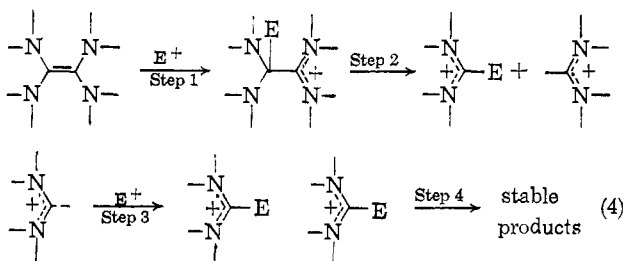


spectrum of this mixture there appeared only a simple doublet corresponding to **5** and **6**; *no absorption attributable to the crossed ethylene 7 was present*. Hence the equilibrium represented by eq. 1 does not occur under conditions as drastic as *any* reported for reactions of tetraaminoethylenes.¹⁻³ A reconsideration of reaction pathways for tetraaminoethylenes is obviously necessary.

Every known reaction of the powerful π -bases can be interpreted in terms of electrophilic attack upon the π -electron system. Whereas the net effect of oxidizing agents such as silver ion and iodine is electron abstraction, leaving the skeleton intact,² most reactions of tetraaminoethylenes lead to products derived from only half of the molecule. It is proposed that the latter class of transformations (air oxidation excepted) conforms to a general mechanism expressed in simplest form by eq. 4, where E^+ represents an electrophile, charged or neutral. Analogy for steps 2 and 3 of eq. 4 is found in the work of Breslow,⁵ who has demonstrated that zwitterions of the type shown are effective both as leaving groups and as nucleophiles. The simplest example illustrating eq. 4 is the facile con-



version of a tetraaminoethylene into two moles of the related formamidinium salt with mineral acid ($E^+ = H^+$), but the proposal applies as well to reactions with hydroxylic substances, aldehydes, ketones, nitro compounds, negatively substituted olefins, etc.¹ In each of these kinds of compound either activated hydrogen or electron-deficient carbon is available as the electrophilic site.

Acknowledgment.—The authors wish to thank the National Science Foundation and the Research Committee of the University of Wisconsin for financial support. They are grateful also to Messrs. R. Lichter and C. Underbrink, who measured n.m.r. spectra.

(5) R. Breslow, *J. Am. Chem. Soc.*, **80**, 3719 (1958).

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RECEIVED MARCH 5, 1964

Electron Pairing and Linear H_3^+

Sir:

Shull¹ has recently criticized the view expressed by Hopton and Linnett² in a paper on linear H_3^+ . We showed that a wave function based on two "one-electron bonds" gave a lower energy than one based on the molecular orbital method or the valence bond method in the Coulson-Fischer form.³ More detailed calcula-

tions by Bowen and Linnett⁴ confirm the results obtained by Hopton and Linnett,² their calculations having been extended to H_3 and H_3^- .

Shull carries out an analysis in terms of natural orbitals. He shows that the MO pair description has a very large overlap with the best wave function (or alternatively that the first occupation number has a value very close to unity). He remarks correctly that the same is true for H_2 .⁵ However this does not alter the very serious fact that the MO pair description for linear H_3^+ leads to a poor energy for that ion, just as it does for H_2 . Moreover, for H_2 , this is true whatever form is allowed for the MO function.⁶ This is the weakness of the molecular orbital approach. It is also the weakness of all analyses in terms of natural orbitals which lay great stress on the large overlaps (or high first occupation numbers) but do not draw attention to the poor energy that is obtained using the first member alone despite its large occupation number. At no point in his paper¹ does Shull record a calculated energy, and in the first paragraph of his paper he states that the conclusions of Hopton and Linnett were based on the large overlaps. They were, in fact, based much more on the values obtained for the energy, the significant fact being that the deviation of the calculated energy from that obtained using the best equivalent CI function was about five times greater using the MO and VB functions than it was using the NP function.⁷ It is the chemist's misfortune that the energies that are of chemical importance are relatively small, being of a magnitude which are also produced by quite small changes in wave functions. Therefore the poor energies obtainable using an MO description (without CI) in nonempirical calculations of the present type are important to the chemist.

If the form of the "best CI function" is examined it can easily be seen that it suggests naturally the function Hopton and Linnett described as NP. Shull points out that this is the description that would be given by introducing electron correlation into a three-center bond description. This certainly provides another way of regarding the situation. Because we used, for our function, a semilocalized orbital involving one HH pair and another involving the other HH pair, and associated one electron with each, we described the distribution as consisting of two one-electron bonds. The spins of the electrons must be opposed (*i.e.*, the state must be a singlet) as otherwise the spin correlation effects would prevent the two electrons ever being simultaneously near the center of the system. Such an effect, driving the electrons onto the end atoms, would produce a considerable increase in energy. It is true therefore that the electron distribution, in this case, may equally well be described in terms of correlation within a three-center bond, or in terms of two one-electron bonds. The final choice between them must depend on which is more fruitful when there is need to transfer our ideas to other more complicated systems. It remains the opinion of the author that descriptions

(4) H. C. Bowen and J. W. Linnett, *Trans. Faraday Soc.*, submitted for publication.

(5) H. Shull, *J. Chem. Phys.*, **30**, 1405 (1959).

(6) C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **34**, 204 (1938).

(7) In recent papers by Bowen and Linnett⁴ and by D. P. Chong and J. W. Linnett (*Mol. Phys.*, accepted for publication), it has been proposed that this method should be described as that of nonpaired spatial orbitals, NPSO.

(1) H. Shull, *J. Am. Chem. Soc.*, **86**, 1469 (1964).

(2) J. D. Hopton and J. W. Linnett, *J. Chem. Soc.*, 1553 (1962).

(3) C. A. Coulson and I. Fischer, *Phil. Mag.*, **40**, 386 (1949).

using one-electron bonds of the type employed here may well prove to be very useful. For example Shull states that "similar cases are involved in the bridge hydrogen bonds of the boron hydrides or in aromatic compounds where electrons are almost completely delocalized." We have completed calculations for the central ring of diborane⁸ and the electrons of the π -system of benzene,⁹ and the results show that a description in terms of similar one-electron bonds is more successful than the others when judged by the calculation of energies. For instance, a function using two adjustable constants which places each of the six π -electrons in benzene in a separate two-center bond orbital leads to an energy only 2 kcal./mole greater than that obtained using the equivalent full CI function needing 21 adjustable constants.¹⁰ An MO description would have to employ many configurations before it could do as well, and no analysis in terms of natural orbitals recording high first occupation numbers can alter this fact.

There are, of course, many molecules for which an analysis in terms of pairs (geminals) is almost certainly the best one as was pointed out by Lewis.¹¹ Molecules for which one Lewis formula may be written would be expected to lend themselves to such an analysis. However there are other molecules for which a single Lewis structure on its own cannot be regarded as satisfactory as was pointed out by Pauling.¹² In such cases an analysis in terms of pairs along the lines advocated by Shull may not provide by any means the best approach.¹³

(8) B. J. Duke and J. W. Linnett, to be published.

(9) P. B. Empedocles and J. W. Linnett, *Proc. Roy. Soc. (London)*, submitted for publication.

(10) J. W. Moskowitz and M. P. Barnett, *J. Chem. Phys.*, **39**, 1557 (1963).

(11) G. N. Lewis, *J. Am. Chem. Soc.*, **38**, 762 (1916).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(13) J. W. Linnett, *J. Am. Chem. Soc.*, **83**, 2643 (1961); "Electronic Structure of Molecules," Methuen, London, 1964.

(14) On leave at the Department of Chemistry, University of California, Berkeley 4, Calif.

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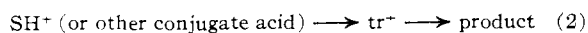
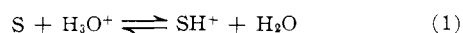
J. W. LINNETT¹⁴

RECEIVED MAY 1, 1964

The Effect of Mineral Acid Medium upon $f_{\text{SH}^+}/f_{\text{tr}^+}$

Sir:

We are reporting the first instance of the direct measurement of the effect of mineral acid medium upon $f_{\text{SH}^+}/f_{\text{tr}^+}$, where f_{SH^+} is the activity coefficient of the conjugate acid of the substrate and f_{tr^+} is that of the transition state in an A-1 reaction. Knowledge of the behavior of such activity coefficient ratios is essential to the proper interpretation of the acidity dependence of reaction rates.



$$k_{\text{obsd}} = \frac{[\text{SH}^+]}{[\text{S}] + [\text{SH}^+]} k f_{\text{SH}^+}/f_{\text{tr}^+} \quad (3)$$

when $[\text{SH}^+] \gg [\text{S}]$

$$k_{\text{obsd}} = k f_{\text{SH}^+}/f_{\text{tr}^+} \quad (4)$$

Under the usually pertaining condition that $[\text{S}] \gg [\text{SH}^+]$ the use of eq. 3 as a criterion of mechanism has traditionally involved the application of two assumptions: (1) that the ratio $[\text{SH}^+]/[\text{S}]$ follows a particular acidity function, *i.e.*, h_0^+ ; and (2) the ratio $f_{\text{SH}^+}/f_{\text{tr}^+}$ is relatively insensitive to medium change.² The former assumption is not always valid (see ref. 3 and references therein).^{2,3} A direct test of the latter assumption is made in the A-1 hydrolysis of the dimethyl acetals of pyridine-2-aldehyde, quinoline-2-aldehyde, and 8-*t*-butylquinoline-2-aldehyde. In lower acid molarities, the rate-controlling step is the heterolysis of the C-O bond of the oxygen conjugate acid, SH^{*+} , although the ground state is the nitrogen conjugate acid, SH^+ . The first term of eq. 5 corresponds to this over-all one-proton A-1 hydrolysis. In higher mineral acid molarities, an over-all two-proton process, involving heterolysis of the C-O bond of the doubly protonated substrate, SH_2^{+2} , may become of increasing importance. This is because of the steep acidity dependence of $[\text{SH}_2^{+2}]/[\text{SH}^+]$ in the two-proton hydrolysis term, the second term of eq. 5.

$$k_{\text{obsd}} = k_1 \frac{K_{\text{SH}^+}}{K_{\text{SH}^{*+}}} f_{\text{SH}^+}/f_{\text{tr}^+} + \frac{[\text{SH}_2^{+2}]}{[\text{SH}^+]} k_2 f_{\text{SH}_2^{+2}}/f_{\text{tr}^{+2}} \quad (5)$$

Consider first the rate results for 2-dimethoxymethylpyridine. In keeping with the mechanistic assignment no catalysis by either molecular acetic acid or acetate ion was observed in acetate buffers at low ionic strength, 0.05 μ (see ref. 4 for accumulated evidence that acetal hydrolysis is A-1). It is evident from the initial decline in k_{obsd} , which goes through a minimum in about 1.6 M HClO_4 , that one-proton hydrolysis predominates in the lower mineral acid range. The rapid increase in k_{obsd} in the highest acid molarities is indicative of the incursion of the over-all two-proton hydrolysis.⁴ These conclusions are confirmed by the solvent isotope effects of Table I.

TABLE I
RATE CONSTANTS AND SOLVENT ISOTOPE EFFECTS IN THE
HYDROLYSIS OF 2-DIMETHOXYMETHYLPIRIDINE AT 60°

HClO_4 , M	$10^4 k_{\text{obsd}}$, ^a sec. ⁻¹	$k_{\text{HClO}_4}/k_{\text{DClO}_4}$ ^b
0.12	4.86	1.06
0.56	4.42	..
1.60	4.19	1.00
1.96	4.20	..
2.72	4.57	0.97
3.10	5.01	..
3.98	7.03	0.87
5.09	15.40	0.70
5.72	30.9	0.61
6.83	147	0.57

^a All first-order rate constants in Tables I and II were obtained by an ultraviolet spectrophotometric method and are duplicable to $\pm 2\%$. ^b Rate in perchloric acid relative to fully deuterated perchloric acid of same molarity.

As regards the ratio $f_{\text{SH}^+}/f_{\text{tr}^+}$, the conclusion is plain that it suffers an initial steady decline as perchloric acid molarity is increased. Whether or not this decline

(1) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(2) W. M. Schubert and R. H. Quacchia, *J. Am. Chem. Soc.*, **85**, 1278 (1963), and references therein.

(3) R. W. Taft, Jr., *ibid.*, **82**, 2695, (1960).

(4) M. W. Fuller and W. M. Schubert, *ibid.*, **85**, 108 (1963).