Tetrahedron Letters Vol. 22, pp 909 - 912
©Pergamon Press Ltd. 1981. Printed in Great Britain

0040-4039/81/0301-0909$02.00/0

THE TWO-PARAMETER LINEAR FREE ENERGY TREATMENT OF THE SUBSTITUENT EFFECTS ON THE HALF-WAVE REDUCTION POTENTIALS AND n,π* TRIPLET ENERGIES OF AROMATIC KETONES. A TEST OF THE VALIDITY OF THE APPROACH.

William J. Leigh, Donald R. Arnold,* and Kim M. Baines
Department of Chemistry
Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

The half-wave reduction potentials of fluoro- and thiomethyl-substituted benzophenones and the n,π* triplet energies of the fluoro-substituted derivatives are found to agree quite closely with values predicted using empirical relations comprised of Hammett σ values and σ· values; the lowest triplet states of the thiomethyl-substituted derivatives are shown to be π,π*.

In the course of our investigation of the effect of merostabilization on the half-wave reduction potential ($E_{1/2}^{red}$) and n,π* triplet energy (E_T) of benzophenone, it was necessary to evaluate the nature of the "normal" substituent effect (i.e. in the absence of merostabilization) on these quantities.[1] For symmetrically disubstituted (i.e. 4,4'-X_2 and 3,3'-X_2) benzophenones, E_T and $E_{1/2}^{red}$ were found to correlate with two-parameter relations comprised of Hammett σ values and a set of parameters (σ·) reflecting substituent effects on benzylic radical stabilities (equations (1) and (2), respectively).

$$(1) \quad E_T(\text{kcal mol}^{-1}) = 69.7 - (1.3\Sigma\sigma + 2.2\Sigma\sigma\cdot)$$

$$(2) \quad E_{1/2}^{red}(\text{eV}) = 2.21 - (8.4\Sigma\sigma + 2.0\Sigma\sigma\cdot)/23.03$$

The relative contributions from polar and radical-stabilizing factors to the substituent effects on E_T and $E_{1/2}^{red}$ can be inferred from the coefficients in equations (1) and (2). It is particularly significant that radical-stabilizing factors contribute about equally to the substituent effects on E_T and $E_{1/2}^{red}$. This is presumably due to the fact that the π*-orbital is singly-occupied in both species; the diphenylmethyl radical has been used as the model for this orbital in benzophenone.[2] Support for the validity of the model is provided by the similarities in the spin densities at the ring carbons in the radical anion[3] and the diphenylmethyl radical[4] as measured by esr spectroscopy. Recent results for the benzophenone n,π* triplet[5] are also suggestive.

Since this sort of treatment of the substituent effects on E_T and $E_{1/2}^{red}$ for aromatic ketones is, as far as we know, unprecedented, we felt it desirable to test the validity of our approach by using (1) and (2) to predict E_T and $E_{1/2}^{red}$ for a few substituted benzophenones and comparing our predictions to experimentally determined values. We therefore chose four benzophenones (1a-d) bearing substituents whose σ and $\sigma\cdot$ values are unique. Fluorine (1a,b) was chosen since it appears to be the only substituent which destabilizes a benzylic radical in the *para*-position[6] ($\sigma\cdot = -.08$), while being mildly electron-withdrawing in the polar sense ($\sigma = .06$). Thiomethyl (1c,d)[7] on the other hand, is a strong radical-stabilizing group[6] ($\sigma\cdot = .43$), while being electronically neutral ($\sigma = 0$). We assume merostabilization to be relatively unimportant in these monosubstituted derivatives.

Half-wave reduction potentials of 1a-d were measured in acetonitrile solution by cyclic voltammetry, while the triplet energies were calculated from the positions of the short wavelength 0-0 band maxima in the phosphorescence emission spectra in EPA[9] at 77K. These results are collected in Table 1, along with the values of E_T and $E_{1/2}^{red}$ predicted using equations (1) and (2).

Table 1. Predicted and observed[a] half-wave reduction potentials ($E_{1/2}^{red}$, eV) and triplet energies (E_T, kcal mol^{-1}) of substituted benzophenones 1a-d.

1[b]	X,Y	$-E_{1/2}^{red}$ (pred)[c]	$-E_{1/2}^{red}$ (expt)[d]	E_T (pred)[e]	E_T (expt)[f]
a	H,F	2.19	2.20	69.8	69.8
b	F,F	2.18	2.19	69.9	70.3
c	H,SCH_3	2.17	2.18	68.7	64.0
d	SCH_3,SCH_3	2.14	2.16	67.8	63.9

[a] Experimental procedures have been reported previously.[1]

[b] All substituents are in the *para*-positions.

[c] Calculated according to equation (2).

[d] In 0.1M TEAP/CH_3CN; vs. Ag/0.1M $AgNO_3$/0.1M TEAP, 25°C; ±0.02

[e] Calculated according to equation (1).

[f] From the 0-0 band maxima in the phosphorescence emission spectra (EPA, 77K); ±0.2.

Excellent agreement between the predicted and experimental values of the half-wave reduction potentials of 1a-d is observed in all cases. The predictive value of equation (2) is most apparent for 1c and 1d, since in these cases consideration of polar factors (i.e. σ values) alone would have lead to the prediction that $E_{1/2}^{red}$ for these compounds should be the same as that for benzophenone itself (2.21 eV).

Good agreement is also observed between the predicted and experimental n,π* triplet energies of 1a and 1b. The triplet energies of the thiomethyl derivatives 1c and 1d however, are significantly less than those predicted by equation (1). This is due to the lowest triplet states of these derivatives being π,π* in nature; we have several pieces of evidence in support of this conclusion.

(i) The long wavelength n,π* transition which is visible in the absorption of 1c,d in hydrocarbon solvents is masked by an intense CT-π,π* absorption[10] in alcohol solution. The solvent shift (hexane/ethanol) of this intense band is ca. 2100 cm^{-1}.

(ii) The vibronic band separation ($\Delta\bar{\nu}_{0-1}$) in the phosphorescence emission spectrum of an n,π* triplet ketone corresponds closely to the carbonyl stretching frequency in the ir spectrum of the compound, while in π,π* triplets, $\Delta\bar{\nu}_{0-1}$ is considerably less than this.[11] For 1c and 1d, $\Delta\bar{\nu}_{0-1}$ = 1490 and 1350 cm^{-1} respectively; this can be compared to the spacings in the emission spectra of 4-dimethylaminobenzophenone (1350 cm^{-1}) and Michler's ketone (1240 cm^{-1}), both of which are known to have CT-π,π* lowest triplet states[11].

(iii) The phosphorescent lifetimes of 1c,d (47 and 31 msec)[12] are characteristic of π,π* triplet states[10] (compare these to 170 and 90 msec for 4-dimethylaminobenzophenone and Michler's ketone)[12].

The characterization of the lowest triplet states of 1c and 1d as π,π* completes our understanding of the effect of electron-donating substituents (CH_3, OCH_3, SCH_3, $N(CH_3)_2$) on the ordering of the n,π* and π,π* triplet states in aromatic ketones. In benzophenone, inversion occurs with thiomethyl substitution. On the other hand, in phenyl alkyl ketones, in which the n,π* and π,π* triplet states lie closer in energy in the parent compound, inversion occurs with methyl substitution.[13]

The two-parameter approach provides a much clearer understanding of the effects of substituents on the n,π* triplet energy and half-wave reduction potential of benzophenone. The predictive value of the approach is succinctly demonstrated by the good agreement observed between calculated and experimental values of E_T and $E_{1/2}^{red}$ for these derivatives.

Acknowledgement This work was supported by a grant from the Natural Sciences and Engineering Research Council (Canada). KMB wishes to thank the Atlantic Provinces Inter-University Committee on the Sciences (APICS) for financial support.

REFERENCES AND NOTES

1. W. J. Leigh, D. R. Arnold, R. W. R. Humphreys, and P. C. Wong, Can. J. Chem., 58, 2537 (1980).
2. A. Streitwieser, Jr., Molecular orbital theory for organic chemists. J. Wiley and Sons, Inc., New York, 1962, Chapter 7.
3. H. R. Falle and F. C. Adam, Can. J. Chem., 44, 1387 (1966).
4. A. R. Bassindale, A. J. Bowles, A. Hudson, R. A. Jackson, K. Schreiner, and A. Berndt, Tetrahedron Letters, 3185 (1973).
5. J. A. Mucha and D. W. Pratt, Chem. Phys. Lett., 37, 40 (1976).
6. a) X. Creary, J. Org. Chem., 45, 280 (1980).
   b) J. W. Timberlake, A. W. Garner, and M. L. Hodges, Tetrahedron Lett., 309 (1973).
7. 1c and 1d were synthesized by Friedel-Crafts acylation of benzene and thioanisole with 4-(thiomethyl)benzoyl chloride. 1c: mp = 76-77.5°C[8]. 1d: mp = 125-126°C[8].
8. A. Schomberg, R. Abelsdorff, H. Kirchrath, W. Malchow, and A. Rosenbach, Annalen, 436, 205 (1924).
9. ether:isopentane:alcohol (5:5:2).
10. G. Porter and P. Suppan, Pure Appl. Chem., 9, 499 (1964).
11. R. N. Griffin, Photochem. Photobiol., 7, 159 (1968).
12. Phosphorescent lifetimes were determined from the rates of phosphorescence decay in degassed EPA at 77K.
13. P. J. Wagner, A. E. Kemppainen, and H. N. Schott, J. Am. Chem. Soc., 95, 5604 (1973).

(Received in USA 15 September 1981)