possible ion-pair structures. A simplified scheme[31] is that shown in Scheme I. The position of the equilibrium strongly depends on the nature of positive ion, negative ion, and solvent. The similar equilibrium scheme involving monomer ion, cluster ion, and diamagnetic dimer or polymer may be quite common to many ion-pair systems. Similarities between some of the processes described here and the other systems should be noted.[32,33]

Acknowledgment. I am very grateful to Professor S. I. Weissman of Washington University for his gift of C^{13}-labeled fluorenone. By his courtesy, studies of temperature dependence of C^{13} splittings were made possible. Financial support from the National Science Foundation (GP-5040) is greatly appreciated.

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(31) The existence of many structurally different monomer ion pairs is neglected in this scheme in order to simplify the illustration.

(32) I. M. Brown, S. I. Weissman, and L. C. Snyder, *J. Chem. Phys.*, **42**, 1105 (1965).

(33) H. Van Willigen, Thesis, Amsterdam, 1965. I thank Dr. H. Van Willigen for sending me a copy of his thesis.

Valence-Shell Expansion in Electronically Excited States of Aromatic Sulfur Compounds[1]

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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana. *Received July 28, 1966*

Abstract: The extent of valence-shell expansion in photoexcited states of aromatic sulfur compounds has been investigated. Acid dissociation constants of phenols with sulfur-containing substituents have been determined in the ground, lowest triplet, and first excited singlet states, by fluorescence, phosphorescence, and ultraviolet absorption spectroscopy. Substituent groups included sulfone, sulfoxide, sulfide, and sulfonium functions. A linear-free-energy treatment of phenols containing sulfone, sulfonium, and sulfoxide groups shows that the extent of electron-attracting conjugation by the substituents is greatly enhanced in photoexcited states, compared with the ground state. In contrast, σ constants for electronically excited sulfides are not appreciably different from those in the ground state unless alkyl groups are situated *ortho* to the sulfide function, in which case a large increase in σ occurs upon excitation. This result suggests that the sulfide group participates in both electron-releasing and -attracting conjugation in the ground state and that the extent of both forms of conjugation increases in a roughly equivalent fashion upon excitation, unless electron-releasing p_π conjugation is sterically inhibited. Steric factors exert very much less influence upon the excited-state acidities of sulfones, sulfoxides, and sulfonium salts, indicating that p_π orbitals in these compounds do not engage in significant conjugation, either electron releasing or withdrawing, in photoexcited states.

There has been continuing interest in the nature of the carbon–sulfur bond in aromatic sulfur compounds, especially with respect to participation of sulfur d_π orbitals in electron-withdrawing conjugation ("valence-shell expansion").[2] It seems generally accepted that such conjugation is significant in the ground electronic states of aryl sulfones, sulfoxides, and sulfonium salts. However, the extent of sulfur electron-accepting conjugation in aryl sulfides remains in some doubt. Recent spectral "substituent interference experiments" reported by Goodman and Taft[3] indicate significant population of sulfur 3d orbitals in the ground states of thiophenols and thioanisoles. Earlier spectral evidence, however, had been interpreted as demonstrating the absence of significant valence-shell expansion in compounds of divalent sulfur.[4] The influence of sulfide groups on the acidities of benzoic acid and phenol also has implied that recognizable expansion of the sulfur valence shell does not occur unless an extremely potent electron donor is present; chemically, the principal conjugative effect of a sulfide substituent frequently appears to be electron *donation*.[5]

While the influence of valence-shell expansion upon the chemical properties of ground-state aromatic sulfur compounds has received considerable attention, surprisingly little has been done to elucidate the extent of the effect in electronically excited states. Beginning with the work of Fehnel and Carmack[6] and Koch,[7] several attempts have been made to relate the nature of conjugative perturbations introduced by sulfur-containing substituents to the direction and magnitude of shifts in the ultraviolet absorption maxima of aromatic compounds. In that manner, it has been concluded that, in aryl sulfides, electron-*donor* conjugation may be appreciably more important in photoexcited states than in the ground state,[7-9] but there is no clear spectral

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(1) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 11-16, 1966.

(2) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press, New York, N. Y., 1962; H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1963; C. Y. Meyers, *Gazz. Chim. Ital.*, **93**, 1206 (1963).

(3) L. Goodman and R. W. Taft, *J. Am. Chem. Soc.*, **87**, 4385 (1965).

(4) See, for example, G. L. Bendazzoli and C. Zauli, *J. Chem. Soc.*, 6827 (1965), and A. Mangini, *Pure Appl. Chem.*, 7, 103 (1963).

(5) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78**, 854 (1956).

(6) E. A. Fehnel and M. Carmack, *ibid.*, 71, 84, 231, 2889 (1949); 72, 1292 (1950).

(7) H. P. Koch, *J. Chem. Soc.*, 387, 408 (1949); 2892 (1950).

(8) A. Mangini and C. Zauli, *ibid.*, 4960 (1956).

(9) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **79**, 717 (1957).

evidence that the importance of electron-*acceptor* resonance is increased by electronic excitation.[4,8,9] Evidence from spectral shifts seems to indicate that photoexcited sulfoxides behave similarly, *i.e.*, excitation produces an increase in electron-donor conjugation.[9,10] In contrast, spectral shifts alone indicate that the relative significance of valence-shell expansion greatly increases upon electronic excitation for aryl sulfones and sulfonium salts.[2,10]

Inference of excited-state chemical properties from ultraviolet absorption frequencies may often be of qualitative utility. However, the interpretation of such data must be carried out with great care. The frequency of maximum ultraviolet absorption is a measure of the difference in electronic energy between the ground and excited states; consequently, absorption frequencies do not provide quantitative information concerning the nature of electronically excited states unless the electronic properties of the ground state are well established—which is seldom the case in complex molecules. Furthermore, the frequency of an absorption maximum includes not only the energy of electronic excitation, but also that of a number of vibrational quanta. Hence, if the spacing or occupation of vibrational energy levels in ground and excited states is significantly different, the energy of an absorption maximum will not serve as a measure of the difference in *electronic* energy between the two states; such information can be obtained only by accurate measurement of the "0–0" absorption frequency, a virtually impossible task for complex molecules in liquid solution. It is clear, therefore, that measurement of ultraviolet absorption frequencies offers, at best, an indirect, qualitative means for investigating the chemistry of excited molecules.[11]

A useful technique for performing relatively "direct" studies of the chemistry of excited molecules is to measure their Brønsted acidities,[12] for it is known that acidity is a sensitive measure of changes in electron density at the site of proton attachment. Previous investigations of excited-state proton-transfer reactions have indicated that very striking enhancements of conjugation (relative to induction) are brought about by photoexcitation. Further, direct conjugative effects between *meta* substituents appear of considerable importance in excited states.[13] Hence, it should be possible to assess the significance of valence-shell expansion, and other forms of conjugation, by noting trends in excited-state pK_a values of dissociable compounds with sulfur-containing substituents. A considerable body of knowledge concerning the excited-state protolyses of substituted phenols is already available;[13,14] accordingly, phenols with sulfoxide, sulfide, sulfone, and sulfonium substituents have been chosen for study.

Experimental Section

All compounds (except *p*-hydroxythioanisole, which is commercially available) were synthesized by published procedures; literature citations are given in Table I. All phenols were carefully purified by one or more of the following procedures: recrystallization, vacuum sublimation, vacuum distillation, fractional freezing, or adsorption chromatography. Purification of solvents has been described.[13a]

Ground- and excited-state acidities were determined in 48% aqueous ethanol, because several of the sulfides were extremely insoluble in water. Ground-state pK_a values were determined by glass-electrode potentiometric titration[15] and spectrophotometric techniques[16] using buffers of constant ionic strength (0.01) similar to those described by Biggs[17] and Perrin.[18] The literature values for the pH of the buffers pertain to aqueous solution, and are obviously inapplicable to the present work. Hence, apparent pH values were measured in 48% ethanol with an ordinary glass-electrode pH meter, and these uncorrected buffer pH values were used to compute apparent pK_a values from spectrophotometric measurements. In addition, it was assumed that the activity coefficient corrections[17] were the same in 48% ethanol as in pure water. Although this assumption is of doubtful validity, the activity corrections are sufficiently small[16–18] that they should not introduce significant error into the apparent pK_a values. Despite the uncertainties in the spectrophotometric procedure, it was found that the spectrophotometric and potentiometric techniques yielded excellent agreement in all cases where both were used. Unfortunately, the aryl sulfides tended to undergo rapid oxidation, especially in neutral or alkaline solution, during the time required to obtain a potentiometric titration curve; the decomposition could not be eliminated by flushing the titration cell with nitrogen.

Excited-state pK_a values were determined by both the Förster cycle[12,19] and "excited-state titration curve"[12] techniques; in the former, both absorption and luminescence data were used.[20] Agreement between the two methods was generally excellent; however, rapid photodecomposition prevented measurement of meaningful titration curves for many compounds. Ultraviolet absorption spectra were measured with either a Bausch and Lomb Spectronic 505 or Cary Model 14 recording spectrophotometer; fluorescence and phosphorescence spectra were obtained with an Aminco-Bowman spectrofluorophotometer. Although 48% aqueous ethanol forms badly cracked glasses at 77°K, it was possible to obtain phosphorescence spectra in this matrix; the spectra compared favorably with those obtained in absolute ethanol, which forms clear glasses.

Results and Discussion

For the various phenols studied, apparent ground- and excited-state pK_a values are presented in Table I. In our notation, pK_a refers to the ground state, p$K_a{}^S$ to the first excited singlet, and p$K_a{}^T$ to the lowest triplet. As expected, electronic excitation greatly enhances the acidity of these compounds in the first excited singlet, while the effect is much smaller in the lowest triplet.[21]

The data have been correlated by the Hammett equation, using $\rho = 2.42$.[10,22] We assume that ρ in the electronically excited states can be set equal to the ground-state value. There is no fundamental justification for this assumption; it has, however, been observed that, for substituted phenols, the slopes of Hammett plots are essentially the same regardless of whether ground- or excited-state acidities are used.[13a] Hence the assumption appears justified in the present case, but it should not be inferred that it will obtain

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[10] S. Oae and C. Zalut, *J. Am. Chem. Soc.*, **82**, 5359 (1960).

[11] It should not be inferred that absorption spectroscopy is useless for this purpose; however, the most valid and useful comparisons are those involving *intensities*, rather than frequencies, of absorption bands.[3]

[12] For reviews, see A. Weller, *Progr. Reaction Kinetics*, 1, 189 (1961), and E. L. Wehry and L. B. Rogers in "Fluorescence and Phosphorescence Analysis," D. M. Hercules, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, pp 125–140.

[13] (a) E. L. Wehry and L. B. Rogers, *J. Am. Chem. Soc.*, **87**, 4234 (1965); (b) H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

[14] E. L. Wehry and L. B. Rogers, *J. Am. Chem. Soc.*, **88**, 361 (1966); W. Bartok, R. B. Hartman, and P. J. Lucchesi, *Photochem. Photobiol.*, **4**, 499 (1965); W. Bartok, P. J. Lucchesi, and N. S. Snider, *J. Am. Chem. Soc.*, **84**, 1842 (1962).

[15] F. G. Bordwell and H. M. Andersen, *ibid.*, **75**, 6019 (1953).

[16] R. A. Robinson in "Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 16.

[17] A. I. Biggs, *Trans. Faraday Soc.*, **52**, 35 (1956).

[18] D. D. Perrin, *Australian J. Chem.*, **16**, 572 (1963).

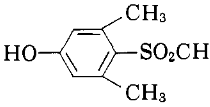
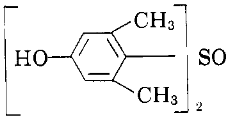
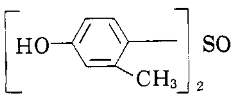
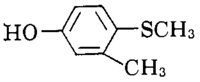
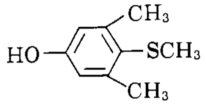
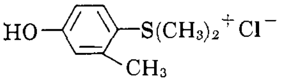
[19] A. Weller, *Z. Elektrochem.*, **56**, 662 (1952).

[20] E. L. Wehry and L. B. Rogers, *Spectrochim. Acta*, **21**, 1976 (1965).

[21] G. Jackson and G. Porter, *Proc. Roy. Soc.* (London), **A260**, 13 (1961).

[22] G. Schwarzenbach and E. Rudin, *Helv. Chim. Acta*, **22**, 360 (1939); H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **78**, 3400 (1956).

Table I. Apparent pK_a Values and Substituent Constants for Phenols in Ground, First Excited Singlet, and Lowest Triplet States

Compound	Synthesis ref	pK_a	Method[a]	pK_a^S [b]	pK_a^T [b]	σ	σ^S	σ^T
Phenol	. . .	10.91	P	4.9	9.6	. . .	. . .	. . .
		10.94	S					
p-$HOC_6H_4SO_2C_6H_5$	*c*	8.67	P	2.1	7.2	0.95	1.2	1.0
		8.65	S					
p-$HOC_6H_4SO_2CH_3$	*d*	9.13	P	2.3	7.6	0.78	1.1	0.83
		9.06	S					
m-$HOC_6H_4SO_2CH_3$	*d*	9.37	P	2.6	7.9	0.52	0.91	0.45
		9.43	S					
	*e*	9.38	P	2.4	7.7	0.65	1.0	0.79
		9.36	S					
p-$HOC_6H_4SOC_6H_5$		9.28	P	2.3	7.9	0.73	1.1	0.70
		9.18	S					
p-$HOC_6H_4SOCH_3$	*g*	9.36	P	2.4	7.6	0.62	1.0	0.83
		9.43	S					
m-$HOC_6H_4SOCH_3$	*g*	9.64	S	2.8	7.9	0.45	0.79	0.58
	*h*	9.07	P	2.3	7.6	0.75	1.1	0.83
		9.13	S					
	*h*	9.01	P	2.3	7.7	0.76	1.1	0.79
		9.11	S					
p-$HOC_6H_4SC_6H_5$	*i*	10.16	S	4.2	8.8	0.32	0.29	0.34
m-$HOC_6H_4SC_6H_5$	*i*	10.46	S	4.4	9.2	0.20	0.21	0.17
p-$HOC_6H_4SCH_3$	. . .	10.53	S	4.4	9.1	0.17	0.21	0.21
m-$HOC_6H_4SCH_3$	*j*	10.37	S	4.4	9.0	0.19	0.21	0.25
	*e*	9.99	S	2.8	8.4	0.39	0.87	0.50
	*e*	10.12	S	3.0	8.7	0.34	0.78	0.37
p-$HOC_6H_5S(CH_3)_2{}^+Cl^-$	*k*	8.84	P	2.0	7.6	0.83	1.2	0.83
		8.93	S					
m-$HOC_6H_5S(CH_3)_2{}^+Cl^-$	*k*	9.22	S	2.2	7.6	0.71	1.1	0.83
	*k*	9.13	S	2.2	7.8	0.75	1.1	0.74

[a] P, potentiometric; S, spectrophotometric. [b] Förster cycle values only; *cf.* Experimental Section. [c] H. H. Szmant and G. Suld, *J. Am. Chem. Soc.*, **78**, 3400 (1956). [d] F. G. Bordwell and G. D. Cooper, *ibid.*, **74**, 1058 (1952). [e] H. Kloosterziel and H. J. Backer, *Rec. Trav. Chim.*, **72**, 185 (1953). [f] M. Gazdar and S. Smiles, *J. Chem. Soc.*, **93**, 1833 (1908). [g] Reference 9. [h] Reference 10. [i] G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, **51**, 1526 (1929). [j] Reference 5. [k] S. Oae and C. C. Price, *J. Am. Chem. Soc.*, **80**, 3425 (1958).

for other classes of compounds. When the assumption is made, substituent constants in ground and excited states can be computed (Table I).

It is noted in Table I that σ values in the first excited singlet state are consistently larger than those in the ground state for *sulfones*, *sulfoxides*, and *sulfonium salts*. If it is assumed that the influence of inductive effects is not changed appreciably by electronic excitation,[13,23] the trend in substituent constants indicates that electron-accepting conjugation is considerably enhanced by photoexcitation, especially in singlet excited states.

This observation by itself provides no information concerning expansion of the sulfur valence shell in excited states, for electron-accepting resonance could involve either $4p_\pi$ or $3d_\pi$ orbitals, or both, on sulfur. It is generally considered that molecular coplanarity is a prerequisite for effective participation of sulfur p_π orbitals in conjugations, but there is little angular requirement for p–d overlap.[2] It is significant, therefore, that substitution of methyl groups *ortho* to a sulfonium, sulfone, or sulfoxide group exerts only a very small effect on the excited-state acidities of phenols containing these substituents. It is extremely unlikely that the hindered compounds are coplanar, even in the ground state. We therefore conclude that the conjugative effect operative in photoexcited aryl sulfones, sulfoxides, and sulfonium salts constitutes an example of valence-shell expansion, and that its significance (relative to induction and other forms of conjugation) is greatly enhanced by photoexcitation.

This conclusion is consistent with that derived from shifts in the ultraviolet absorption maxima of aryl

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(23) W. F. Hammer and F. A. Matsen, *J. Am. Chem. Soc.*, **70**, 2482 (1948); H. Sponer, *J. Chem. Phys.*, **22**, 234 (1954); L. Goodman and H. Shull, *ibid.*, **27**, 1388 (1957).

sulfones[9,10] and sulfonium salts.[2,10] However, in the case of sulfoxides Bordwell and Boutan[9] and Koch[7] concluded, from absorption studies, that electron-*donor* resonance involving sulfur $3p_\pi$ orbitals is enhanced by electronic excitation. The present results cannot be rationalized in that way. The increase in σ produced by excitation is too large and consistent to be coincidental; furthermore, steric hindrance does not appear to effect significant changes in the relative magnitudes of ground- and excited-state substituent constants. There is no evidence from the acidities for appreciable p_π conjugation, either electron releasing or attracting, in photoexcited aryl sulfoxides.

We turn now to the results for *sulfides*. The nature of conjugation in ground states of aryl sulfides has been a subject of controversy; it is generally (but by no means universally) accepted that, in the ground state, the sulfide group engages in both $3p_\pi$ electron-donating and $3d_\pi$ electron-accepting conjugation.[2,24] The present results are consistent with that viewpoint.

Magnitudes of conjugative effects in substituted benzenes can be estimated *via* the Taft[25] inductive-resonance equation

$$\log\left[\frac{K_x}{K_0}\right] = \sigma_I\rho_I + \sigma_R\rho_R \qquad (1)$$

where

$$\sigma_I\rho_I = \left[\frac{1}{1-\alpha}\right]\left[\log\left(\frac{K_x{}^m}{K_0}\right) - \alpha\log\left(\frac{K_x{}^p}{K_0}\right)\right] \qquad (2)$$

in which α denotes the magnitude of the resonance effect at a *meta* position, compared to that of the same substituent at a *para* position, and K_0, $K_x{}^p$, and $K_x{}^m$ have their usual meanings. We assume $\alpha \cong 0.33$[25] for the SCH_2 and SC_6H_5 substituents. From the data in Table I, together with tabulated σ_I values,[25] we can compute σ_R values for the sulfide groups in the ground states of the unhindered sulfides. For m-SCH_3, p-SCH_3, and m-SC_6H_5, σ_R values all lie between -0.01 and -0.06 while, for p-SC_6H_5, $\sigma_R = +0.09$. It is important to note that the precise resonance substituent constant, $\sigma_R{}^\circ$, for SCH_3 is -0.17.[26] Deviations of measured σ_R values from $\sigma_R{}^\circ$ can in principle be ascribed to specific substituent effects.[27] In the present case, the measured σ_R values are all more positive than $\sigma_R{}^\circ$. This observation is consistent with the view that the SR substituent in ground-state sulfides engages in both $3p_\pi$ donor and $3d_\pi$ acceptor conjugation, with the latter increasing in importance relative to the former as the electron-withdrawing power of R increases (note particularly the positive σ_R for p-SC_6H_5).

It is noted in Table I that the results for photoexcited aryl sulfides differ importantly from those for the other sulfur-containing substituents. For the sulfides, σ, σ^S, and σ^T, are all approximately equal, and there is no clear evidence for enhanced valence-shell expansion. If, however, both donor and acceptor conjugation are significant in the ground state, and the importance of both increases in a roughly equivalent fashion upon photoexcitation, the lack of appreciable change in σ upon excitation can be understood. The experimental results for hindered sulfides are consistent with that conclusion. Insertion of methyl groups *ortho* to the sulfide function in p-hydroxythioanisole causes a very significant increase in σ^S relative to σ. This result indicates that valence-shell expansion in aryl sulfides does indeed increase with photoexcitation, but that this effect is "masked" by a concomitant increase in p_π donor conjugation, unless the latter is sterically inhibited.

Goodman and Taft[3] have measured intramolecular F^{19} nuclear magnetic resonance shielding effects in a number of hindered aryl sulfides. Their nmr data indicate that $\sigma_R{}^\circ$ for the SCH_3 group increases from -0.17[26] in an unhindered sulfide to approximately $+0.03$ when two methyls are placed *ortho* to the SCH_3. Since p_π donor resonance is presumably of negligible importance in the hindered compound, we may take $\sigma_R{}^\circ = +0.05$ to be a reasonable estimate of the extent of valence-shell expansion in ground-state thioanisole derivatives. For the excited singlet states of the hindered sulfides, however, we calculate $\sigma_R{}^S \cong +0.7$.[28] Comparison of that value with the ground-state σ_R for hindered thioanisoles demonstrates that a dramatic increase in valence-shell expansion is produced by excitation to the first singlet.[29] Clearly, the effect is very much less significant in the lowest triplet.

For all compounds in which substituent constants increased upon excitation, enhancements were noted in *meta*-, as well as *para*-, substituted phenols. This is consistent with previous observation of direct conjugative interactions between *meta* substituents in photoexcited aromatic compounds.[13,30] A semiquantitative evaluation of the magnitude of conjugation involving *meta* substituents can be performed with the Taft inductive-resonance expression. Rearrangement of eq 2 yields an expression for α, the resonance "fall-off factor"

$$\alpha = \frac{\sigma_I\rho_I - \log\left[K_x{}^m/K_0\right]}{\sigma_I\rho_I - \log\left[K_x{}^p/K_0\right]} \qquad (3)$$

Data from Table I have been used to compute excited-state α values for unhindered SCH_3, $SOCH_3$, and SO_2CH_3 groups. They are compared with the ground-state values in Table II. We note that the excited-state values for SO_2CH_3 and $SOCH_3$ are considerably larger than those for the ground state. The α^S and α^T values for SCH_3 are, in contrast, very nearly equal to the ground-state value. This comparison provides

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(24) R. R. Beishline, *J. Org. Chem.*, **26**, 2533 (1961).

(25) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); *Tetrahedron*, **5**, 210 (1959).

(26) R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(27) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959).

(28) Here we assume that ground-state ρ_I and σ_I values can be applied to the first excited singlet. This is equivalent to assuming that the inductive effect does not change upon excitation;[23] we have, in fact, already made this assumption (*vide supra*). In addition, it has been assumed that substituent constants are additive in excited states. There exists at present virtually no experimental evidence pertaining to the validity of that assumption; in fact, it seems rather unlikely that it will be of general applicability. Our experience has been that, at least for alkyl substituents, the assumption of additivity should not introduce significant error. Hence, the $\sigma_R{}^S$ value for hindered sulfides has been corrected for the methyl groups, assuming $\sigma_{CH_3}{}^m = -0.03$.[13a]

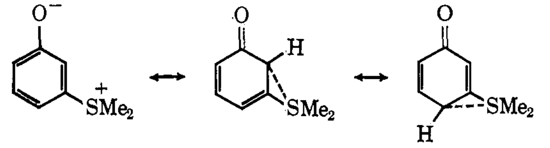
(29) The author is indebted to a referee for suggesting this comparison.

(30) For examples of such observations in photochemical reactions see R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Am. Chem. Soc.*, **87**, 2945 (1965); H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963); H. E. Zimmerman and S. Somasekahara, *ibid.*, **85**, 922 (1963); E. Havinga, R. O. de Jongh, and W. Dorst, *Rec. Trav. Chim.*, **75**, 378 (1953).

Table II. Calculation of α in Ground and Excited States

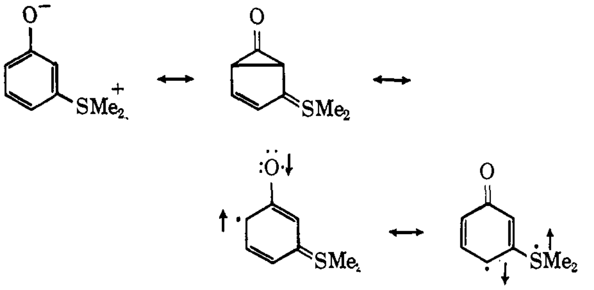
Substituent	σ_I	α	α^S	α^T
SO_2CH_3	0.59	0.18	0.8	0.5
$SOCH_3$	0.52	0.16	0.7	0.6
SCH_3	0.25	0.31	0.3	0.2

further evidence that no net enhancement of conjugation is noted in photoexcited aryl sulfides unless p_π-donor resonance is sterically unfavorable. It would be most interesting to compute α values for hindered sulfides; unfortunately, however, attempts to prepare hindered derivatives of *m*-hydroxythioanisole were not successful.



(4)

Direct conjugation between the phenolic group and sulfonium function may be responsible to some unusual frequency shifts in the ultraviolet spectra of *m*-dimethylsulfoniophenol. It has previously been assumed[31] that conjugative interactions in that compound involve canonical forms with external three-membered rings, particularly in photoexcited states. The present results suggest that conjugation in *m*-sulfoniophenols is not significantly different from that exhibited in excited singlet states of other *meta*-substituted phenols, in which "Dewar structures" are considered to make important contributions. This similarity suggests that the postulation of canonical forms with external three-membered rings in excited states of *meta*-substituted sulfonium salts is unnecessary. A more suitable description of the first excited singlet of these compounds would involve contributions from (*inter alia*) structures such as those in eq 5. The essential point is that, while any description of excited-state charge distributions in terms of contributing structures is likely to be highly imprecise, descriptions based solely upon data obtained from absorption spectra should be viewed with particular reservation.[20]



(5)

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(31) See Table I, footnote *k*.

Vibrational Spectra of Polynuclear Hydroxy Complexes of Lead(II)[1a]

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Abstract: Raman spectra for solutions and Raman and infrared spectra for crystals containing polynuclear hydroxy complexes of lead(II) are reported. The close similarity of Raman spectra for solutions and crystals indicates the presence of identical structural units in the two phases, for a hydroxyl:lead ratio of both 1.00 and 1.33. In the former case, where $Pb_4(OH)_4^{4+}$ is the complex present, the vibrational features are entirely consistent with the tetrahedral structure previously proposed on the basis of solution X-ray scattering measurements. In the latter case, where the complex is probably $Pb_6(OH)_8^{4+}$, the spectrum is interpretable on the basis of an octahedral structure, although other structures are not excluded. There is no vibrational evidence of perchlorate binding to any of the lead species, either in solution or in the crystals.

Recently we presented the results of an infrared and Raman spectroscopic investigation of a polynuclear product of bismuth(III) hydrolysis.[2] We now wish to report on a similar study of the hydrolytic polymers of lead(II).

Lead(II) is isoelectronic with bismuth(III), and they share the convenient characteristic that their hydrolysis leads predominantly to the formation of a single polynuclear complex which is highly soluble in water. Whereas, however, for bismuth(III) the main product is

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(2) V. A. Maroni and T. G. Spiro, *J. Am. Chem. Soc.*, **88**, 1410 (1966).