Fig. 5.—Proton spin relaxation times for Np(V) ions 25°, 40 megacycles: $\odot$, T_1; $\bullet$, T_2; 1.03×10^{-2} M Np(V) *ca.* 0.1 M HClO$_4$; [UO$_2^{+2}$] $= 0$, $\mu = 3.0$ Mg(ClO$_4$)$_2$.

on T_1 and T_2. The paucity of the data does not warrant any more extended discussion of possible details of the ionic interactions, but it is to be em-phasized that the observations are indicative of specific interaction between the Np(V) and uranyl ions.

Conclusion

Three separate types of measurements are consistent with the concept of specific interaction between the Np(V) and uranyl ions in acid solution. No evidence has been obtained for the participation of anions in this complex.

The association quotient determined by spectrophotometric and potentiometric methods agrees within the limits of error despite the drastically different assumptions made in the two types of measurements. Weighting the individual determinations (perchlorate solutions only) according to their listed uncertainties, we obtain a final weighted mean value for the association quotient at 25° and ionic strength of three; $K = 0.690 \pm 0.013$ l./mole.

Reactions of Permanganate Ion with Borohydride Ion

By T. FREUND AND N. NUENKE

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The reactions between BH$_4^-$ and MnO$_4^-$ in basic solutions were investigated. The products of the reaction were shown to include BO$_2^-$, MnO$_4^-$, MnO$_2$ and H$_2$. Interestingly, all the H$_2$ was shown to originate from the BH$_4^-$. The second-order specific rate constant was found to be 2×10^3 l./mole-sec. at 20°. The proposed mechanism involves hypomanganate.

Introduction

On mixing basic solutions of borohydride and permanganate ions the following was observed: first the solution was pink (MnO$_4^-$), then grey or colorless (at about equal concentrations of MnO$_4^-$ and MnO$_4^=$ the visible absorption spectrum is almost flat since the absorbancies of the two species complement each other), then green (MnO$_4^=$) and much later yellow-brown (MnO$_2$). These color changes varied with the order of mixing. If BH$_4^-$ was added to MnO$_4^-$, the following sequence was seen: pink, grey, green and then yellow-brown. If the reverse addition was used the pink persisted for a longer time, instead of grey the solution looked colorless, and the solution did not get as intensely green before turning yellow-brown. This paper reports a study of these reactions.

Extensive studies of the reducing properties of borohydride ion toward organic oxidants have been published.[1] However, relatively few reactions[2,3] of BH$_4^-$ with inorganic species have been intensively investigated. Permanganate oxidations of inorganic ions in basic solution resulting in MnO$_4^=$ have been investigated,[4] but only in a few cases are the kinetics known.[5-8] Jensen[9] was the first to study the BH$_4^-$ reduction of MnO$_4^-$; he investigated this reaction as a basis for a quantitative potentiometric titration.

We became interested in this reaction for two reasons. First, it is an oxidation of analytical interest occurring in strongly basic solution in contrast to the iodometric[9] or gas evolution[9] methods which are performed in acid solution. Second, the rate of reaction[8] approaches the speed of the "electron transfer" reaction[10] between permanganate and manganate.

Experimental

The reactions of BH$_4^-$ in basic solutions were examined with initial concentrations of BH$_4^-$ from 0.002 to 500 mM, of MnO$_4^-$ from 0.02 to 500 mM and in OH$^-$ from 10 to 200 mM. The ratio of inital concentrations of MnO$_4^-$ to BH$_4^-$ after mixing was varied from 0.5:1 to 33:1. The effect of the order of mixing was investigated. For convenience, the discussion of the experiments has been divided into the following: (a) gas evolution, (b) spectrophotometry, (c) potentiometry, (d) chemical analysis by separation and (e) kinetics.

(a) **Gas Evolution.**—In base concentrations from 0.05 to 0.2 M the addition of 0.4 M MnO$_4^-$ to 0.04 M BH$_4^-$ or the reverse liberated only one gas, H$_2$. An experiment using borohydride in heavy water showed that all the hydrogen liberated is derived from the hydridic hydrogens of the borohydride ion.

The volume of H$_2$ gas evolved was followed as 0.15 M MnO$_4^-$ was added in dropwise increments to 0.5 M BH$_4^-$ in 0.1 M OH$^-$. Each addition of MnO$_4^-$ evolved 0.33 of moles H$_2$ per mole of MnO$_4^-$, until 2.3 moles of MnO$_4^-$ had been added per mole of BH$_4^-$, after which no more H$_2$

(1) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

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

(3) T. Freund, *J. Inorg. Nucl. Chem.*, **9**, 264 (1959).

(4) A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 435 (1953).

(5) M. C. R. Symons, *ibid.*, 3956 (1953).

(6) A. Webster and J. Halpern, *Trans. Faraday Soc.*, **53**, 51 (1957).

(7) R. Stewart and R. Van der Linden, *J. Canadian Chem.*, **38**, 2237 (1960).

(8) T. Freund, *J. Inorg. and Nucl. Chem.*, **15**, 371 (1960)

(9) E. H. Jensen, "A Study of Sodium Borohydride," Nyt Nordisk Forlang, Copenhagen, 1954.

(10) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957).
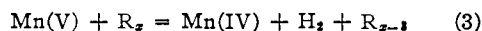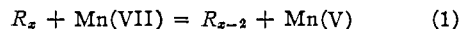
was produced on further addition of MnO_4^-. At this sharp "end-point" no BH_4^- was left as shown by the lack of gas evolution when the solution was acidified.

In contrast the reverse addition, dropping BH_4^- into MnO_4^-, liberated less than half the amount of hydrogen; and a plot of moles of hydrogen liberated on the ordinate vs. moles of BH_4^- added on the abscissa gives an "S" shaped curve. The gas evolution ceased at 2.0 moles of MnO_4^- per mole of BH_4^- added, giving a total of 0.3 mole of hydrogen per mole of borohydride. As expected, more rapid mixing, with either order of addition, gave intermediate values for the amount of hydrogen produced.

This H_2-producing reaction does not involve the reduction of MnO_4^- since H_2 was still produced in large amounts when MnO_4^- was added to a BH_4^- solution containing Ba^{++}. The above reasoning is based on the assumption that the reportedly[11] fast precipitation of $BaMnO_4$ is faster than the reduction of MnO_4^- in this reaction system. Further confirmation is found in the following experiment. When a drop of MnO_4^- was allowed to fall into a BH_4^- solution, no visible gas bubbles formed. The drop technique is capable of showing H_2 formation since bubbles were observed when MnO_4^- was dropped into a BH_4^- solution.

Although bubbles of gas appeared to be released from the surface of the MnO_2 particles when a drop of MnO_4^- fell into a solution of BH_4^-, no bubbles were seen when BH_4^- was added to freshly prepared MnO_2 suspensions. We interpret the above as evidence that the MnO_2 is not catalyst for the decomposition of BH_4^- but that the H_2 and MnO_2 are formed simultaneously.

These experiments as well as those described in later sections are consistent with the hypothesis that some of the Mn(VII) (permanganate) is reduced to Mn(V) (hypomanganate) followed by two competing reactions of the Mn(V). The first is oxidation by Mn(VII) (reaction 2) and the second is reduction with the liberation of hydrogen gas (reaction 3). Let R_x represent a reducing species, borohydride or some partially oxidized species derived from the borohydride ion. "x" represents the number of equivalents per mole of reducing capacity and is eight for BH_4^-. Reaction 2

$$R_x + Mn(VII) = R_{x-2} + Mn(V) \quad (1)$$

$$Mn(V) + Mn(VII) = 2Mn(VI) \quad (2)$$

$$Mn(V) + R_x = Mn(IV) + H_2 + R_{x-1} \quad (3)$$

is reported[12] to be very fast. With a high Mn(VII) to BH_4^- ratio (dropping borohydride into permanganate) less hydrogen should be produced because of the predominance of reaction 2 over reaction 3. One cannot say whether the path represented by reaction 3 occurs in one step or not, nor whether the reducing agent is borohydride or some intermediate. It is interesting that the hydrogen does not come from the solvent, in contrast to other reactions of borohydride which liberate hydrogen. Previously, we have shown that the hydrolysis of borohydride in heavy water[3] yields hydrogen deuteride and that the hydrogen accompanying the reduction of ferricyanide also contains solvent hydrogen.[3]

(b) **Spectrophotometry.**—Spectrophotometric examinations for MnO_4^- and MnO_4^- were made at 530 and 610 mμ, respectively, for solutions with ratios of initial molar concentrations of MnO_4^- to BH_4^- of 0.5:1 to 33:1. Although the presence of MnO_2 affected the absorbancy measurements, certain features were clearcut. In all cases the number of moles of MnO_4^- reduced was greater than the number of moles of MnO_4^- formed. In dilute solution even at the lowest ratio of MnO_4^- to BH_4^- not all the MnO_4^- was reduced to manganese dioxide. For MnO_4^-/BH_4^- ratios of 5:1 to 33:1 (excess of MnO_4^-) approximately four moles of MnO_4^- react per mole of BH_4^- and three moles of MnO_4^- are produced. In more concentrated solution where the manganese dioxide coagulation is more complete it was found that 1.0 mole of manganese dioxide was formed per mole of borohydride reacted. Even with large excesses of Ba^{++} and MnO_4^- it was not possible to stop the reaction at the manganese stage. This was in contrast to experiments with other reducing agents which were studied by Drummond and Waters.[4]

The change in absorbancy at appropriate wave lengths in the visible and the ultraviolet during the reaction was exam-

ined for absorbing species such as hypomanganate. Nothing was found that could not be ascribed to MnO_4^- or MnO_4^-.

The very beautiful color changes described in the Introduction are consistent with reactions 1, 2, 3. Three differences in the color changes were observed depending on whether BH_4^- was added to MnO_4^- or MnO_4^- to BH_4^-. The pink stage persisted longer when MnO_4^- was added to BH_4^-. This can be ascribed to the formation of relatively less MnO_4^- (green) than MnO_2 (colorless before polymerization) and hence the pink was not masked by the green. This would be expected when reaction 3 predominated over reaction 2. The second difference was that the second color-stage was colorless when MnO_4^- was added to BH_4^- in contrast to grey when BH_4^- was added to MnO_4^-. The apparent lack of color indicated lower concentrations of both MnO_4^- and MnO_4^-. Again reaction 3 should predominate over reaction 2 since BH_4^- was in excess. The third difference was the lower intensity of the green (third color-stage) when MnO_4^- was added to BH_4^-. Again, if reaction 3 predominated over reaction 2, less MnO_4^- would be produced before the green color is masked by the yellow-brown of polymerized MnO_2.

(c) **Potentiometric.**—As Jensen[9] reported, a potentiometric titration (platinum versus calomel electrodes) could be made with fair precision by titrating BH_4^- with MnO_4^-. He assumed the end-point corresponded to the reaction

$$3BH_4^- + 8MnO_4^- = 3BO_2^- + 8MnO_2 + 8OH^- + 2H_2O$$
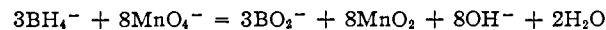
With more dilute solutions, we also found a sharp end-point, but it came between seven and seven and one-half equivalents of borohydride. However, we found that the reverse titration was useless giving very small potential changes which were time dependent. Interestingly enough, Ba^{++} was almost without effect on the titration. These potentiometric studies confirm that the course of the reaction is dependent on the order of addition and that MnO_4^- is produced by a secondary reaction.

Polarographic studies also were made. The anodic BH_4^- wave is known[2] to be irreversible on Hg. Attempts were made to use a spinning platinum electrode in order to go more anodic than mercury will allow. No steady potentials were obtained.

(d) **Chemical Analysis by Separation.**—Several complete chemical analyses of the reaction were made on solutions with initial concentrations: 0.03 mM BH_4^-, 0.3 mM MnO_4^- and 50 mM OH^-. The procedure after rapidly mixing the reactants was: Toepler pump to remove hydrogen gas for mass spectrometric analysis, addition of tetraphenylarsonium chloride (TPAC) to precipitate the MnO_4^- as $TPAMnO_4$, filter to remove the precipitated MnO_2 and $TPAMnO_4$, spectrophotometrically analyze for MnO_4^- in a sample of the filtrate, to the rest of the filtrate add Ba^{++} to precipitate the MnO_4^- leaving only BH_4^- in solution. The BH_4^- was titrated iodometrically to a potentiometric end-point. The first precipitate containing MnO_2 and $TPAMnO_4$ was extracted with pyridine previously distilled from $KMnO_4$ under N_2. The resulting pyridine solution containing $TPAMnO_4$ was analyzed spectrophotometrically for MnO_4^-. The remaining manganese dioxide pad was dissolved in concd. HCl, evaporated to dryness and then oxidized to MnO_4^- with IO_4^- in aqueous H_3PO_4.

The results of the analyses were slightly less than 4 moles of MnO_4^- reacted per mole of BH_4^- to yield 3 moles of MnO_4^-, 0.7 mole of MnO_2 and 0.5 mole of H_2.

Certain qualitative experiments were performed that also shed some light on the mechanism of the reaction. The lack of precipitation of $TPAMnO_4$ when TPAC was added to a solution of Mn(VI) and BH_4^- showed that the sequence

$$Mn(VII) \longrightarrow Mn(V) \longrightarrow Mn(IV) + Mn(VII)$$
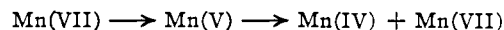
is not important. It had been shown previously that MnO_4^- reacts very slowly with borohydride. In addition we found that I_3^- could not generate an intermediate derived from BH_4^- that can reduce MnO_4^-.

(e) **Kinetic Studies.**—Some forty experiments were made by either following the disappearance of permanganate at 530 mμ or the appearance of manganate at 610 mμ with a Beckman DK1 spectrophotometer. For the more rapid reactions the output of the photomultiplier tube was amplified by a d.c. amplifier whose output was recorded on a Visicorder. Three types of mixing were used. For the highest concentrations, degassed reactant solutions were forced by nitrogen pressure to mix in a 1.5 mm. three way

(11) A. Carrington and M. C. R. Symons, J. Chem. Soc., 3676 (1954).
(12) A. Carrington and M. C. R. Symons, ibid., 3373 (1956).

"T" stopcock and proceed into a previously evacuated cell. For some of the more dilute solutions an absorption cell with a side arm was used. For the most dilute solutions a third method involving the use of a two compartment flask and then pouring the mixed solution into the cell was employed.

The concentration ranges covered were: 0.01 to 0.1 M base, initial MnO_4^- from 0.01 to 0.5 mM and initial BH_4^- from 0.001 to 0.2 mM. The rate for each kinetic experiment was evaluated assuming first order each in BH_4^- and MnO_4^-. For about three quarters of the runs this rate constant remained constant to 25% over at least 75% of the reaction. About half of the runs gave rate constants in the range of 1500 to 2500 liter/mole-second. The rest of the runs ranged up to 70,000 liter/mole-sec. Sources of chemicals, cleaning procedures for glassware, time of standing of solutions before use, glass surface area, addition of manganese dioxide and variation in O_2 content of the solutions were without effect on the rate. The rates were measured at 20°.

Conclusion

Despite the complexity of this system (which is evident from the fact that the reducing agent contains eight equivalents per mole and manganese has many possible oxidation states) we can be confident of many features of the mechanism.

Permanganate oxidations in basic solution resulting in manganate are usually considered to proceed by one of two mechanisms. The first mechanism is by the generation of hydroxyl radicals (the active oxidizing agent) as shown by

$$MnO_4^- + OH^- = MnO_4^- + OH\cdot \qquad (4)$$

The second mechanism is a two-equivalent reduction of MnO_4^- by a reducing agent (R) to give hypomanganate which is followed by the rapid generation of MnO_4^- as shown by equations 5 and 6

$$MnO_4^- + R = MnO_4^{-3} + R' \qquad (5)$$

$$MnO_4^- + MnO_4^{-3} = 2MnO_4^- \qquad (6)$$
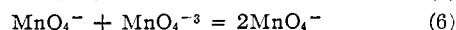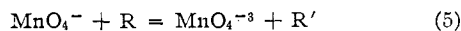
It should be noted that the hydroxyl radical mechanism implies a hydroxide ion dependence.

The evidence for the hypomanganate mechanism for the borohydride case includes: (a) the absence of a strong hydroxide ion dependence, (b) the observation that the rate of reduction of manganate by borohydride is slow, (c) the impossibility of stopping the reduction at the manganate stage

with barium and (d) the lack of influence of barium on the potentiometric manganese dioxide end-point. According to the hypomanganate mechanism, the manganate formed arises from the oxidation of hypomanganate by permanganate (reaction 2). Some of the hypomanganate follows another path —reduction to manganese dioxide with the liberation of hydrogen (reaction 3). The hydrogen producing path may consist of more than one step. The path involved in the H_2 production does not involve the catalysis of the hydrolysis of BH_4^- since all the H_2 was shown to originate from the BH_4^-. Since both manganese dioxide and manganate are found, hypomanganate must be very reactive toward both reduction and oxidation.

The transition state for a two equivalent reduction of MnO_4^- by BH_4^- may be analogous to the transition state suggested by Halpern and Taylor[13] for the $HCOO^-$ reduction of MnO_4^-. They suggest that the covalently bound H in $HCOO^-$ is transferred as a hydride to an oxygen of MnO_4^- giving Mn(V) with a formula $HOMnO_3^=$. Both BH_4^- and $HCOO^-$ are negative ions and have covalently bound H.

Speculation on the transition state for the reaction producing H_2 should wait until it is known whether both hydrogen atoms come from the same ion of BH_4^- or a poly-boron species is involved.

All reductions by borohydride have been reported to be kinetically first order in borohydride.[2,3,9] The order with respect to oxidants has been reported to be one for organic oxidants and zero for ferricyanide.[3] The order with respect to acid is one for water,[2,14,15] one for ferricyanide[3] and has not been reported for organic oxidants. The MnO_4^-–BH_4^- reaction is the first for which no acid dependence has been found.

Acknowledgment.—Mr. R. Fox assisted with some of the experiments.

(13) J. Halpern and S. M. Taylor, *Disc. Faraday Soc.*, **29**, 177 (1960).

(14) J. B. Brown and M. Svenson, *J. Am. Chem. Soc.*, **79**, 4241, 6581 (1957).

(15) R. E. Davis and C. G. Swain, *ibid.*, **82**, 5949 (1960).

Decaborane, "6-Benzyl" B₁₀H₁₃ Chemistry

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Benzyldecaborane has been prepared by alkylation of decaboranylsodium with benzyl bromide in ether solution. Chemical, mass spectral and n.m.r. evidence lead to the conclusion that the benzyl group is substituted on either the 1 or 6-boron atom of decaborane. Arguments are presented for the preferred 6-position. Decaboranylsodium in ether reacts with iodine to produce iododecaborane, ethoxydecaborane and ethoxyiododecaborane.

Introduction

Decaborane (I), a strong monoprotic acid in water–alcohol and water–dioxane solutions, can be titrated potentiometrically with a strong base. Back titration with aqueous hydrochloric acid re-

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produces the titration curve, and I may be recovered in good yield from the acidified solution.[2] I behaves as a weak monoprotic acid in acetonitrile and as a stronger diprotic acid in dimethylformamide.[3]

(2) G. A. Guter and G. W. Schaeffer, *J. Am. Chem. Soc.*, **78**, 3546 (1956).

(3) R. Atterberry, *J. Phys. Chem.*, **62**, 1458 (1958).