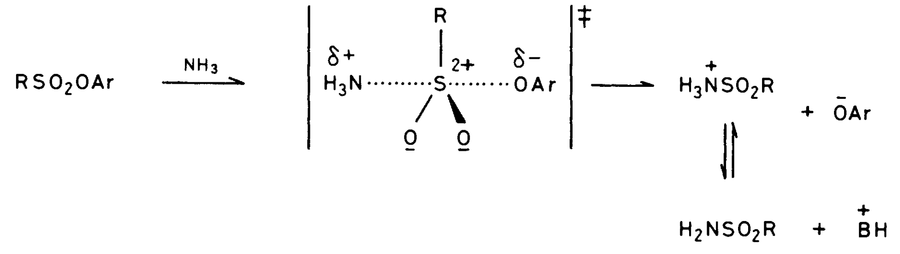
Experimental

Materials.—Aryl toluene-4-sulphonate esters were prepared according to the following general procedure. A solution of the appropriate phenol (0.1 mol) in dichloromethane (100 ml) was cooled by an ice-bath and stirred by a magnetic stirrer. Triethylamine (0.1 mol) was added and then a solution of sulphonyl chloride (0.1 mol) in dichloromethane added over 5 min. The solution was stirred overnight (18 h) and the triethylammonium chloride by-product extracted with dilute HCl (3 × 25 ml; 2M) and the solvent layer dried over $MgSO_4$ and evaporated *in vacuo*. The products were recrystallised from absolute ethanol to constant m.p. Yields of the recrystallised material were *ca.* 50—80% and the i.r. and ^1H n.m.r. spectra were consistent with the expected structures. M.p.s and analyses are presented in Table 1.

Methods.—In order to obtain pseudo-first-order kinetics the ammonia buffer concentration was maintained in large excess over that of the esters. Ethanol was used as a co-solvent (30% v/v) to keep both sulphonate ester and product sulphonamide in solution. Ionic strength was maintained at 1M with aqueous ethanolic potassium chloride. Ammonolyses of the aryl toluene-4-sulphonate esters were followed initially by repetitive scanning of the u.v. spectrum during reaction in buffer with a Pye–Unicam SP 800 spectrophotometer to ob-



(1)

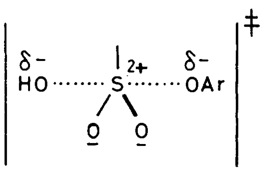


(2)

Table 1. Analytical and physical data for aryl toluene-4-sulphonate esters

		Found (%)					Calculated (%)			
Aryl substituent	M.p. (°C)	C	H	N	S	Formula	C	H	N	S
1 2,4-Dinitro	122—123 [a]	46.2	3.0	8.3	9.4	$C_{13}H_{10}N_2O_7S$	46.1	3.0	8.3	9.5
2 2-Methyl-4,6-dinitro	165—166	47.5	3.3	7.7	9.3	$C_{14}H_{12}N_2O_7S$	47.7	3.4	8.0	9.1
3 4-Nitro	95—96 [b]	53.4	3.8	4.8	11.2	$C_{13}H_{11}NO_5S$	53.2	3.8	4.8	11.0
4 2-Nitro	81—82 [c]	53.2	3.8	4.8	11.0	$C_{13}H_{11}NO_5S$	53.2	3.8	4.8	11.0
5 2-Chloro-4-nitro	106—107	47.5	3.1	4.3	9.8	$C_{13}H_{10}ClNO_5S$	47.6	3.1	4.3	9.8
6 4-Chloro-2-nitro	61—62	47.8	3.1	4.4	9.8	$C_{13}H_{10}ClNO_5S$	47.6	3.1	4.3	9.8
7 2,6-Dinitro	134—135	46.2	2.8	8.2	9.7	$C_{13}H_{10}N_2O_7S$	46.1	3.0	8.3	9.5
8 2,5-Dinitro	115—117	46.1	3.0	8.2	9.4	$C_{13}H_{10}N_2O_7S$	46.1	3.0	8.3	9.5
9 2-Chloro-4,6-dinitro	154.5—155.5	42.1	2.5	7.4	8.7	$C_{13}H_9ClN_2O_7S$	41.9	2.4	7.5	8.6
10 3-Chloro-4-nitro	94—95	47.8	3.2	4.4	9.8	$C_{13}H_{10}NO_5S$	47.6	3.1	4.3	9.8

[a] Lit.,[d] 121 °C. [b] Lit.,[d] 97 °C. [c] Lit.,[d] 83 °C. [d] A. Vogel, ' Textbook of Practical Organic Chemistry,' Longman, London, 1978.



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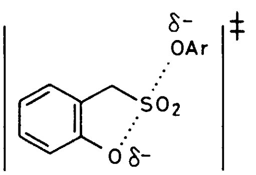


(IV)

tain the best wavelength for kinetic study; the kinetic observations were made at the chosen wavelengths with the same instrument linked with a Servoscribe potentiometric recorder. A typical experiment involved adding a solution of the ester in ethanol stock solution (20—50 ml) to give a final concentration of *ca.* 10^{-4}—10^{-5}M on the flattened tip of a glass rod to the buffer solution (2.5 ml) in a stoppered silica cell in the thermostatted cell compartment (25 ± 0.1 °C) of the spectrophotometer and the change in optical density recorded as a function of time. The dead time of the mixing operation was negligible compared with the half-life. Pesudo-first-order rate constants (k_{obs}) were calculated from plots of $A_t - A_\infty$ *versus* time on two-cycle semi-logarithmic graph paper. For those reactions too slow to measure by complete reaction the method of initial rates was employed ($k_{obs} < 10^{-6}$ s^{-1}); the absorbance at infinite time was obtained by hydrolysis of an equivalent amount of substrate in aqueous ethanolic KOH (0.5 ml) followed by acidification to the appropriate pH and dilution to 2.5 ml. Thus, for slow reactions the rate constant could be obtained from a number of initial rate measurements [$k_{obs} = (dA/dt)_0/(A_0 - A_\infty)$].

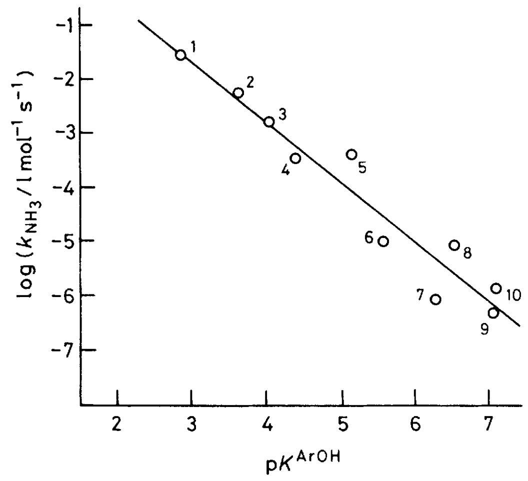
The pH of the reaction mixture was measured after completion in the cell with a Radiometer PHM-26 instrument calibrated with E.I.L. buffer standards to ±0.01 pH units; this ensured that the fraction of base species, determined from the composition of the buffer, was constant throughout a series of runs.

Product analysis was carried out by taking advantage of the characteristic u.v. spectra of the products.

Table 2. Rate constants for the ammonolysis of substituted phenyl toluene-4-sulphonate esters (k_{NH_3}) [a]

Substituent	k_{NH_3}/ l mol^{-1} s^{-1}	N [c,d]	pK^{ArOH}	λ_k[b]/nm
2-Chloro-4,6-dinitro	2.44×10^{-2}	8	2.87	380
2,6-Dinitro	0.65×10^{-2}	8	3.71	430
2,4-Dinitro	0.16×10^{-2}	16	4.11	360
2,4-Dinitro-6-methyl	3.0×10^{-4}	8	4.44	370
2,5-Dinitro	4.0×10^{-4}	8	5.22	440
2-Chloro-4-nitro	9.6×10^{-6}	8	5.64	410
3-Chloro-4-nitro	7.9×10^{-7}	8	5.83	400
4-Chloro-2-nitro	8.6×10^{-6}	8	6.64	430
4-Nitro	4.4×10^{-7}	8	7.14	410
2-Nitro	1.4×10^{-6}	8	7.23	420

[a] Measured using ammonia–ammonium chloride buffers at fractions of base (FB) 0.2 and 0.5 at 25 °C, 30% v/v ethanol–water, and 1.0M ionic strength. [b] Wavelength employed in the measurement of the kinetics. [c] Number of data points. [d] Total ammonia concentration change for each substrate was from 0.1 to 1.0M.



Dependence of log k_{NH_3} for the ammonolysis of aryl toluene-4-sulphonates on the pK of the phenol leaving group. Data and identification of the points are taken from Table 2 and the line is calculated from equation (3)

Results

The decomposition of the sulphonate esters was pseudo-first-order over at least 90% of the total progress curves for those substrates reacted to infinite time. The first-order rate constants are linear in total ammonia concentration and the slopes of plots of k_{obs} *versus* total ammonia concentration are proportional to the basic fraction (FB) of the buffer indicating that only neutral ammonia is responsible for the degradation of the esters. Neutral and alkaline hydrolyses are negligible at pH values of the buffer solutions employed. The intercept of the above slopes on the axis at FB = 1 gives the rate constant k_{NH_3}, the second-order rate constant for attack of ammonia on the ester. The Brønsted-type plot of log K_{NH_3} *versus* the pK of the leaving phenol is linear [equation (3)].

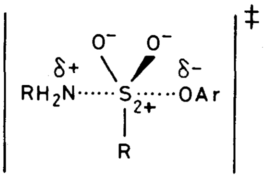
$$\log k_{NH_3} = (-1.08 \pm 0.13)\ \mathrm{p}K^{\mathrm{ArOH}} + 1.49 \pm 0.69\ (r\ 0.937) \quad (3)$$

Product analysis through the u.v. spectra of the products indicated that a negligible amount of the anilide had been formed by aromatic nucleophilic displacement in each ester reacted. The 2,4-dinitrophenyl ester was studied in detail as this is most likely to undergo aromatic substitution. The product spectrum coincided precisely with that of a mixture of 2,4-dinitrophenol and toluenesulphonamide in concentrations equivalent to that of the starting ester and under identical conditions. This is quite a sensitive test as the ratio of extinction coefficients for the 2,4-dinitroaniline at 380 and 330 nm is 0.709 and for the 2,4-dinitrophenol is 1.769. Extinction coefficients for spectral peaks are: toluenesulphonamide, 225 nm, $10^{4.305}$; 2,4-dinitrophenol, 360 nm, $10^{4.196}$; 2,4-dinitroaniline, 345 nm, $10^{4.238}$ (at pH 9.5, 30% v/v ethanol–water, ionic strength 1M). The upper limit estimated for the presence of the aniline in the product is no more than 5%; we regard this as negligible and have made no corrections to the kinetic data.

$$\mathrm{RNH_2} + \mathrm{RSO_2{-}O{-}Ar} \rightleftharpoons \overset{+}{\mathrm{R}}\mathrm{NH_2{-}SO_2R} + \overset{-}{\mathrm{O}}\mathrm{Ar} \quad (4)$$

Discussion

The ammonolysis rate constants for aryl toluene-4-sulphonates (k_{NH_3}) exhibit a β_{lg} value of -1.08 *versus* the ionisation of the corresponding phenol compared with the transfer of a sulphonate group from a phenol to a constant acceptor which has a β_{eq} of -1.83.[3] The change in effective charge on the leaving oxygen is -1.08 from ground to transition state compared with a total change of -1.83 units. Such a large change in effective charge is consistent with considerable bond fission between sulphur and oxygen; the alkaline hydrolysis of aryl acetates has a change in effective charge of only -0.4 in -1.7 where it is known that the C–O bond is not breaking in the rate-controlling transition state.[5] A case where C–O bond cleavage is rate limiting, namely the alkaline hydrolysis of aryl carbamates, has a change in effective charge of -1.15 in -1.8,[6] comparable with the present system. The absence of general base catalysis of the ammonolysis reaction indicates that the proton absent in the product sulphonamide is removed *after* the rate-controlling step as is depicted in equation (2) where reactions succeeding the $RSO_2NH_3^+$ intermediate are fast. It is not possible as yet to measure the value of β_{eq} for process (4) where the varying group is the amine nucleophile. Thus the value of β_{nuc} observed for aminolysis of sulphonate esters may not yet be used strictly to estimate the effective charge on the nitrogen in the transition state. Values obtained for β_{nuc},[7] however, suggest that there is substantial change in charge on the nitrogen consistent with the proposed concerted mechanism. A value of 0.66 was found for the aminolysis of the 5-nitro-2-hydroxyphenylmethanesulphonic acid sultone [7a] and Kice found [7b] that aminolysis of phenyl α-disulphones has the same selectivity to amine structure as does the reactivity of carboxylic acid esters, pointing to large changes in charge on the attacking nitrogen.



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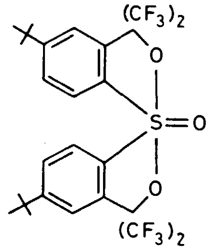


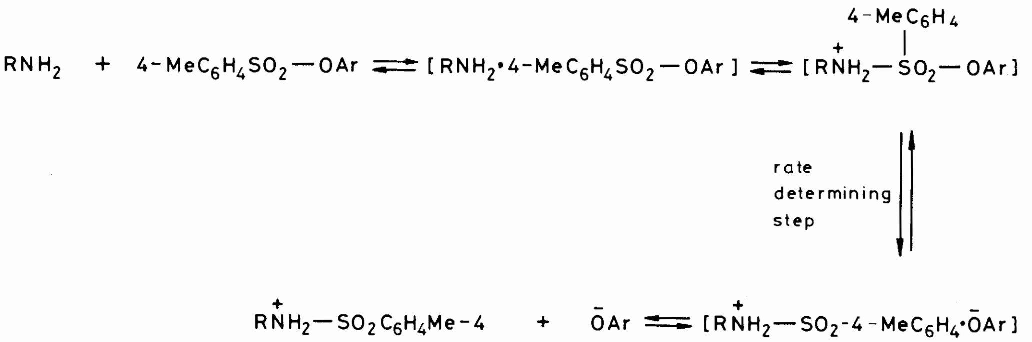
(VI)

It is interesting to speculate on the structure of the transition state for the sulphonyl group transfer to the amine. This is presumably essentially a trigonal bipyramidal structure with apical entering and departing groups (V). Martin and his co-workers have succeeded in isolating an analogue (VI) of this trigonal bipyramidal structure and they find that the apical bonds are longer than single (tetraco-ordinate) S–O bonds by *ca.* 0.2 Å.[8] The isolation of an analogue of the structure does not mean that the structure itself is at an energy well consistent with a stable molecule. For example Martin has also isolated analogues of the S_N2 transition-state structure [9] but there is no question that in alkyl substitution a pentaco-ordinate carbon intermediate does not exist. It is hardly surprising that the analogue prepared by Martin [8] is relatively stable as it is an example of a 'no-bond' resonance compound; [10] decomposition by S–O fission would yield a species which would revert rapidly to reagent [equation (5)]. The distinction between a stepwise process and a concerted one is in the present case strictly between the relative stabilities of pentaco-ordinate structures in equations (1) and (2). Thus one would expect an intermediate such as (I) to exist long enough for a vibration to occur ($t_{\frac{1}{2}} > 10^{-13}$ s) and the concerted process will be the favoured path when such an intermediate has a half-life shorter than a vibration ($< 10^{-13}$ s). Since proton transfer is not rate limiting and proton transfer from the ammonium moiety in the intermediate (I) would be expected to be at a diffusion-controlled rate constant we can only say that if an intermediate exists it must have a half-life $< 10^{-10}$ s. It is conceivable that the mechanism could be that in equation (6) where the pentaco-ordinate intermediate in the encounter complex decomposes to protonated sulphonamide (in the encounter complex) faster than the base can diffuse in to deprotonate the ammonium ion.

(5)

We show here that the mechanism for the sulphonyl group transfer reaction involves passage through a pentaco-ordinate structure with weak entering and leaving bond-order consistent with large changes in effective charge at the donor and acceptor atoms as depicted in equation (7); the effective charge of -0.25 on the aryl oxygen in the transition state is derived from β_{lg} (-1.08) and the effective charge in the ground-state ($+0.83$).[3] We have shown that there is substantial charge change in donor and acceptor atoms for other sulphonyl group transfer reactions.[3,4]

It is unlikely that oxygen-18 incorporation esperiments of the type used by Bender [11,12] will distinguish between the concerted and stepwise paths. Since the pentaco-ordinate intermediate, if formed, is required to decompose faster than diffusion the proton transfer step must be slower than decomposition and thus incorporation *via* mechanism 'A' in equation (8) should not occur. The possibility of a fast intramolecular proton transfer should not be completely ruled



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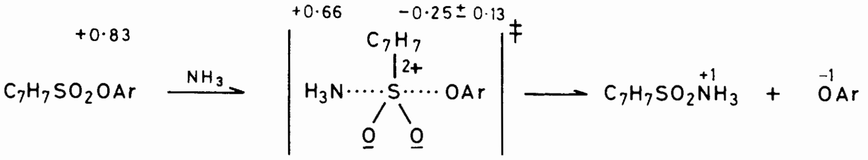

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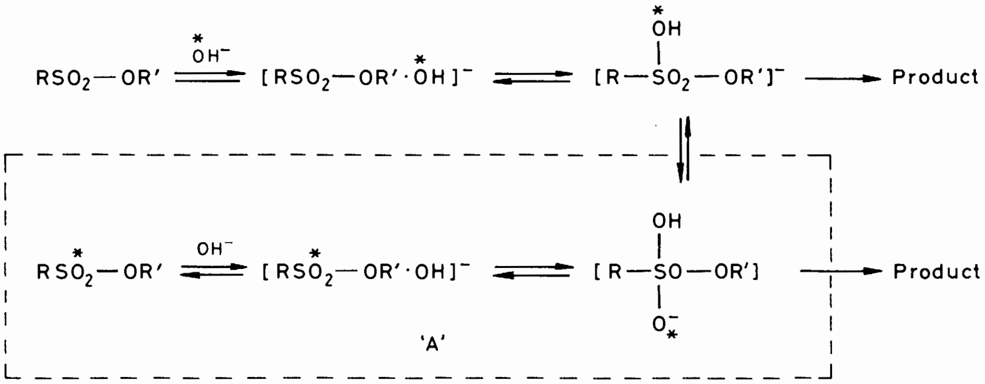
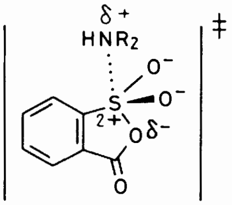


(8)

out but is unlikely to be favoured over one involving transporter molecules.[13]

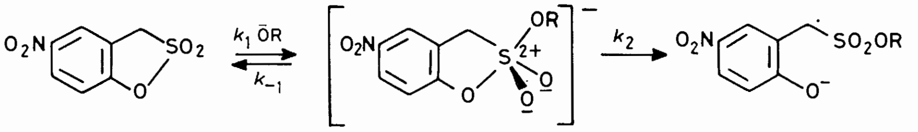
We shall now discuss the existence of intermediates (I) and (II) for equation (1). If the decomposition of (II) were rate limiting, as indicated by the large change in effective charge on the phenol oxygen, the rate law would include an hydroxide term. Such a rate-limiting step would also not be consistent with the relatively large β_{nuc} for aminolysis of sulphonate esters[7] which suggests considerable positive charge on nitrogen in the transition state. We are thus forced to conclude that, if equation (1) holds, the decomposition of (I) to protonated sulphonamide is required to be rate limiting. Partitioning of (I) through the protonated sulphonamide requires that this step be faster than the proton-transfer reaction to intermediate (II); the proton transfer is a diffusion-controlled step since it is thermodynamically favourable. Thus equation (1) can only hold if the decomposition rate constant of (I) to sulphonamide exceeds the diffusion-controlled rate, that is, (I) must decompose to sulphonamide in the encounter complex before it can diffuse into the bulk solution. The decomposition of (I) is thus diffusion controlled and no selectivity is expected for changing the phenol leaving group, contrary to the experimental results.



(VII)

The recent structure–reactivity data for the hydrolysis of 2-carboxybenzenesulphonamides[14] indicate charge changes on nitrogen, sulphur, and attacking oxygen (VII) consistent with either a stepwise process or a concerted one with advanced S–O bond formation and advanced N–S bond fission. The unsymmetrical nature of the transition state might be expected since the carboxylate anion is a relatively weak nucleophile.

The reaction of oxyanions with the 5-nitrosultone [equation (9)] gives us direct evidence that there is not an intermediate species because there is no indication of a break in the Brønsted-type plot.[3] Since the reactivity of the sultone is probably due to angle strain[15] the intermediate species would ring open



(9)

(k_2) faster than the return (k_{-1}) for leaving groups of equal pK (6.00). Thus we should expect a break to occur at pK values for the attacking RO$^-$ species lower than pK 6. There is no evidence of a break and the slope of the Brønsted correlation ($\beta_{\text{nuc}} = 0.87$) is much too large for the k_1 step to be rate limiting.

It is interesting at this stage to reopen the question of the meaning of bond orders less than unity. Martin and his co-workers [8] showed that the increased bond lengths of the apical S–O bonds in their pentaco-ordinate analogues were consistent with bond orders of between 0.4 and 0.7 using Pauling's equation.[16] This interpretation indicates that there should be negative charge on the apical oxygens so that estimation of negative charge on the acceptor and donor atoms would not necessarily distinguish between concerted and stepwise paths. There are some difficulties with the interpretation of bond order. The first is that a bond order between zero and unity must be derived from an extrapolation procedure rather than the interpolation as used in bond-order measurements for, say, aromatic C–C bonds; in the application to C–C bonds the π-bonding is the variant whereas the much stronger σ-bonding is constant. A second problem is that although the *s* and *p* orbitals will give a trigonal bipyramidal structure with a three-centre four-electron bond (one bonding and one non-bonding orbital filled) [8b] the interaction of *d*-orbitals especially the d_z-orbital is neglected. If *d*-orbitals are included the apical *pd*-hybrid orbitals provide normal two-centre two-electron apical bonds which will not be as polarised as those involving the three-centre orbital. The different hybridisation between S–O bonds from the tetrahedral compounds and pentaco-ordinate species could easily explain the bond length differences observed by Martin. In any case there seems no justification in taking the tetrahedral S–O bond as being a ‘ single ’ bond for ‘ bond order ’ estimations; it might very well be that this has some double-bond character.

Acknowledgements

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