reduced molecular symmetry tends to mix the v and w orbitals with the e, f, and g orbitals.

Thus, the estimation of several excited state pK's for each compound considered seems established, and may provide an additional tool useful in band assignment.

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                RECEIVED MAY 11, 1964

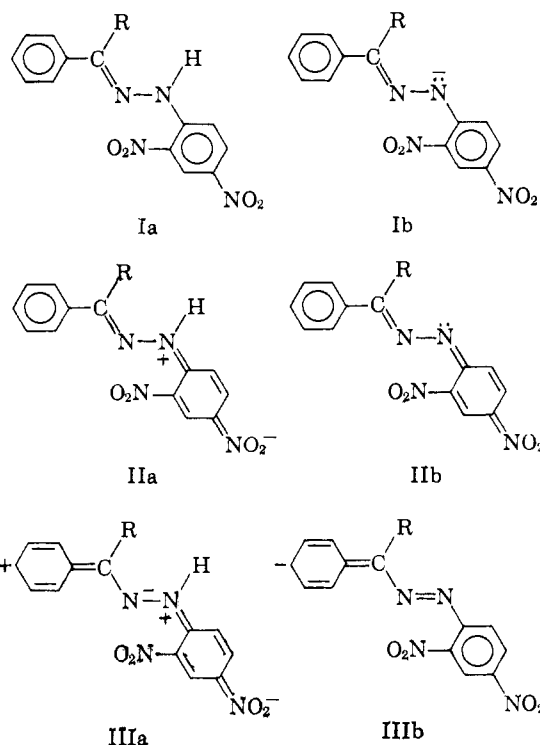## Excited State pK's. II. $\Delta\nu$–σ Relations[1]

Sir:

C. K. Hancock and his students[2] have observed that $\Delta\nu$, the difference between absorption frequency of free acid and conjugate base, can be correlated with Hammett substituent constants (σ) in some favorable cases. Examples were the 2,4-dinitrophenylhydrazones of a series of substituted benzaldehydes and acetophenones and 4-substituted 2-nitrophenols. No adequate explanation for this observation has been advanced.

According to the Förster cycle,[3] this $\Delta\nu$ represents the difference, $\Delta pK = pK^* - pK$, between the pK of the ground state and the pK^* of the excited singlet reached by the absorption process. It then appears that this ΔpK correlates with substituent constants. Since it has been shown in all of the above cases that the ground state pK's correlate with the *same* substituent constants, it follows that the same is true for the pK^*'s. This is the first instance of such a correlation to have been encountered.

In the 2,4-dinitrophenylhydrazones[2a,c] of the benzaldehydes and acetophenones, the pK^*'s are highly satisfactorily correlated with σ's, correlation coefficients running in the order of 0.98. One possible explanation for this behavior might be that the substituted ring is not strongly involved in the chromophore and the acidic center. This explanation appears highly improbable when one examines either resonance structures or the ρ-value (ρ^*) for the pK^*'s. Conversion of the $\Delta\nu$'s into pK units leads to a value of ρ^* of 4.00 for the aldehyde and of 4.88 for the ketone series, some ten times larger than in the ground state. This implies a very strong interaction between substituent and acidic center.

Maybe the situation is best interpreted in terms of the following resonance structures (Ia–IIIb). IIIa must be important in the excited state of the free acid since the p-amino group produces a *strong* bathochromic shift, the p-nitro group a much lesser one. On the other hand, IIIb is important in the conjugate base since here the p-nitro group produces the strong bathochromic shift, the p-amino group a much lesser one. No reasonable structure analogous to IIIa can be written in the base, nor one analogous to IIIb in the acid. Structure IIIa, however, apparently makes practically no contribution to the ground state of the acid, since the ground state pK does not require

(1) Part I: *J. Am. Chem. Soc.*, **86**, 2982 (1964).

(2) (a) L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960); (b) M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Am. Chem. Soc.*, **83**, 3489 (1961); (c) L. A. Jones and N. L. Mueller, *J. Org. Chem.*, **27**, 2356 (1962).

(3) T. Förster, *Z. Elektrochem.*, **54**, 42 (1950).

σ^+-values, for p-alkoxy and p-amino groups. Since a σ^--value is needed for the p-nitro group one must conclude that IIIb is involved importantly in the ground state of the conjugate base. All these relations are consistent with the intuitive energy orders Ia < IIa < IIIa and Ib < IIb $\approx$ IIIb.

In series of 4-substituted phenols,[4] 2,6-di-t-butylphenols,[4] and 2-nitrophenols,[2b] the $\Delta\nu$'s for the ^1L_a band are not too well correlated with σ's, but the pK^* values for the ^1L_a state calculated by use of the Förster cycle correlate reasonably well; ρ^*-values of -4.97, -8.36, and -2.62, larger than the ground state ρ's by about a factor of two and with r values of 0.94, 0.97, and 0.99, respectively, are obtained. These correlations required the use of σ^+ and σ^- constants for mesomerically electron-donating and -withdrawing substituents, respectively, presumably because of the high polarity of the ^1L_a state of the phenols. Use of the data from the same work[4] for the ^1L_b band yields quite small $\Delta\nu$, and consequently a ρ-value not very different from that of the ground state. Bartok, *et al.*,[5] using absorption and fluorescence data obtained widely differing results for three of the same phenols in the ^1L_b state.

Spectra and pK's of azo- and azoxybenzene derivatives have been extensively investigated in this laboratory.[6a–c] A fair pK^*–(σ^+, σ^-) correlation is observed for the monosubstituted azobenzenes.[6a] In the p-N,N-dimethylaminoazobenzene[6b] series, reasonable correlations between pK_1^* and pK_2^* are found while pK_3^* and pK_4^* are substantially insensitive.[7] For the azoxy-

(4) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963); L. A. Cohen and W. M. Jones, *ibid.*, **85**, 3402 (1963).

(5) W. Bartok, P. J. Lucchesi, and N. S. Snider, *ibid.*, **84**, 1842 (1962), have obtained data which are not in agreement with this finding; repetition of their experiments (W. Bartok, private communication), however, has brought their results in line with the above statement.

(6) (a) H. H. Jaffé and R. W. Gardner, *ibid.*, **80**, 319 (1958); (b) M. Isaks and H. H. Jaffé, *ibid.*, **86**, 2209 (1964); (c) C.-S. Hahn and H. H. Jaffé, *ibid.*, **84**, 949 (1962).

(7) The labeling pK_1, pK_2... etc. follows the diagram of S. J. Yeh and H. H. Jaffé, *ibid.*, **81**, 3283 (1959).

benzenes no satisfactory $pK^*-\sigma$ correlation was found.[6c]

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Equilibration of 4-Substituted Thiane 1-Oxides[1]

Sir:

There is much current interest in stereochemical aspects of sulfoxides. We have previously reported on a stereoselective method of inversion of configuration of sulfoxides.[2] Subsequently, Mislow and co-workers[3] have described the hydrogen chloride catalyzed racemization of sulfoxides and Henbest and Khan,[4] the thermal isomerization of sulfoxides.

For 4-*t*-butylthiane 1-oxides (1) thermally-induced equilibrium (190° in decalin) was reported to exist at a *cis*:*trans* ratio of 20:80, although no arguments were presented for the assigned configurations.[4] We have also prepared these sulfoxides[5] and our results indicate that the previous stereochemical assignments are in error. This work further demonstrates that in 4-substituted thiane 1-oxides *the isomer bearing the axial oxygen is more stable.*

The geometries of the 4-*t*-butylthiane 1-oxides were ascertained by physical and chemical analogies with the corresponding 4-*p*-chlorophenylthiane 1-oxides (2) of known configuration.[2a] Periodate oxidation of sulfide 5 provides a 70:30 mixture of 2a:2b, whereas peroxide oxidants yield approximately 30:70 mixtures.[2a] By analogy, the *cis* configuration (1a) is assigned to the predominant product (75%) obtained by periodate oxidation of 4 and *trans* (1b) to the isomer predominating in peroxide oxidations.[6] In each case, the compound of *cis* assignment is found to predominate under equilibrating conditions (see below). This chemical evidence is corroborated by a correspondence in physical behavior of compounds of like assignment. In each case the compound assigned the *cis* structure had the

R = (CH₃)₃C   1a   1b   4
R = *p*-ClC₆H₄   2a   2b   5
R = CH₃   3a   3b   6
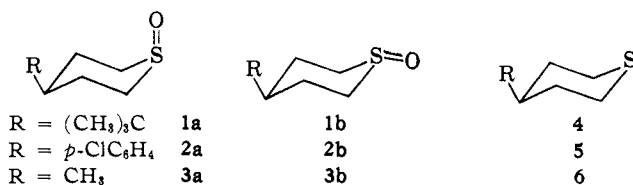
higher melting point (1a, m.p. 70-71°, lit.[4] 49-50°; 1b, m.p. 57-59°, lit.[4] 68-70°; 2a, m.p. 172.5-173°; 2b, m.p. 120-120.5°); the *cis* compounds are eluted prior to the *trans* isomers in both column and gas

(1) We gratefully acknowledge support by the National Science Foundation (Grant No. GP-1159).
(2) (a) C. R. Johnson, *J. Am. Chem. Soc.*, **85**, 1020 (1963); (b) C. R. Johnson and J. B. Sapp, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 23Q.
(3) K. Mislow, T. Simmons, J. T. Mellillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964). We are grateful to Professor Mislow for providing us with details of this method prior to publication.
(4) H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1964).
(5) Satisfactory analyses have been obtained on compounds herein reported.
(6) A detailed study of the stereochemistry of oxidation at sulfur will be published: C. R. Johnson and D. McCants, Jr. in preparation.

chromatography[7]; there is a striking similarity in the sulfoxide stretching region (1000 to 1100 cm.⁻¹) of the infrared spectra for the compounds of like assignment.

Thermal equilibrations were run in purified decalin at 190° employing a quartz flask and nitrogen atmosphere. Mixtures of the 4-*t*-butylthiane 1-oxides (*cis*:*trans*, 75:25 and 25:75) rapidly provided an equilibrium composition of 80% *cis* and 20% *trans*. With pure samples of 1a and 1b, approach to equilibrium is very slow and significant side reactions could not be avoided. Thermal equilibration of 2 was also found to be impractical because of partial decomposition.

Treatment of pure 1a, 1b, or mixtures thereof with hydrochloric acid-dioxane[3,8] for 20 min. is sufficient to provide a *cis*:*trans* equilibrium mixture of 90:10. Similar equilibrium compositions were obtained for compounds 2 and 3 (Table I).

TABLE I

EQUILIBRATION OF 4-SUBSTITUTED THIANE 1-OXIDES

Com-pounds	Method (°C.)	Equilibrium composition *cis*	*trans*	ΔF, kcal./mole
1	HCl (25)	90	10	1.3
2	HCl (25)	80	20	0.8
3	HCl (25)	80	20	0.8
1	Decalin (190)	80	20	1.3
3	Declain (190)	65	35	0.6
1	N₂O₄ (0)	81	19	0.8
3	N₂O₄ (0)	76	24	0.6

We have found that dinitrogen tetroxide, a useful reagent for the conversion of sulfides to sulfoxides,[9] is also capable of isomerization of sulfoxides. Treatment of sulfide 4 and sulfoxide 1a or 1b yields a mixture composed of 81% 1a and 19% 1b. Optically active (+)-benzyl *p*-tolyl sulfoxide is rapidly racemized by this reagent.

As can be seen from the data in Table I, there is considerable variation in the equilibrium composition dependent upon conditions and the identity of the 4-substituent; however, there is always a marked preference for the isomer with the axial oxygen. The best value for the conformation free-energy difference for the sulfoxide within the six-membered ring is probably that (1.3 kcal./mole) obtained with the very bulky and nonpolar 4-*t*-butyl group from both thermal and hydrogen chloride catalyzed equilibrations. In the dinitrogen tetroxide reaction, free sulfoxides are probably not involved in the equilibration observed.[9]

The question remains open as to why an axial oxide on sulfur in thianes is energetically favored over the equatorial configuration. One explanation is that this preference simply reflects the relative steric requirements of oxygen *vs.* the free electron pair. If this were true, it would be unlikely that the electron pair of sulfoxides is located in a 3s orbital as has been proposed.[10] On the other hand, the lone pair could reasonably be

(7) Gas chromatography employing a 6-ft. silicone gum nitrile (GE XE-60) column provided excellent resolution of the sulfide the two sulfoxides, and the sulfone.
(8) Use of anhydrous hydrogen chloride in benzene (ref. 3) was found to result in a mixture of sulfide, α-chlorosulfide, and sulfoxides.
(9) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 2705 (1956); L. Horner and F. Hubenett, *Ann.*, **579**, 193 (1953).
(10) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962.