conversion of the complex to a diamagnetic ground state explaining the absence of detectable epr signals in the EtMgCl-treated solutions.

A conceivable alternative would be that the diamagnetic complex formed in the presence of EtMgCl is the di-$\mu$-nitrido derivative, which then would be protonated to I and II. In this case, however, two different epr signals would be expected in the course of the protonation, which was not observed.

The identification of II as the product of the reaction between the hydride complex III and nitrogen (Scheme I) leaves no reasonable doubt that the reduction of molecular nitrogen $N_2$ has occurred via a double insertion of $N_2$ into the two metal–hydride bonds of III, presumably with a $\pi$-bonded nitrogen complex IV as intermediate. This complex IV is certainly too unstable to be directly detectable. However, such a slight nuclear displacement is necessary only to convert this species to the di-$\mu$-imino complex V that quite small concentrations of IV might be sufficient to allow for the observed smooth reaction.

Though the six reduction equivalents, which are necessary to conduct the reduction of $N_2$ to the ammonia state, require that a titanium(IV) complex of structure V be the product of the insertion reaction proper, the identification of the corresponding titanium(III) compounds I and II in the reaction solution is not in contradiction with this mechanism; V is to be expected to be susceptible, like the corresponding dicyclopentadienyltitanium(IV) chloride, to reduction by the Grignard reagent which is present in excess in the reaction mixture.

The chemistry of this and related reactions will be considered in detail in a subsequent communication.

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# A Linear Enthalpy–Free Energy Correlation as Supporting Evidence for Hammett's Indicator Overlap Method[1,2]

*Sir:*

We wish to report a remarkably good correlation between the heats of protonation of a series of primary amines in concentrated sulfuric acid and the estimated $pK_a$ values of their conjugate acids in water. As shown in Figure 1, this correlation covers a very wide range, nearly 16 $pK$ units and 30 kcal/mole. It is especially significant because many of the amines are weakly basic indicators whose $pK_a$ values in water could only be estimated by a lengthy extrapolation using the Hammett overlap method.[3,4] Since this could easily result in serious cumulative errors,[4] it is important to have an

(1) Paper II in the series Weak Bases in Strong Acids.
(2) Supported by National Institutes of Health Grant G.M. 10872.
(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.
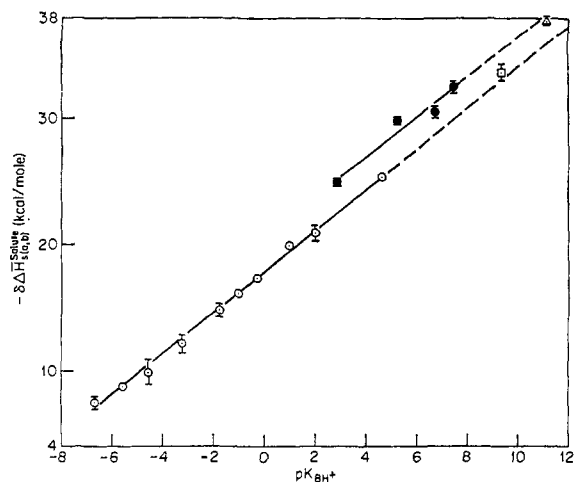(4) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).



Figure 1. Partial molal heats of transfer $\Delta \bar{H}_a$ for amines from *sym*-tetrachloroethane to 96.48% sulfuric acid *vs.* the $pK_a$ value of their conjugate acids in water. The solid points ● refer to pyridines with the following $pK_a$'s: 2,4,6-collidine (7.43), 2,6-lutidine (6.72), pyridine (5.25), 3-bromopyridine (2.84). The open circles ○ refer to primary anilines of the following $pK_a$'s: aniline (4.60), 2,4-dichloroaniline (2.00), *p*-nitroaniline (1.00), *o*-nitroaniline (−0.29), 4-chloro-2-nitroaniline (−1.02), 2,5-dichloro-4-nitroaniline (1.78), 2,6-dichloro-4-nitroaniline (−3.27), 2,4-dinitroaniline (−4.53), 2,6-dinitroaniline (−5.54), 2-bromo-4,6-dinitroaniline (−6.68). □ refers to benzylamine and △ refers to piperidine. The $pK_a$ values used here were taken from M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963), or D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth, Inc., Washington, D. C., 1965.

independent test of the reliability of the overlap method. We believe that the results presented here help to meet this need.

Because of wide differences in basicity, there is no reliable analytical method that will permit measurement of the ionization constants of all of these amines in a single medium. However, their relative heats of ionization are measured easily (as described below) in a single acid solution of sufficient strength. In the present case, the heats of attenuation of the bases from their pure liquid or crystalline standard states to highly dilute ($10^{-3}$ to $10^{-4}$) solution in an inert solvent (*sym*-tetrachloroethane) were used to correct the heats of solution of the amines from the same liquid or crystalline standard states to concentrated sulfuric acid. The $\Delta \bar{H}_a$ values therefore represent standard heats of transfer for the amine from solution in the former solvent to the latter in which it is completely ionized.

The close correlation of heats of ionization in one medium with free energies in another suggests strongly that both properties are proportional to the same energy term, the internal energy of ionization at 25°. Following Hepler,[5] the standard free energy of ionization ($\Delta G_i°$) in a given medium can be considered in terms of internal (int) and external (ext) components, thus

$$\Delta G_i° = \Delta H°_{int} - T\Delta S°_{int} + \Delta H°_{ext} - T\Delta S°_{ext}$$

For a series of closely related compounds in aqueous media, the last two terms tend to compensate each other and the difference in $T\Delta S°_{int}$ is insignificant. Therefore, the structural variation ($\delta_s$) of the measured free energy change corresponds to that of the internal

(5) L. G. Hepler, *J. Am. Chem. Soc.*, **85**, 3089 (1963), and earlier papers cited therein.

energy ($\delta_s\Delta G°_{int} \approx \delta_s\Delta H°_{int} \approx \delta_s\Delta E_{int}$) in conformity with a vast array of free energy–structure correlations in highly aqueous media,[6-8] even for acids[6] and amines[9] in water where the $\Delta H_{ext}$ and $\Delta S_{ext}$ terms are large and erratic.[9,10]

A number of other workers have measured the heats of interaction for several series of amine bases with various strong acids of both the protonic (*e.g.*, methanesulfonic acid in nitrobenzene,[11] trichloroacetic acid in benzene[12]) or Lewis-type[11,13,14] (both in the gas phase and inert media). In the absence of steric hindrance, they have usually found, as we do, a good correlation between the free energy of ionization in water and the heat of acid–base interaction in their chosen medium. Furthermore, each class of amine generates its own correlation line as we find for the pyridines (upper line).

Since their results have all dealt with strong amine bases of well-established $pK_a$ values, they do not anticipate the results presented here (testing the $H_0$ overlap method over a wide basicity range).

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

(7) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 32, 1333 (1936).

(8) R. W. Taft, Seminar, University of California at Irvine, 1966.

(9) A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949).

(10) C. Douty and J. Burke, unpublished work.

(11) H. C. Brown, D. H. McDaniel, and O. Häfliger, "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955, p 640.

(12) T. E. Mead, *J. Phys. Chem.*, 66, 2149 (1962).

(13) L. Sacconi, G. Lombardo, and R. Ciofalo, *J. Am. Chem. Soc.*, 82, 4183, 6266 (1960).

(14) F. G. A. Stone, *Chem. Rev.*, 58, 101 (1958).

Preliminary results of F. Jones in this laboratory indicate that the heat of ionization of di- and triarylcarbinols to carbonium ions in sulfuric acid will correlate with their $pK_R$ values[15] in water.

In recent years, there has been much discussion of extrathermodynamic $\Delta H$–$\Delta S$ correlations.[6,7] We wish to emphasize that whenever a true relationship (not due merely to correlated errors) of this kind is found, it automatically requires that there be correlation of $\Delta G$ and $\Delta H$. These latter two properties can be determined independently and one is often much harder to measure than the other, so that an extensive knowledge of *bona fide* $\Delta G$–$\Delta H$ correlations should be of considerable use in estimating unknown values of either of these properties.

The heats of solution in sulfuric acid and tetrachloroethane were measured conveniently in a simple solution calorimeter[16] on carefully purified and protected amines. It is mandatory that exactly the same strength of acid be used for all bases to be compared, since $\Delta H_a$ is very sensitive to the concentration of sulfuric acid.

(15) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955).

(16) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, 87, 1541 (1965).

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# Book Reviews

**Advanced Quantum Chemistry. Theory of Interactions between Molecules and Electromagnetic Fields.** By HENDRIK F. HAMEKA, Department of Chemistry, University of Pennsylvania. Addison-Wesley Publishing Co., Inc., Reading, Mass. 1965. x + 277 pp. 16 × 23.5 cm. $13.75.

The title of Hameka's book is "Advanced Quantum Chemistry." The stated purpose of the book is to bridge a communications gap between physicists and chemists in the area of the theoretical description of interactions between molecules and electromagnetic fields.

In his preface Hameka interprets and attempts to extend Coulson's 1959 classification of quantum chemists into *ab initio* ists and *a posteriori* ists. His interpretation of Coulson's categorization is that both groups have as their primary objective determination of more or less approximate molecular wave functions and corresponding energies. The extension of Coulson's classification is described by a passage from Dante which, somewhat loosely translated, means, "I thought how many worthy souls there were suspended in that Limbo." Somewhat earlier in Canto IV occurs a perhaps more appropriate passage, "Death-pale, the Poet spoke: 'Now let us go into the blind world waiting here below us. I will lead the way and you shall follow'." If one were to accept both Coulson's polarization of the field and Hameka's further resolution into higher order moments, then at least one other emerging overlap area can be identified where exchange may prove to be even more fruitful, namely, scattering theory and chemical reactivity, and this brings us to the first of several minor criticisms.

The title of the book, "Advanced Quantum Chemistry," is misleading. The qualifying statement following the title, "Theory of Interactions between Molecules and Electromagnetic Fields," would have been more appropriate as a title. Anyone stimulated by the title into picking up the book may reasonably expect to find a presentation of closed-shell, open-shell, and extended Hartree–Fock theory, Brillouin's theorem, natural orbitals, nonbonding interactions, scattering theory, and a host of other subjects.

Chapter 4 is entitled "Approximate Methods in Quantum Theory" while Chapter 5 is entitled "Time-Dependent Perturbation Theories." The author index is incomplete.

The book is somewhat uneven in level. On one hand a derivation is given for the Thomas factor of $1/2$ in the expression for the energy of a spinning electron in an electromagnetic field, while on the other hand neither the Breit equation nor the problem of retardation is discussed.

Hameka's remarks on page 67 relating to perturbation theory and direct analytical solution of the equations for certain cases are well illustrated in the book by H. A. Bethe and E. E. Salpeter, "Quantum Mechanics of One- and Two-Electron Atoms," Academic Press Inc., 1957, on pages 27 and 229. In fact, those stimulated to apply some of the theories discussed by Hameka will find much helpful material in Bethe and Salpeter's book where the stated second aim is to be of some use to graduate students who wish to learn "applied quantum mechanics."

Although English is not Hameka's native tongue, about the only trace apparent is his use of "Apparently . . . ." instead of "It is apparent that . . . ." as on page 61.