electron would be expected to move in a nonlocalized orbital, it does not appear to have been previously observed for the case of magnetic electrons associated with a normal paramagnetic atom.

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THE STRONG ACID BEHAVIOR OF DECABORANE

Sir:

Decaborane, in sharp contrast to the lower boranes, dissolves in alcohols, water–alcohol, water–dioxane and other protolytic solvents without rapid hydrolysis[1]; further, the rate of hydrogen evolution as observed by H. C. Beachell and W. A. Mosher[2] for the alcoholysis of decaborane exhibits a marked induction period. These observations suggest that a reasonable stable intermediate, a precursor to the hydrogen-producing reactions, is formed.

Consistent with these observations we have noted that the solution of decaborane in these solvents produces a strong monoprotic acid without the evolution of hydrogen and that decaborane is recoverable in part from such solutions. Typically, the titration of 122 mg. (1.00 millimole) of decaborane (approx. 95% pure) dissolved in 75% ethyl alcohol–water with 0.10 *N* sodium hydroxide was followed potentiometrically. The titration curve so obtained was characteristic of a strong monoprotic acid, the end-point being observed after the addition of 0.96 milliequivalent of base. Back titration with aqueous hydrochloric acid reproduced the same titration curve. That the decaborane structure is probably not destroyed in the formation of the strong acid is demonstrated by the recovery of decaborane (identified by melting point and mixed melting point, 97–98°) from alkaline water or alcohol–water solution in 35% yield by acidification. A large fraction of the decaborane apparently is lost through hydrolysis or alcoholysis as indicated by vigorous evolution of gas.

The formation of the strong acid is sufficiently slow so that its rate of growth can be followed potentiometrically, spectrophotometrically or conductimetrically. The last method, in 75% water–dioxane, yielded results sufficiently satisfactory for kinetic treatment. The rate ($-\log k_{9.4} = 3.16$; $-\log k_{15.2} = 3.00$; $-\log k_{21.5} = 2.71$; $-\log k_{25.5} = 2.57$) is first order in decaborane and independent of hydrogen ion. From the data is derived $\Delta H^{\neq} = 14.2$ kcal. mole^{-1}.

It is proposed that the hydrogen ion originates either by reaction between decaborane and the solvent

$$B_{10}H_{14}(\text{soln.}) + H_2O = [B_{10}H_{14}OH]^-(\text{soln.}) + H^+(\text{soln.})$$

or by loss of a proton from the decaborane

$$B_{10}H_{14}(\text{soln.}) = [B_{10}H_{13}]^-(\text{soln.}) + H^+(\text{soln.}).$$

Either process would fit the observed kinetics. Deuterium exchange and kinetic experiments which should help to distinguish between them are now in progress.

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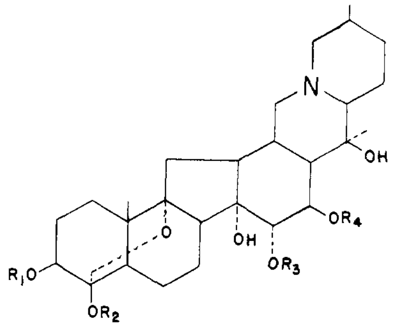
[1] W. H. Hill and M. S. Johnson, *Anal. Chem.*, **27**, 1300 (1955); H. C. Beachell and T. R. Meeker, THIS JOURNAL, **78**, 1796 (1956).

[2] H. C. Beachell and W. A. Mosher, private communication.

ZYGADENUS ALKALOIDS. VII. ON THE STRUCTURE OF ZYGADENINE

Sir:

The alkamine zygadenine[1] ($C_{27}H_{43}O_7N$) and its ester alkaloid derivatives have been shown to occur, alongside germine and its esters, in several species of *Zygadenus*[1–4] and *Veratrum*.[5,6] I wish to report evidence for structure I for zygadenine.



I, $R_1 = R_2 = R_3 = R_4 = H$
II, $R_1 = R_3 = R_4 = Ac$; $R_2 = H$
III, $R_1 = R_2 = R_3 = R_4 = Ac$
V, $R_1 = R_4 = Ac$; $R_2 = R_3 = H$
VI, $R_1 = Ac$; $R_2 = R_3 = R_4 = H$

The order of stability of the zygadenine isomers [zygadenine (3-β-hydroxy-4,9-hemiketal) < isozygadenine[7] (3-β-hydroxy-4-keto-9-α-hydroxy-A/B *trans*) < pseudozygadenine (3-α-hydroxy-4,9-hemiketal)][2] parallels that of the veracevine isomers and differs from that of the germine series.[8] Zygadenine forms a triacetate (II) upon acetylation with acetic anhydride alone; acetylation with acetic anhydride–pyridine affords a tetraacetate (III).[3] Acetylation of zygacine acetonide[3] (zygadenine-14,15-acetonide-3-acetate) with acetic anhydride yields zygadenine-14,15-acetonide-3,16-diacetate (IV), m.p. 271–272° dec., $[\alpha]^{23}\text{D} - 29°$ (py.). Found: C, 66.33; H, 8.35; acetyl, 13.61. Hydrolysis of IV with dilute mineral acid affords zygadenine-3,16-diacetate (V), m.p. 255–257° dec., $[\alpha]^{23}\text{D} - 50°$ (py.). Found: C, 64.69; H, 8.17; acetyl, 14.83; equiv. wt., 582. Periodate titrations indicate the following uptakes: zygadenine (I), 3 mole; zygacine[3,4] (VI), 2 mole; zygadenine diacetate (V), 1 mole; zygadenine triacetate (II), 0 mole; zygacine acetonide, 0 mole. Formulation I for zygadenine was first conceived as a reasonable rationalization of the above facts.

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[1] F. W. Heyl, F. E. Hepner and S. K. Loy, THIS JOURNAL, **35**, 258 (1913); F. W. Heyl and M. E. Herr, *ibid.*, **71**, 1751 (1949).

[2] S. M. Kupchan and C. V. Deliwala, *ibid.*, **75**, 1025 (1953).

[3] S. M. Kupchan, D. Lavie and R. D. Zonis, *ibid.*, **77**, 689 (1955).

[4] S. M. Kupchan, C. V. Deliwala and R. D. Zonis, *ibid.*, **77**, 755 (1955).

[5] A. Stoll and E. Seebeck, *Helv. Chim. Acta*, **36**, 1570 (1953).

[6] M. W. Klohs, M. D. Draper, F. Keller, S. Koster, W. Malesh and F. J. Petracek, THIS JOURNAL, **75**, 4925 (1953).

[7] I propose the name isozygadenine for the amorphous carbonyl-containing isomer of zygadenine described in reference 2.

[8] S. M. Kupchan and C. R. Narayanan, *Chemistry and Industry*, in press.