structure derived from that of pentaborane through removal of a proton (most likely a bridge proton) from a basal boron.[1] Apparent equivalence of basal borons at ambient temperature can be accounted for by assuming averaging of chemical shifts through tautomerism, as is used to account for the boron-11 nmr spectrum of hexaborane(10).[3]

Addition of an equivalent quantity of $(CH_3)_4NCl$ to an ether solution of LiB_5H_8 at −78° followed by warming and stirring 48 hr at ambient temperature results in the formation of a pale yellow solid mixture containing LiCl and $(CH_3)_4NB_5H_8$.[4] Lithium chloride was extracted with cold alkaline aqueous solution and the residual $(CH_3)_4NB_5H_8$ was recrystallized from acetone–water solution.

Anal. Calcd for $C_4H_{12}NB_5H_8$: C, 35.5; B, 39.7. Found: C, 36.0; B, 40.0.

A plot of equivalent conductance of $(CH_3)_4NB_5H_8$ in dilute acetonitrile *vs.* the square root of equivalent concentration gave a slope of 301, a reasonable value for a 1:1 electrolyte.[5] A cryoscopic molecular weight measurement determined with a 0.05 *m* solute concentration in acetonitrile is consistent with complete ionization 1:1 electrolyte. *Anal.* Calcd for $(CH_3)_4N^+B_5H_8^-$: mol wt, 68.6; Found: mol wt, 66.6. The X-ray powder diffraction pattern of this salt can be indexed in the cubic system. Though not complex in appearance, the boron-11 nmr spectra of $(CH_3)_4NB_5H_8$ and $(CH_3)_4NB_5D_8$ differ markedly from the spectra of the corresponding alkali metal salts; we are unable to discuss them satisfactorily at the present time. Conceivably the $B_5H_8^-$ ion in the tetramethylammonium salt is a structural isomer of the corresponding ion in the alkali metal salts.

The $B_5H_8^-$ ion appears to be degraded to $B_3H_8^-$ by isopropyl alcohol.

$$(CH_3)_4NB_5H_8 + 6i\text{-}C_3H_7OH \longrightarrow (CH_3)_4NB_3H_8 + 3H_2 + 2B(OC_3H_7)_3$$

A solution of $(CH_3)_4NCl$ in isopropyl alcohol was added to an equivalent amount of LiB_5H_8 in diethyl ether at −78°. Upon warming, the solution was stirred for 1 hr and filtered under nitrogen. The white solid isolated was $(CH_3)_4NB_3H_8$ in 75% yield. It was identified by chemical analyses and its boron-11 nmr spectrum. A similar degradation of $(CH_3)_4NB_9H_{12}$ by methanol to give $(CH_3)_4NB_3H_8$ has been reported.[6]

Through tensiometric titrations at −78° in diethyl ether and in glyme, it was determined that alkali metal $B_5H_8^-$ salts react with diborane in equimolar ratios. This reaction appears to produce unsymmetrical cleavage of diborane.

$$B_2H_6 + MB_5H_8 \longrightarrow MBH_4 + B_6H_{10}$$

The alkali metal borohydrides were identified from their boron-11 nmr spectra and their X-ray powder diffraction patterns. For the time being, it is believed that in the reaction cited above a BH_2^+ is inserted into the basal plane of the $B_5H_8^-$ ion, giving a product which is an isomer of normal B_6H_{10}. The nmr spectrum of this new material consists of two doublets: an upfield doublet which is in excellent agreement with that assigned to the apical boron of hexaborane(10) with respect to coupling constant and chemical shift, and a downfield doublet which is some 27 ppm upfield from the value assigned to the basal borons of hexaborane(10).[7] This material will distil away with the solvent diethyl ether from the reaction mixture at −20°. Upon standing at room temperature in solution, it appears to convert at least partially to normal hexaborane(10). The boron-11 nmr spectrum of an ether solution which was permitted to stand at room temperature for 30 min showed that the low-field doublet assigned to hexaborane(10) had appeared, while the doublet some 27 ppm upfield from it had diminished in intensity. The upfield doublet was unchanged.[8]

By refluxing glyme solutions of the B_6H_{10} product obtained from the reaction of diborane with either NaB_5H_8 or KB_5H_8, we have been able to obtain $B_{10}H_{14}$ in 20–30% yields. Decaborane(14) was characterized by its X-ray powder diffraction pattern, its melting point, and its boron-11 nmr spectrum. Efforts are continuing to elucidate the nature of the B_6H_{10} product and to improve the yield of $B_{10}H_{14}$ from the alkali metal $B_5H_8^-$–B_2H_6 systems.

Acknowledgment. We wish to acknowledge, gratefully, the support of this work by the National Science Foundation. We are also grateful to Mr. Frank Parker of the University of Michigan for taking nmr spectra at 32.1 Mc.

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(3) R. E. Williams, *J. Inorg. Nucl. Chem.*, 20, 201 (1961).

(4) A reported attempt to prepare $(CH_3)_4NB_5H_8$ yielded $(CH_3)_4NB_3H_8$; experimental conditions were not given.[2]

(5) R. D. Feltham, and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(6) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 83, 2669 (1961).

(7) T. P. Onak, H. Landesman, R. W. Williams, and I. Shapiro, *J. Phys. Chem.*, 63, 1533 (1959).

(8) NOTE ADDED IN PROOF. The normal form of hexaborane(10) was isolated from the mixture and identified by its boron-11 nmr spectrum and by its mass spectrum.

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Isomerization of Maleic Acid by Vanadous Ion

Sir:

cis–trans isomerism brought about by a variety of agents such as heat, free radicals, etc., is well known and accounted for by a number of mechanisms.[1] None of these cases, however, involves electron transfer to the double bond through other parts of the molecule. On the other hand, Fraser and Taube suggested,[2] in connection with their work on electron-transfer reactions, that activation of the double bond of maleic acid leading to isomerization may be possible by "remote attack" by the reducing agent on the carboxyl group. The conjugation of the maleic acid molecule and the high reducibility of its double bond are factors that make such an expectation plausible. The present experiments show that this idea was essentially correct though its manifestation in the system in which it was originally reported now seems open to question.[3] When vanadous ion is added to a maleic acid aqueous solution, isomerization to fumaric acid does take place, along with reduction to

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(1) See, for example, R. B. Cundal, *Progr. Reaction Kinetics*, 2, 165 (1964).

(2) R. T. M. Fraser and H. Taube, *J. Am. Chem. Soc.*, 81, 5514 (1959); 83, 2242 (1961).

(3) H. Taube, private communication. It was not found possible to doublicate the positive experimental evidence reported in ref 2.

succinic acid. In fact, the failure to observe it in the case of the reduction by Cr^{2+} or V^{2+} of the Co^{III} complex containing maleic acid as ligand[3] may prove to be a useful clue for the elucidation of the mechanism of the electron-transfer process. In this communication we report some observations on the isomerization. Data on the reduction are available.[4]

Figure 1 shows the fumaric acid produced in two reaction mixtures differing only in their perchloric acid content. Replacement of $HClO_4$ by HCl in a solution containing initially 0.0113 M V^{2+}, 0.156 M maleic acid, and 0.85 M H^+ did not affect the amount of fumaric acid obtained upon complete consumption of the V^{2+}. Included in Figure 1 is the V^{2+} consumption in the parallel reduction of maleic acid.[4] The isomerization is caused by V^{2+}; it does not take place if V^{2+} is not present, other conditions being constant. The other oxidation states of vanadium (V^{3+}, VO^{2+}) do not cause isomerization. The inverse, thermodynamically unfavorable, conversion of fumaric to maleic acid was not observed. Determination of fumaric acid in the presence of maleic and succinic acids was made polarographically under the conditions suggested by Warshowsky, *et al.*[5] The aliquots from the reaction mixture were exposed to air or mixed with a Fe^{3+} solution to stop the reaction and were analyzed polarographically after removing the metal ions on a Dowex 50 column. Fumaric acid, because of its limited solubility, is precipitated from reaction mixtures containing relatively high concentrations of maleic acid and was also identified by taking its melting point and ir spectrum. Analogous but slower isomerization with that of maleic acid is also observed with its derivative citraconic acid which is converted to mesaconic acid.

The study of the temperature dependence is made difficult because of the parallel oxidation of V^{2+} and the establishment upon mixing of a complex formation equilibrium between V^{2+} and the organic acids.[4] Nevertheless, it is mentioned that in two identical reaction mixtures containing 0.168 M maleic acid, 0.0113 M V^{2+}, and 0.058 M $HClO_4$ at 20 and 60° the percentage of fumaric acid formed over the initial maleic acid was 29.6 and 24.3, respectively. The determination was made after all the V^{2+} had been oxidized. Increase in temperature seems to favor reduction over isomerization.

In a preliminary attempt to follow more closely the isomerization and to find out what happens locally at the double bond, we did an experiment in deuterated water (50% D_2O) and determined by nmr the fraction of CD bonds in the fumaric acid produced. The mixture contained initially 0.25 M maleic acid, 0.05 M V^{2+}, and 0.1 M $HClO_4$. The fraction of CD bonds found in the fumaric acid which precipitated was 20–22%. Fumaric acid itself, without V^{2+}, does not undergo exchange. Figure 1 shows that formation of fumaric acid is faster at lower hydrogen ion concentration. Using the empirically determined[4] rate law and rate constant for the oxidation of V^{2+} and assuming first-order dependence of the isomerization on (V^{2+}), we can obtain from the data estimates of the rate constant for isomerization. We find then that the increased rate of production of fumaric

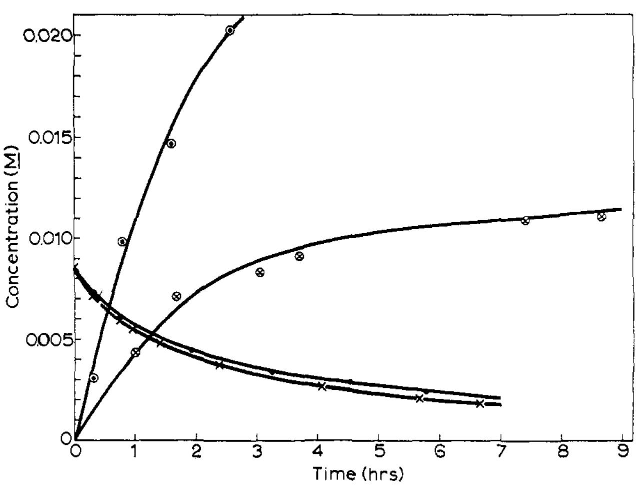
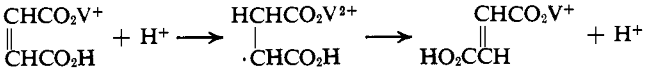


Figure 1. Isomerization of maleic acid by vanadous ion. Initial concentrations: $(V^{2+})_0$ = 0.009 M, (maleic acid)$_0$ = 0.156 M. ⊙ and ⊗ fumaric acid produced; and ● and ×, the corresponding V^{2+} concentrations in 0.43 and 0.85 M $HClO_4$, respectively.

acid at lower acid is mainly due to an inverse dependence on (H^+) of the isomerization itself and to a lesser extent to the decreased rate of the competing oxidation of V^{2+}. In a qualitative way, this fact is illustrated in Figure 1 where it is seen that the curves of (V^{2+}) *vs.* time depend much less on acid than those of (FA) *vs.* time. The significance of this observation is that it provides a link between the isomerization and the complex formation equilibrium between V^{2+} and maleic acid.

The factors affecting exchange of the double-bond hydrogens and its relation to isomerization can best be illustrated with the aid of a specific reaction scheme



$$\begin{matrix}\text{CHCO}_2\text{V}^+\\ \| \\ \text{CHCO}_2\text{H}\end{matrix} + \text{H}^+ \longrightarrow \begin{matrix}\text{HCHCO}_2\text{V}^{2+}\\ | \\ \cdot\text{CHCO}_2\text{H}\end{matrix} \longrightarrow \begin{matrix}\text{CHCO}_2\text{V}^+\\ \| \\ \text{HO}_2\text{CCH}\end{matrix} + \text{H}^+$$

If there is no labilization of the hydrogens in the intermediate, the statistically expected fraction of CD's in 50% D_2O is 12.5%. The fact that we observe more than this minimum indicates that the hydrogens of the intermediate become labile or that we have large isotopic discrimination, or that the first step in the above scheme is reversible. In addition, an analogous scheme for exchange can be written for the fumaric acid produced in the system. The evaluation of the relative importance of all these factors is the subject of further investigation.

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Stereospecific Reaction of Growing Ends of Polyacrylate Anions with Water, Hydrochloric Acid, and Acetic Acid

Sir:

A series of oligomers was prepared by adding H_2O, HCl, or CH_3COOH to a polymerization solution of isopropyl acrylate-α,β,β-d_3 in toluene after 2 min of

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[4] E. Vrachnou-Astra, Ph.D. Thesis, submitted to the National Technical University, Athens, Greece.

[5] B. Warshowsky, P. J. Elving, and J. Mandel, *Anal. Chem.*, **19**, 161 (1947).