

fact that sulfides form adducts with  $^1\text{O}_2$ ,<sup>10</sup> but further work will be required to establish this.

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## A Linear Free Energy-Enthalpy-Entropy Relationship for the Ionization of Benzoic Acids

Sir:

It can be shown<sup>1</sup> that a linear relationship between the free energies of two reaction series can be expected only if each reaction series shows one of the following types of behavior: (a)  $\Delta H^\circ$  is constant throughout the series, (b)  $\Delta S^\circ$  is constant, or (c)  $\Delta H^\circ$  is linearly related to  $\Delta S^\circ$ . Of the many linear free-energy relationships now known, the Hammett equation is undoubtedly the most widely used, yet, as many reviewers have noted (e.g., ref 1-3), its defining reaction series, the ionization of benzoic acids, does not appear to belong to any one of these categories. This, as Shorter<sup>2</sup> has commented, makes the empirical success of the Hammett equation something of a mystery and it also, to some extent, reduces our confidence in the use of enthalpies and entropies as quantitative indexes of substituent effects on chemical reactivity.

Recently Larson and Hepler<sup>4</sup> have drawn attention to large discrepancies existing between sets of measurements of enthalpies of ionization of benzoic acids and also to the antiquity of some of the most frequently quoted measurements.

combine to make accurate calorimetric measurements difficult. Furthermore, the very small  $\Delta H^\circ_{25}$  value means that the  $pK_a$  values show very little variation with temperature, making van't Hoff-type determinations of  $\Delta H^\circ_{25}$  also subject to large errors unless unusual precautions are taken.

After a thorough appraisal of the factors most likely to reduce accuracy in these systems we have now re-determined the enthalpies and entropies of ionization in water of benzoic acid and 11 meta- and para-substituted benzoic acids. For ten of these compounds we used an emf-spectrophotometric technique which has been shown to give reliable results for the heats and entropies of proton ionization of phenols<sup>5</sup> and anilinium ions<sup>6</sup> and for which good agreement has been observed between the results obtained and calorimetrically determined data. This method has the advantage that for acids of the benzoic acid charge type no extrapolation to zero ionic strength is required, thus removing one major source of uncertainty in the final results. For the two nitro-substituted acids we used a variation of an indicator spectrophotometric method described by Robinson and Bower.<sup>7</sup> This method required an extrapolation to zero ionic strength but this was carried out on a computer to minimize subjective influences on the final results, and the method was found to be highly reproducible. All of the acids were measured in several solutions of differing ionic strength and, wherever experimentally feasible, in more than one type of buffer solution.

In making these measurements great attention was paid to the accuracy and control of temperature and as wide a range of temperature as was experimentally possible (5-60°) was used. With such small variation in  $pK_a$  with temperature, different mathematical methods of determining  $\Delta H^\circ/\Delta S^\circ$  from the  $pK_a$ -temper-

Table I. Thermodynamic Functions of Ionization of Benzoic Acids in Water at 25°

Acid	$\Delta G^\circ_{25}$ , cal mol <sup>-1</sup>	$\Delta H^\circ_{25}$ , cal mol <sup>-1</sup>	$\Delta S^\circ_{25}$ , cal deg <sup>-1</sup> mol <sup>-1</sup>	$\Delta C_p^\circ_{25}$ , cal deg <sup>-1</sup> mol <sup>-1</sup>
Benzoic	5732 (±2) <sup>a</sup>	-67 (±19)	-19.44 (±0.04)	-42 (±3)
m-Methoxybenzoic	5583 (±1)	22 (±12)	-18.65 (±0.04)	-23 (±2)
m-Toluic	5800 (±1)	-91 (±13)	-19.75 (±0.05)	-34 (±2)
m-Chlorobenzoic	5234 (±1)	178 (±17)	-16.95 (±0.06)	-38 (±3)
m-Bromobenzoic	5198 (±1)	197 (±17)	-16.77 (±0.06)	-45 (±3)
m-Nitrobenzoic	4720 (±2)	421 (±25)	-14.41 (±0.08)	-41 (±4)
p-Methoxybenzoic	6130 (±2)	258 (±26)	-19.69 (±0.09)	-45 (±4)
p-Toluic	5962 (±1)	-134 (±9)	-20.44 (±0.03)	-39 (±1)
p-Chlorobenzoic	5437 (±2)	100 (±26)	-17.90 (±0.09)	-44 (±4)
p-Bromobenzoic	5403 (±1)	107 (±28)	-17.76 (±0.09)	-35 (±2)
p-Iodobenzoic	5450 (±1)	78 (±15)	-18.01 (±0.04)	-32 (±2)
p-Nitrobenzoic	4671 (±1)	432 (±36)	-14.21 (±0.12)	-25 (±2)

<sup>a</sup> The number in parentheses is the standard error of the measurement at the 95% confidence level.

The thermodynamic enthalpies of ionization of meta- and para-substituted benzoic acids are extremely difficult to measure accurately. The acids are usually very insoluble in water, especially at temperatures below ambient, and the value of  $\Delta H^\circ_{25}$  is usually of the order of 100-400 cal mol<sup>-1</sup>. These two factors

ature data can give significantly different results.<sup>8</sup> We have used the full-multiple regression procedure of Clarke and Glew.<sup>9</sup>

Table I lists the values of the measured thermodynamic functions and their standard errors calculated

(5) P. D. Bolton, J. Ellis, and F. M. Hall, *J. Chem. Soc. B*, 1252 (1970), and references contained therein.

(6) P. D. Bolton and F. M. Hall, *ibid.*, 1247 (1970), and references contained therein.

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(2) J. Shorter, *Chem. Brit.*, **5**, 269 (1969).

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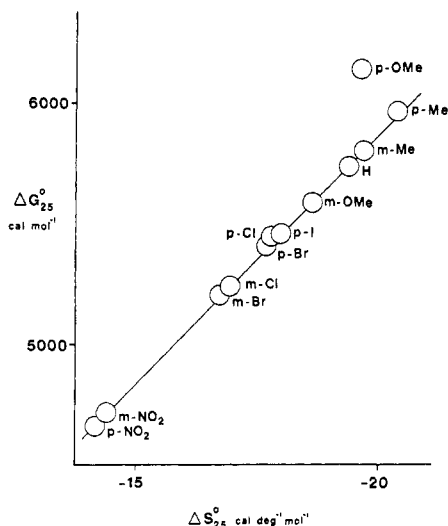


Figure 1. Linear relationship between the standard free energies and entropies of ionization of meta- and para-substituted benzoic acids.

at the 95% confidence level by the method of Clarke and Glew.<sup>9</sup> It should perhaps be emphasized that these are estimates of the precision of the results and they should not be interpreted as measures of the absolute error.

The consistently high precision of these results leads us to believe that they are the best set of data now available for the assessment of substituent effects on the ionization of benzoic acids. Certainly they appear to be free of most of the inconsistencies of the older data which were drawn from different sources of widely varying precision. As Figure 1 shows, providing the *p*-methoxy substituent is omitted from the correlation, a plot of the free energies of ionization against the corresponding entropy values is highly linear ( $r = 0.9999$ ). Similar linearity, again with the *p*-methoxy substituent deviating significantly, is found for plots of  $\Delta H^\circ$  against  $\Delta S^\circ$  ( $r = 0.9992$ ) and for  $\Delta G^\circ$  against  $\Delta H^\circ$  ( $r = 0.9984$ ). Thus the ionization of benzoic acids can now be placed in category c above. It is also interesting to note that the least-squares slope of the plot of  $\Delta G^\circ$  against  $\Delta S^\circ$  is  $-205^\circ\text{K}$ , which is very close to the value of  $-218^\circ\text{K}$  predicted by classic electrostatic theory.<sup>10</sup>

It is possible that the deviation of the *p*-methoxy substituent has its origin in the cross-conjugation effects<sup>11</sup> arising when the +M *p*-methoxy substituent is located para to the carboxyl reaction center.

**Acknowledgment.** We thank the Australian Research Grants Committee for financial support.

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## Pyridinyl Hetero Diradicals. Intramolecular Interaction between Two Different Pyridinyl Radicals

Sir:

Pyridinyl diradicals<sup>1</sup> associate intramolecularly to form molecular complexes which are regarded as rad-

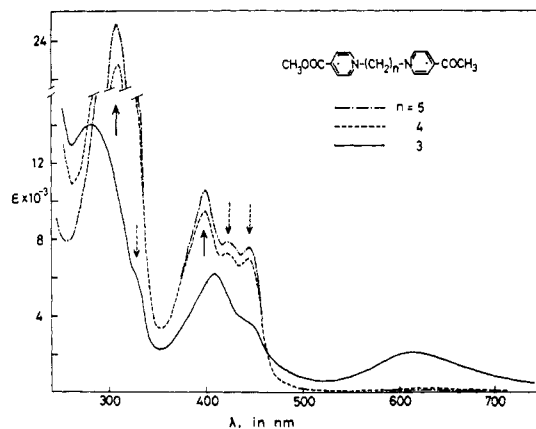
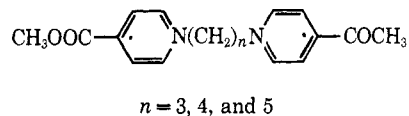


Figure 1. The absorption spectra of the hetero diradicals **3**, **4**, and **5** in MTHF at room temperature ( $27-28^\circ$ ): --- and - - - show absorption bands due to 4-carbomethoxy- and 4-acetylpyridinyl moieties, respectively. Concentration of the diradical was determined by electron-transfer reaction to methylviologen (E.M. Kosower and J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964)).

ical dimers.<sup>2</sup> In a previous paper,<sup>3</sup> we reported the intramolecular electronic interaction in the pyridinyl cation radicals in which the pyridinyl radical and pyridinium cation were connected with tri- or tetramethylene groups. The intramolecularly associated cation radicals were considered to be dimer radicals.<sup>4</sup> While numerous studies of the radical dimers and dimer radicals have been carried out, only few spectroscopic studies of the electronic interaction between two kinds of radicals have been reported.<sup>5,6</sup>

We now report a new series of pyridinyl hetero diradicals for which the hetero diradical for  $n = 3$  asso-



ciates intramolecularly to show charge-transfer interaction (closed form<sup>1,3</sup>) between two different pyridinyl moieties. The previous papers demonstrated that the diradicals (homo) and the cation radicals consist of the open and closed forms in equilibrium, respectively. However, no direct observation of the equilibrium was presented. Now the equilibrium of the open and closed forms of the hetero diradical ( $n = 3$ ) has been directly observed by temperature dependence of the absorption spectra.

The pyridinyl hetero diradicals (**3** for  $n = 3$ , **4** for  $n = 4$ , and **5** for  $n = 5$ ) were prepared by reduction of the corresponding diiodides or dibromides in the manner previously described.<sup>1,3</sup> 2-Methyltetrahydrofuran (MTHF) was used as the extractant. The absorption spectra of the MTHF solutions of **3**, **4**, and **5** were determined at room temperature ( $27-28^\circ$ ), as shown in Figure 1. It is noteworthy that the spectrum of **3** shows a new absorption band at 615 nm, while the

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