change to contribute to the line width. Moreover, the line width remains constant over a tenfold range in concentration.

A characteristic of the additional spin-orbit relaxation mechanisms proposed[9,10,11] is that the line width is independent of frequency. To check this point, line widths of *t*-butylperoxy radical in 20% hydroperoxide in pentane were determined by Dr. W. C. Landgraf of Varian Associates at 35 Gc. At 25 and −35°, line widths of 27.8 and 16.0 gauss, respectively, were obtained. At X-band, in our laboratory, the same sample gave 29.0 and 18.9 gauss, respectively.[21] All measurements have about a ±0.7 gauss reliability. Consequently, it seems most plausible to attribute the dominant spin relaxation process in *t*-butylperoxy radicals to the spin-orbit processes of ref 9-11.

The exact nature of the most important spin-orbit mechanism is still a question under investigation. Most recently Atkins and Kivelson have concluded[11] that a spin-rotation interaction, involving the spin and the magnetic field created by rotation of the radical (coupled by an interaction tensor proportional to the square of the *g* value variance from that of the free electron), is more important in most cases than the rotational spin-orbit mechanism of ref 9 which requires a combined spin and orbital electronic transition. When dominated by rotational motions of the radical, the line width is expected[11] to be proportional to $(g - 2.0023)^2T/a^3\eta$ where a is the diameter of the radical, η the viscosity, and T the absolute temperature. Qualitatively the effects of temperature and viscosity shown in Figures 1 and 2 upon the line width as well as the influence of radical size shown in Figure 1 at 25° (*t*-butyl > cumyl > methyldiphenylmethyl)[22] are consistent with this expectation.

The vibrational spin-orbit process introduced by Lloyd and Pake[3,10] affords a possible mechanism to explain the drop of line width from its viscosity-limited value of 14 gauss at 25° to its low temperature limited value of 3 gauss in Figure 1. However, Atkins and Kivelson[11] conclude that this mechanism suffers the same restriction which limits the rotational spin-orbit mechanism and that it will, in general, be unimportant. In this event the discrepancy might possibly be accounted for by an effective increase in the size of the radical *via* hydrogen-bonding solvation with hydroperoxide at low temperatures.

Acknowledgment. The author is grateful to Dr. W. C. Landgraf, Varian Associates, for the 35-Gc measurements; to Dr. J. Q. Adams for helpful discussion; and to Professor D. Kivelson for his conclusions prior to publication as well as helpful correspondence.

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(21) Radical concentrations were not determined in these two sets of experiments. The radically different experimental equipment used, including method and intensity of irradiation, further dispels concern that the measured line widths are a function of radical concentration.

(22) Cumylperoxy was prepared in the same solvent as *t*-butylperoxy. Methyldiphenylmethylperoxy was prepared by oxidation of the hydroperoxide in methanol with Ce^{4+}; *g* values were the same as for *t*-butyl to within ±0.0001 for cumyl and ±0.001 for methyldiphenylmethyl.

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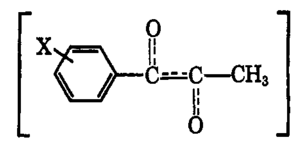
Electron Spin Resonance Studies of Substituent Effects. Correlations with σ Constants

Sir:

Much data have been obtained in recent years concerning substituent effects on hyperfine splitting constants (hfsc) in radical ion series. Correlations of nitrogen hfsc with Hammett σ constants have been sought for the nitrobenzene anion radicals[1] and the phenyl *t*-butyl nitroxides.[2] Even though the σ constant is interpreted as a measure of a substituent effect on electron density at an atom,[3] a correlation with splittings of this type will not be very good because the nitrogen hfsc is a function of the spin density at the attached atoms as well as the spin density on nitrogen.[4]

We present here preliminary results on an anion radical system in which hyperfine splitting constants vary linearly with spin densities, which shows large sensitivity to substituent, and which gives an excellent correlation with σ constants for many substituents. Radical anions of substituted 1-phenyl-1,2-propanediones (I) can be readily formed by base-catalyzed oxidation of the corresponding propiophenones in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%).[5] These radicals have sizable methyl splittings which are readily evaluated. Furthermore, the methyl splitting will be *directly proportional* to the spin density at the attached carbon atom.[6] Table I shows results for a variety of derivatives,[7] together with σ constants taken from the compilation of McDaniel and Brown.[8]



I

Four substituents, *p*-CF$_3$, *p*-Ph, *p*-F, and *p*-N(CH$_3$)$_2$, are anomalous in that the methyl splittings fall out of the order of the σ constants while the methyl splitting for *p*-CN is obviously far less than would be predicted from its σ constant. For all other substituents, however, the methyl splitting reproduces the vagaries of the σ constants, *i.e.*, the strong electron-supplying effect of *p*-OCH$_3$ compared to the electron-withdrawing effect of *m*-OCH$_3$, the stronger electron-withdrawing effect of *meta* halogens compared to *para* halogens, and the order of electron withdrawal within the series Br, Cl, F.

Figure 1 shows a plot of $A^{\mathrm{H}}_{\mathrm{Me}}$ *vs.* σ together with the least-squares line. The correlation coefficient for the 16 "well-behaved" points is 0.995. The correlation

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(1) P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, 1136 (1964).

(2) H. Lemaire, Y. Marechal, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. France*, 372 (1965).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp 186-194.

(4) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961); P. H. Rieger and G. K. Fraenkel, *ibid.*, **39**, 609 (1963). For arguments that in nitroxides the nitrogen hfsc is a function only of the nitrogen spin density, see H. Lemaire and A. Rassat, *J. Chim. Phys.*, **61**, 1580 (1964), and G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. France*, 1975 (1965).

(5) G. A. Russell and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 744 (1964).

(6) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958), H. Fischer, *Z. Naturforsch.*, **20a**, 428 (1965).

(7) Spectra for the important *m*- and *p*-nitro derivatives could not be obtained by this method because of complications involving electron transfer to un-ionized nitro compound (G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962)).

(8) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

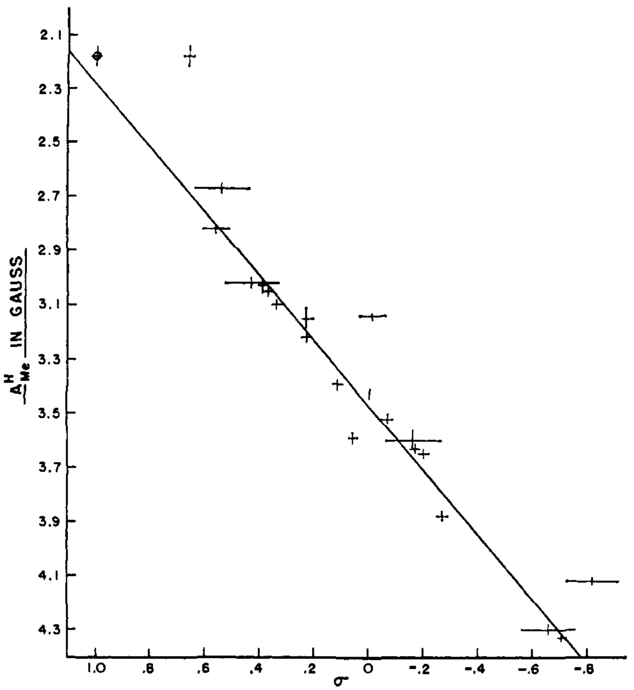

Figure 1. Plot of methyl hfsc *vs.* σ. Ordinate: methyl hfsc, uncertainties are average deviations; abscissa: σ, uncertainties are estimates of McDaniel and Brown (uncertainties of $\sigma_m^-{}_{-O}$ and $\sigma^-{}_{p-CN}$ are arbitrary). Circle indicates $\sigma^-{}_{p-CN}$ point.

coefficient between σ and nitrogen hfsc for those substituents in common, omitting anomalous substituents, is 0.942 (seven values) for nitrobenzene anion radicals in aqueous acetone[1] and 0.778 (six values) for phenyl *t*-butyl nitroxides in $(CH_2OH)_2$.[2] The methyl hfsc also show far greater variation with substituent than do the nitrogen hfsc. The ρ values for methyl splittings, nitrogen splittings in nitrobenzene radicals,[1] and nitrogen splittings in nitroxides[2] are −0.84, −0.30,[9a] and −0.39,[9b] respectively.

Table I. Methyl Hfsc for Substituted 1-Phenyl-1,2-propanesemidiones

Substituent	A^H_{Me}	σ
p-CN	2.18	0.66 ($\sigma -$ = 1.00[a])
p-CF_3	2.67	0.54
m-CN	2.82	0.56
m-CF_3	3.02	0.43
m-Br	3.03	0.391
m-Cl	3.05	0.373
m-F	3.10	0.337
p-Ph	3.14	−0.01
p-Br	3.15	0.232
p-Cl	3.22	0.227
m-OCH_3	3.39	0.115
p-H	3.43	0.000
m-CH_3	3.52	−0.069
p-F	3.59	0.062
m-NH_2	3.60	−0.16
p-CH_3	3.63	−0.170
p-$C(CH_3)_3$	3.65	−0.197
p-OCH_3	3.88	−0.268
p-$N(CH_3)_2$	4.12	−0.83
p-NH_2	4.30	−0.66
m-O^-	4.33	−0.708[a]

[a] Taken from H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

The excellent correlation with σ for the "well-behaved" substituents may in part be due to the fact that σ constants derived from ionization constants of benzoic acids measure a substituent effect on electron density at an atom β to the benzene ring as do the methyl hfsc. The deviations of *p*-F, *p*-Ph, *p*-CF_3, and *p*-CN may indicate that these substituents have different effects on unpaired and paired electron density.[10] The *p*-F group is also anomalous in promoting the rearrangement of 2-methyl-2-phenyl-1-propyl radicals.[11] The normal behavior of *m*-F indicates the anomaly stems from resonance interactions involving the p electrons. Unpublished work of Janzen demonstrates that hfsc within a series better correlate for −R groups with σ^- than σ.[12] The plot shows, accordingly, that the σ^- point for *p*-CN is quite close to the least-squares line.

The deviation of *p*-$N(CH_3)_2$ possibly stems from experimental uncertainty in the σ constant, due to the difficulty in correcting for zwitterion. The value for this substituent taken from Jaffé's compilation,[13] −0.600, fits reasonably well with the other data.

Other radicals which should give good correlations with σ are substituted monaryl nitroxides (the -NH splitting) and radical anions of substituted acetophenones, benzaldehydes, and phenylglyoxals (the -CH and $-CCH_3$ splittings). Additional data may reveal the necessity of a new set of σ constants, $\sigma^{-}\cdot$, necessary to correlate one electron delocalization. Work is in progress in this area.[13a]

Acknowledgment. The author is very grateful to Mr. R. Petkun for synthesis of many of the starting materials and to Drs. J. Weinstein and E. G. Janzen for helpful discussions.

(9) Calculated omitting anomalous substituents: (a) 17 values; (b) 13 values. The Figure 1 *x*-axis direction is opposite to that used in the calculation.

(10) See A. Streitwieser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1964); B. D. Gilliom and B. E. Wood, *ibid.*, **87**, 3944 (1965).

(11) C. Ruchardt and S. Eichler, *Ber.*, **95**, 1921 (1962).

(12) Private communication from E. G. Janzen.

(13) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(13a) NOTE ADDED IN PROOF. The substituent parameter for *p*-CF_3 measured from the ionization of anilinium ions, 0.65 (W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965)), puts this group on the correlation line. This could be interpreted as additional evidence for fluorine 1,3 p–π conjugation.

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A Photochemical 1,3 Cycloaddition of Olefins to Benzene[1]

Sir:

We wish to report a photochemical cycloaddition of olefins to benzene different from that recently reported[2] by Srinivasan and Hill for cyclobutene. We find that the adducts from *cis*-but-2-ene (Ib), cyclopentene (Ic), and 2,3-dimethylbut-2-ene (Id) are substituted tricyclo[5.1.0.$0^{4,8}$]oct-2-enes (I). They correspond to addition of an olefin across a cyclopropyl ring of benzvalene (II).

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. Srinivasan and K. A. Hill, *J. Am. Chem. Soc.*, **87**, 4653 (1965).