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STERIC EFFECTS ON ACIDITY OF METHYLENEBIS-(DIALKYLSULFONIUM) SALTS

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The substituents R and R' have a sizable effect on the acidity of the methylenebis-(dialkylsulfonium) salts 1 - 3. (1)

$$RR'\overset{+}{S}\text{-}CH_2\text{-}\overset{+}{S}RR' \quad 2BF_4^-$$

1 R = R' = methyl
2 R = methyl, R' = ethyl
3 R = R' = ethyl

Replacement of methyl groups by ethyl groups enhances acidity in the series 1 - 3. This trend is unexpected since it runs counter to that anticipated on the basis of the relative electron donating power of methyl and ethyl groups (Table 2). We can now report that pK_a data from a more complete series of bissulfonium salts confirms the trend originally observed in compounds 1 - 3.

We have prepared the bissulfonium fluoroborates 4 - 7* (see table 1) by treatment of bis-(n-propylthio)methane and bis-(i-propylthio)methane with triethyloxonium and trimethyloxonium fluoroborates as described previously (1). The pK_a values of these bissalts in aqueous solution are reported in Table 1.

The $\delta_R\ pK_a$ value for replacement of methyl by ethyl (1 vs. 2 and 2 vs. 3) is -0.7 to -0.8 while replacement of ethyl by i-propyl (2 vs. 5 and 3 vs. 7) gives a $\delta_R\ pK_a$ of -0.6 to -0.8. Exchange of ethyl and n-propyl groups has no significant effect on the pK_a value. These data show clearly that as the effective size of the alkyl substituents increases, the acidity of the bissulfonium salts increases, the reverse of predictions based on polar effects. These effects do not parallel the Taft E_s values (Table 2) however.

We propose that the unusual substituent effects on acidity observed in compounds 1 - 7 are caused by steric hindrance of solvation in the bissulfonium dications. Loss of a proton from bissulfonium salt 8, which has two localized

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* All new compounds have been characterized by NMR spectroscopy and elemental analysis.

TABLE 1

pK_a in Water of Methylenebis-(dialkylsulfonium) Fluoroborates

$RR'\overset{+}{S}-CH_2-\overset{+}{S}RR'$

Compound	R	R'	Average pK_a[a,b]
1	methyl	methyl	9.19 ± 0.01 (9.10)[c]
2	methyl	ethyl	8.51 ± 0.02 (8.35)[c]
4	methyl	n-propyl	8.52 ± 0.02
5	methyl	i-propyl	7.76 ± 0.03
3	ethyl	ethyl	7.71 ± 0.02 (7.43)[c]
6	ethyl	n-propyl	7.63 ± 0.02
7	ethyl	i-propyl	7.14 ± 0.01

a. Determined by potentiometric titration of ca. 0.002 M. aqueous solutions with 0.115 N. alkali. Values are not corrected for ionic strength effects.

b. Ranges are standard deviations for three to five determinations. The probable error in the pK_a values should be ± 0.10 to ± 0.20 units.

c. Values reported in reference 1.

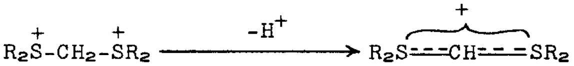
TABLE 2

Taft Polar and Steric Substituent Constants

	[a]	E_s [b]
methyl	0.00	0.00
ethyl	-0.100	-0.07
n-propyl	-0.115	-0.36
i-propyl	-0.190	-0.47

a. Ref. 2, page 619 b. Ref. 2

unit charges, gives ylide 9 (3), which bears a net unit charge delocalized over three atoms. (4)



$$R_2\overset{+}{S}-CH_2-\overset{+}{S}R_2 \xrightarrow{-H^+} R_2\overbrace{S\text{- - -}CH\text{- - -}S}^{+}R_2$$

8 9

Clearly, the bissalts should have higher solvation energies than their respective conjugate bases. Replacement of small alkyl groups on sulfur by larger ones should hinder solvation, particularly in the bissalts where charge is localized on sulfur. Thus larger alkyl substituents would destabilize the bissalt relative to its conjugate base and enhance its acidity.

Relief of steric interactions between the large R_2S- groups owing to an increase in the S-C-S angle on going from **8** to **9** might account for part of the observed effect. However, because of the shortening of the S-C bond length in the ylides owing to dπ - pπ overlap (5), the sulfur-sulfur distance should change but little. For example, a 15° increase in the S-C-S angle from 115° to 130° accompanied by a decrease in the C-S bond length from 1.82 Å in **8** to 1.70 Å in **9** results in only an 0.05 ± .01 Å increase in the sulfur-sulfur distance.

It is not surprising that the effects of alkyl substituents in these compounds do not correlate well with their Taft E_s values. The steric effects of alkyl groups in methylenebis-(dialkylsulfonium) salts would be expected to differ significantly from those observed in the hydrolysis of aliphatic esters. In addition, the observed effects are certainly not purely steric effects but are presumably the result of a strong steric effect superimposed on a weaker polar effect.

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REFERENCES

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2. R.W. Taft in *Steric Effects in Organic Chemistry*, M. Newman, Ed., John Wiley and Sons, New York, 1956.

3. C.P. Lillya and P. Miller, *J. Am. Chem. Soc.*, **88**, 1560 (1966).

4. Such delocalization by d - p overlap is well established for sulfonium and phosphonium ylides, Cf. A.W. Johnson, *Ylide Chemistry*, Academic Press, New York, 1966.

5. This is well documented for phosphorous ylides: P-C$_{ave.}$ ∼ 1.85 Å and P=C (ylide)$_{ave.}$ ∼ 1.72 Å. Cf. Ref. 4, pages 80 and 124 and D.E.C. Corbridge in *Topics in Phosphorous Chemistry*, E.J. Griffith and M. Grayson, Ed., Vol. III, Interscience, New York, 1966, page 295.