

The data show that (1) carbethoxynitrene is about ten times as selective as the corresponding carbene, (2) the selectivity depends little on the solvent, and (3) the nitrenes generated by photolysis and by α -elimination have nearly the same selectivity. This is best explained by assuming that the carbethoxynitrene in solution is energetically in equilibrium with its environment and does not contain excess vibrational energy.

From our work with cyclohexene⁵ we can estimate that the double bond in cyclohexene reacts about 36 times faster than do the CH₂ groups in positions 4 and 5 (the nonallylic CH₂ groups of cyclohexene). We might, somewhat arbitrarily, equate the reactivities of these CH₂ groups with that in 2-methylbutane. The cyclohexene double bond then would be estimated to react 360 times faster than the primary C-H bond in the methyl groups in 2-methylbutane. This corresponds to a difference in free energies of activation of about 3.5 kcal./mole.

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(5) W. Lwowski and T. W. Mattingly, Jr., to be published.

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

WALTER LWOWSKI
TOM J. MARICICH

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The Hydrolysis of Sodium Tetrahydroborate. Identification of an Intermediate

Sir:

The kinetics of the general acid catalyzed hydrolysis of sodium tetrahydroborate (NaBH₄, sodium hydroborate, sodium borohydride), has been recently reported by Davis, Bromels, and Kibby,¹ by Stockmayer, Miller, and Zeto,² and by Mesmer and Jolly,³ in whose work earlier literature is cited. In a polarographic study, Marshall and Widing⁴ found the anodic wave of the BH₄⁻ ion at an $E_{1/2}$ of -0.15 v. vs. s.c.e., and another much smaller wave at an $E_{1/2}$ of -0.64 v. vs. s.c.e. Pecsok⁵ studied the former wave and used it in his polarographic determination of the rate of hydrolysis of NaBH₄. Mochalov and Gil'manshin⁶ reported that the small wave decreased in height as the NaBH₄ solution decomposed and was larger at lower pH values. They attributed it to the oxidation of an intermediate in the hydrolysis process. We have found that the height of this small wave first increases and then decreases after a solution is prepared and have postulated that it stems from an intermediate in a stepwise hydrolysis process, whose kinetics can be described by a sequential first-order scheme. Polarographic limiting currents, resulting from the oxidation of BH₄⁻ at -0.01 v. and

(1) R. E. Davis, E. Bromels, and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962).

(2) W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, **65**, 1076 (1961).

(3) R. E. Mesmer and W. L. Jolly, *Inorg. Chem.*, **1**, 608 (1962).

(4) E. D. Marshall and R. A. Widing, "Polarography of Sodium Borohydride," Atomic Energy Commission Document No. 2914 (1950).

(5) R. L. Pecsok, *J. Am. Chem. Soc.*, **75**, 2862 (1953).

(6) K. N. Mochalov and G. G. Gil'manshin, *Dokl. Akad. Nauk SSSR*, **132**, 134 (1960); *Proc. Acad. Sci. USSR, Chem. Sect.*, **132**, 467 (1960).

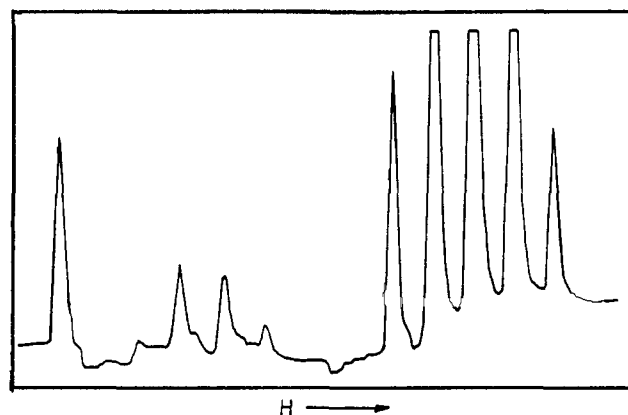


Fig. 1.—B¹¹ n.m.r. spectrum of base-stabilized, partially hydrolyzed NaBH₄ solution.

the oxidation of the postulated intermediate at -0.5 v., fit such a scheme. Thus, the intermediate is formed by the pseudo-first-order reaction of BH₄⁻, and it is consumed in a second, faster process, which is first order in concentration of the intermediate. Rate constants for these processes have been calculated and will be presented in detail elsewhere⁷; here we report the results of confirmatory experiments, bearing on the identity of this intermediate, which have been performed on solutions, which, according to the kinetic results, have the maximum concentration of the intermediate.

Samples of partially hydrolyzed NaBH₄ solutions, which contained the highest possible concentration of intermediate, were prepared by allowing a fresh solution of NaBH₄ to hydrolyze briefly and then quickly adding base to make the pH 12.5 or greater. A typical procedure, used for preparing samples for n.m.r. work, follows. To 20 ml. of a solution 8 M in NaBH₄ (98% as received from Metal Hydrides, Inc.) and 0.05 M in NaOH, 6 M HCl was rapidly added at $25 \pm 0.1^\circ$ until the pH dropped to 8.8. After keeping the solution at this pH for 1 min., the pH was raised to 12.5 or greater by the addition of 19.8 M NaOH. The polarographic limiting current at -0.5 v. vs. s.c.e. indicated a concentration of the intermediate of about 0.16 M in the sample. The half-life of the intermediate in such a solution, determined by observation of the decay of the polarographic limiting current, was 3.7 hr. Polarograms of the solutions exhibited only the two known waves ($E_{1/2} = -0.15$ and -0.64 v. vs. s.c.e.).

It should be noted that the amount of intermediate available for study in the final solution was but a few per cent of the BH₄⁻ present. This situation did not affect the n.m.r. spectroscopy, since the concentration of the intermediate was within the limits of detection of the spectrometer, but it did limit the chemical and electrochemical tests which could be done.

Boron-11 n.m.r. spectra were recorded on a Varian HR-60 spectrometer equipped with a 19.3-Mc. oscillator. A 15-mm. sample tube was used. The B¹¹ spectrum of a base-stabilized, partially hydrolyzed NaBH₄ solution is shown in Fig. 1. The spectrum consists of the borate singlet at low field, a quartet, and a quintet at high field. The quintet is the familiar BH₄⁻ spectrum, first studied by Ogg.⁸ The quartet of

(7) J. A. Gardiner, "The Hydrolysis of Sodium Hydroborate," Ph.D. Dissertation, Graduate School of The Ohio State University, 1964.

(8) R. A. Ogg, *J. Chem. Phys.*, **22**, 1933 (1954).

lines, found only in spectra of solutions which have large polarographic limiting currents at -0.5 v., is the resonance for the intermediate. It arises from splitting of the B^{11} resonance by three equivalent protons and is in fair agreement with the predicted intensity ratio of 1 : 3 : 3 : 1 for this splitting. The spin-spin coupling constant, J , is 82 c.p.s. for the quartet, the same as that for the hydroborate quintet, and its center of gravity is 13.9 p.p.m. upfield from the borate singlet.

The proton n.m.r. spectrum of the sample was identical with the spectrum of a basic NaBH_4 solution.⁹ Thus, we conclude that the screening of the protons on the BH_4^- ion is unaffected by conversion to the $-\text{BH}_3$ entity.

The presence of the $-\text{BH}_3$ group in the base-stabilized, partially hydrolyzed NaBH_4 solution has also been indicated by: (1) electrolyzing the solution at a mercury anode at a constant potential, (2) measuring the H_2 given off in a lengthy hydrolysis of the solution, (3) determining its reducing power toward iodate ion. The details of these experiments will be reported. The results are consistent with the postulation of a $-\text{BH}_3$ -containing entity in the mixture, which might be aquated borine,¹⁰ $\text{H}_3\text{B}\cdot\text{OH}_2$, or trihydrohydroxyborate ion,¹¹ BH_3OH^- . The latter formulation is favored by the analogy between the effect of ionic strength on the rates of reaction of the intermediate and the BH_4^- ion. Thus, for the reaction between BH_4^- and HCO_3^- , the rate was little changed by change in ionic strength, whereas for the reaction between BH_4^- and NH_4^+ the rate decreased with increasing ionic strength. The rates of reaction of the intermediate with the same two general acids show an identical dependence on ionic strength. Although the ionic strengths in the kinetic work (0.2, 0.5, 1.0) were too high to allow the straightforward application of the Brønsted salt effect equation,¹² the similar change in the rates of reaction of the two species may permit the choice of the negatively charged species, BH_3OH^- , as the more probable formula of the intermediate.

(9) In agreement with results of Mesmer and Jolly, ref. 3.

(10) Species postulated by Davis, *et al.*, ref. 1.

(11) J. Goubeau and H. Kallfass, *Z. anorg. allgem. Chem.*, **299**, 160 (1959).

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 150 *et seq.*

(13) Allied Chemical Foundation Fellow, 1963-1964.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

JOHN A. GARDINER¹³
JUSTIN W. COLLAT

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Electron Spin Resonance of Alkyl Nitrenes

Sir:

We have obtained the first direct physical evidence for primary, secondary and tertiary alkyl nitrenes, $\text{R}-\text{N}\cdot$. Such species have been postulated as intermediates in the decomposition of alkyl azides.¹ The electron spin resonances (e.s.r.) of several aromatic nitrenes have been reported.^{2,3} These were shown to

(1) D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962). One of us (G. S.) has made numerous attempts to repeat this work without success. In no case was it found possible to achieve a nitrene insertion reaction even though several different commercially available quartz-enclosed medium pressure mercury lamps were used and the procedures described by Barton and Morgan were followed as well as variations on these procedures.

be ground-state triplets with significant delocalization occurring into an adjacent aromatic system.

The samples were prepared by dissolving the azide precursor⁴ in hexafluorobenzene or perfluorodimethylcyclobutane and irradiating with an HBO-200 mercury lamp at 4°K. Observations of the spectrum were made by means of a Varian V-4500 spectrometer (9.3 kMc.) with 100 kc. modulation. At 4°K the spectra persisted for hours after irradiation indicating a ground-state triplet or a thermally accessible triplet lying not more than a few cm^{-1} above the ground state. The only significant absorption observed with these materials was near 8000 gauss. The shapes of the absorptions indicated that we were observing those molecules in the randomly oriented nitrenes for which the external magnetic field was approximately perpendicular to the C-N bond, the z -axis.⁵

The spectra may be described in terms of the two parameters, D and E , which are proportional to the averages of $1/r^3 - 3z^2/r^5$ and $(y^2 - x^2)/r^5$ for the two unpaired electrons.⁶ The values obtained, assuming $g = 2.0023$, were n -propyl nitrene, $D = 1.607 \text{ cm}^{-1}$, $E = 0.0034 \text{ cm}^{-1}$; 2-octyl, 1.616, 0.0019; cyclohexyl, 1.599, <0.002 ; cyclopentyl, 1.575, <0.002 ; α -carboethoxybenzyl, 1.659, <0.002 ; and t -butyl, 1.625, <0.002 . Since E is a measure of the difference in the unpaired electron distribution along the x - and y -axes, the small values are compatible with an approximately cylindrical distribution about the C-N bond expected for these nitrenes. Symmetry would require that t -butyl nitrene have $E = 0$ if there were no distortions due to the matrix.

The assignment of the spectra to nitrenes receive support from a comparison with the D of N-H. Dixon deduced a value of 1.86 cm^{-1} from the ultraviolet spectrum observed on flash photolysis of HNCO .⁷ Theoretical values of D for N-H are 1.8⁸ or 1.9 cm^{-1} .⁹ The somewhat smaller values of the substituted compounds mentioned above are compatible with some spin delocalization into the adjacent groups. Such delocalization is known to occur with substituted methyl radicals.¹⁰ The less concentrated spin would reduce the dominant contribution to D , the interaction of the unpaired electrons on the nitrogen atom.

Additional support for the nitrene assignment is based on a comparison with an alkyl methylene. Both triplets have the unpaired electrons primarily in two p -orbitals on the same atom. D should be proportional to Z^3 where Z is the effective nuclear charge for the 2 p -orbital.⁹ Then

$$D_{\text{RCH}} = (Z_{\text{C}}/Z_{\text{N}})^3 D_{\text{RN}} = (3.25/3.9)^3 \cdot 1.6 \sim 0.9 \text{ cm}^{-1}$$

(2) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962).

(3) G. Smolinsky, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, **35**, 576 (1963).

(4) The azides were prepared by reaction of sodium azide with the corresponding halide (usually the bromide) in boiling aqueous methanol solutions. All the alkyl azides thus prepared exhibited infrared absorption in the region 2100 cm^{-1} characteristic of the N_3 group [E. Lieber, C. N. Rao, T. S. Chao, and C. W. W. Hoffman, *Anal. Chem.*, **29**, 9161 (1957)].

(5) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, to be published.

(6) M. Gouterman and W. Moffitt, *ibid.*, **30**, 1107 (1959); J. H. Van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959).

(7) R. N. Dixon, *Can. J. Phys.*, **37**, 1171, (1959).

(8) J. Higuchi, private communication.

(9) As may be deduced from H. Sternlicht, *J. Chem. Phys.*, **38**, 2316 (1963). An interchange of the y - and z -axes is necessary.

(10) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).