to form HF. On the other hand, it is reasonable to assume that an electron transfer reaction of the type $PhH + F \rightarrow PhH^+ + F^- \rightarrow Ph + H^+ + F^-$ may take place.

This reaction is analogous to that of nitrite ions which were also found to be efficient scavengers: $NO_2^- + F \rightarrow NO_2 + F^-$. It is suggested that aromatic compounds scavenge *fluorine atoms* by electron transfer rather than by a hydrogen transfer process, because compounds of higher pi-electron density are shown to be relatively better scavengers (3.4–3.5, 3.16–3.17). The lower labelling yields of aromatic compounds with high pi-electron density may be explained by the competitive scavenging property of these compounds, because the homolytic substitution by fluorine atoms should hardly be affected by *ortho–para* directing substituents. A similar behavior of aromatic compounds was observed towards OH radicals.[16]

It may be concluded therefore that fluorine atoms are the active species in organic systems; their behavior in aqueous solutions is discussed below.

Formic acid and nitrite ions act as scavengers in aqueous solutions (4.14, 4.15, 416); higher values of E_H are obtained for aliphatic as compared with aromatic solutes at equal concentrations (4.7–4.26; 4.9–4.12; 4.11–4.21) and higher labelling yields are obtained for phthalic acid as compared with benzoic acid (4.17–4.23) and for benzoic acid as compared with phenol (4.12; 4.25). All these findings are in complete agreement with the results obtained in non-aqueous systems, and it is reasonable to assume that the same mechanism prevails in both media.

The fact that the labelling efficiency per hydrogen of solute (E_H) increases significantly in dilute solutions again exludes the participation of "hot" fluorine atoms, and it means that water is a relatively poor competitor for fluorine atoms when compared with organic substrates. Water may react with fluorine atoms in three ways: either by hydrogen abstraction $F + H_2O \rightarrow HF + OH$, by direct substitution $F + H_2O \rightarrow FOH + H$ or by electron transfer $F + H_2O \rightarrow F^- + H_2O^+$; $H_2O^+ \rightarrow H^+ + OH$. The direct substitution reaction seems energetically less probable compared with the hydrogen abstraction. It was shown that at $pH = 13$ no appreciable scavenging effect is observed (4.4–4.5, 4.12–4.13) due to the reaction $F + OH^- \rightarrow F^- + OH$; this suggests that the electron transfer processes in aqueous solutions may be of little importance as compared with the hydrogen abstraction reaction. It should be noted that this hydrogen transfer process is a rather slow process when compared with hydrogen substitutions on a carbon atom. It might be stated that the fluorine atoms have a finite lifetime in aqueous solutions, long enough to interact with electron donors like nitrite ions or with hydrocarbons. A question of interest is the chemical structure of a solvated fluorine atom in water, however little can be inferred from the results of the present study.

(16) M. Anbar and M. Bobtelsky, to be published.

[CONTRIBUTION FROM THE GENERAL DYNAMICS/CONVAIR SCIENTIFIC RESEARCH LABORATORY, SAN DIEGO, CALIFORNIA]

The Kinetics of the Reduction of Iodate Ion by Borohydride Ion in Basic Aqueous Solutions

BY T. FREUND[1a] AND N. NUENKE

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In this study it was shown that the chemistry of basic aqueous solutions containing IO_3^- and BH_4^- can be described by two independent chemical reactions: $BH_4^- + 2H_2O = BO_2^- + 4H_2$ and $3BH_4^- + 4IO_3^- = 3BO_2^+ + 4I^- + 6H_2O$. The rate of disappearance of IO_3^- is first order in IO_3^-, BH_4^-, H^+ and independent of I^-. The third order specific rate constant at 25° is $7.4 \times 10^7\ M^{-2}\ \text{sec.}^{-1}$ and has a temperature coefficient corresponding to an activation energy of 7.9 kcal. The rate of disappearance of BH_4^- was shown to be given by the expression $k_H[H^+][BH_4^-] - {}^3/_4 d[IO_3^-]/dt$, where k_H is the specific rate constant for the hydrolysis of BH_4^-. The mechanism of the iodate reaction will be considered in terms of the various oxidation states of iodine. Also the behavior of this chemical system will be compared with our previous work on the reactions of BH_4^- with $Fe(CN)_6^{-3}$, MnO_4^-, Sn(III) and $(CH_3)_2CO$.

Introduction

This investigation was undertaken as part of a series of studies on the mechanisms of the reduction of common oxidizing agents by the borohydride ion in aqueous solutions. The mechanisms for aqueous borohydride reductions have been investigated for water,[1a-6] for ferricyanide,[7,8] for permanganate[9] and for antimonyl tartrate.[10] Some chemical studies[5,11,12] have been made in which the kinetics were not investigated.

Our kinetic studies of the ferricyanide and hydrolysis reactions have shown that the rate determining step for both reactions is the same; the activated complex has the chemical composition, $H^+BH_4^-$. In contrast, the kinetics of the permanganate reaction show that the activated complex of the rate determining step contains only permanganate and borohydride ions but no hydrogen ion.

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This paper reports a third type of activated complex for borohydride reactions; the activated complex for the rate determining step of the reaction of iodate with borohydride contains three ions, borohydride, iodate and hydrogen.

Experimental

Materials.—Triple-distilled water was used throughout. Sodium or potassium borohydride, both recrystallized and unrecrystallized (98+%), was used. The rest of the substances were reagent grade. Appropriate buffers of HPO_4^{-2}-PO_4^{-3}, $H_2PO_4^-$-HPO_4^{-2}, HCO_3^--CO_3^{-2} and OH^- were used to maintain constancy of the hydrogen ion concentration for the individual experiments which ranged from *p*H 9.8 to 13.0. In most experiments $NaClO_4$ or KCl was used to bring the reaction mixtures to an ionic strength of 0.7.

Analytical Procedures. IO_3^-.—The iodate concentration was determined either polarographically or spectrophotometrically. In the polarographic procedures[13] a dropping mercury electrode, maintained at −1.6 volts *vs.* s.c.e., was used to measure the iodate diffusion current. The spectrophotometric procedure was to measure the absorbancy at 276 mμ where the molar extinction coefficient for iodate is 11.45 and for iodide is 1.10.

BH_4^-.—Only titrimetric procedures were used since borohydride does not absorb either in the near ultraviolet or visible regions of the spectrum and since iodide interferes with the polarographic determination of borohydride. The Jensen[5] iodometric procedure for the titration of borohydride is to add a known excess of iodate and an excess of iodide to a basic solution containing borohydride and then add sufficient acid to make the solution *p*H 0–1. After waiting two minutes, the excess tri-iodide is titrated with thiosulfate. Jensen's procedure was followed closely, with the exception that the titration was begun immediately after acidification. We found that the two minute waiting period was unnecessary and that this procedure is quantitative even at concentrations lower than 0.01 millimolar when the end-point is detected potentiometrically.

For a solution containing iodate in addition to borohydride, the determination of borohydride by the iodometric method depends on the concentration of iodate in the solution. Therefore, in some cases a titration for borohydride was performed by the hypobromite method,[14] which is independent of the iodate concentration.

H^+.—The hydrogen ion was determined with a glass electrode at the temperature of the reaction. The standardization of the glass electrode was performed at the reaction temperature on standard buffers.

Experimental Procedures. Stoichiometry.—The stoichiometry of the BH_4^--IO_3^- reaction was established from experiments involving measurements in two solutions. In a BH_4-IO_3^- solution, the changes in concentration of iodate and of borohydride were measured. In a solution identical with the first, except that the iodate was replaced on a mole basis with an inert salt, the borohydride hydrolysis was measured. The borohydride was measured by the iodometric titration and the iodate either polarographically or spectrophotometrically.

Rate of Hydrolysis.—The rate of hydrolysis of BH_4^- was measured in buffered solutions identical with the iodate-containing reaction mixture except that the iodate was replaced with an inert salt in order to avoid changes in ionic strength.

Rate of IO_3^--BH_4^- Reaction.—The rate of reaction was determined in a buffered solution at ionic strength of 0.7 by one of three procedures, A, B or C, depending on the concentration range and ratio of reactants to be investigated. In general, the borohydride salt was dissolved in the basic constituent of the buffer and the potassium iodate was dissolved in the acidic constituent. The two solutions were brought to the desired temperature and mixed. The mixture was transferred to a cell kept at constant temperature. The concentrations in the reaction mixture were generally followed to 90% completion of the reaction. Procedure A employed a dropping mercury electrode to follow the iodate concentration continuously. This polarographic method was limited to concentrations of iodate no greater than 4 m*M* and became quite inaccurate below 0.2 m*M*. Procedures B and C were employed for reaction solutions which contained BH_4^- and IO_3^- of comparable concentrations. In both procedures aliquots from the reaction mixture were quenched by the addition of base, resulting in a solution 0.2 *F* in NaOH. In procedure B only spectrophotometric analyses for iodate were made. In procedure C, analyses for both iodate and borohydride were made.

Methods of Calculation. Stoichiometry.—These calculations were used to show that the borohydride ion in an alkaline solution containing iodate disappears by two independent paths: hydrolysis and reaction with iodate. These two paths can be described by

$$BH_4^- + 2H_2O = BO_2^- + 4H_2 \qquad (1)$$

$$3BH_4^- + 4IO_3^- = 3BO_2^- + 4I^- + 6H_2O \qquad (2)$$

The rate of hydrolysis of borohydride in a buffered solution in the absence of iodate is given by

$$-d[BH_4^-]/dt = K_H[BH_4^-] \qquad (3)$$

The rate of disappearance of borohydride in a buffered solution containing iodate when two independent paths exist is given by equation 4, where "*a*" is the number of moles of borohydride consumed by reaction with one mole of iodate.

$$-d[BH_4^-]/dt = -a\ d[IO_3^-]/dt + K_H[BH_4^-] \qquad (4)$$

The integrated form of equation 4

$$\Delta[BH_4^-] = a\ \Delta[IO_3^-] + K_H \int [BH_4^-]dt$$

was used to evaluate "*a*."

Hydrolysis Rate.—The specific rate constant for hydrolysis K_H was evaluated from the slope of a plot of log borohydride concentration *vs.* time.

IO_3^- Rate, Procedure A.—In these experiments the borohydride concentrations were very much larger than the iodate concentration. Therefore, negligible error is made in the calculation of K_I by assuming that all the borohydride disappears by the hydrolytic path. Thus, the borohydride concentration at time *t*, $[BH_4^-]$, is given in terms of the initial borohydride concentration $[BH_4^-]_0$, by equation 5 which is the integrated form of equation 3. Equation 6

$$[BH_4^-] = [BH_4^-]_0 \exp(-K_H t) \qquad (5)$$

$$-d[IO_3^-]/dt = K_I[BH_4^-][IO_3^-] \qquad (6)$$

describes the rate of disappearance of iodate in a buffered solution. If equation 5 is substituted into equation 6 and equation 6 is then integrated, equation 7 results.

$$\ln [IO_3^-]_0/[IO_3^-] = K_I[BH_4^-]_0\{1 - \exp(-K_H t)\}/K_H \qquad (7)$$

IO_3^- Rate, Procedure B.—In procedure B the BH_4^--IO_3^- reaction mixture was analyzed for iodate only. Equation 8, from which the specific rate constant was evaluated, requires for borohydride only a knowledge of the initial concentration in addition to the specific rate constant for hydrolysis. This equation does not involve any approximations and is based solely on equations 4 and 6.

$$K_I = \frac{\Delta \ln [IO_3^-] + K_H \int_1^2 \ln \{[IO_3^-]_0/[IO_3^-]\}dt}{\Delta t\{[BH_4^-]_0 - {}^3/_4[IO_3^-]_0\} + {}^3/_4 \int_1^2 [IO_3^-]\ dt} \qquad (8)$$

IO_3^- Rate, Procedure C.—In this procedure the reaction solution was analyzed for both iodate and borohydride. If both analyses are performed it is not necessary to measure the hydrolysis rate since the iodate rate constant can be evaluated from

$$\log [IO_3^-]_1/[IO_3^-]_2 = K_I \int_1^2 [BH_4^-]\ dt \qquad (9)$$

Results

Stoichiometry.—The values of "*a*" averaged 0.8. This value is considered to be in agreement with 0.75, the value predicted by equation 2. These experiments established that the chemistry of the borohydride–iodate reaction mixtures can be described by two independent chemical reactions, hydrolysis of borohydride (equation 1) and oxidation of the borohydride by iodate (equation 2).

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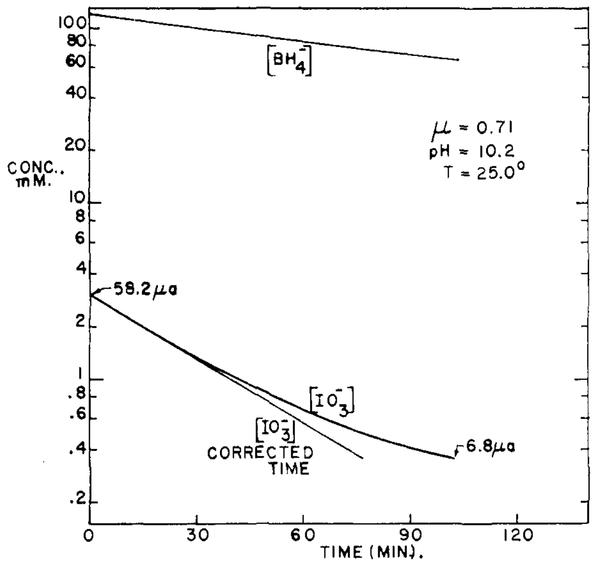

Fig. 1.—Concentrations for a typical rate determination: log [BH_4^-] *vs.* time; log [IO_3^-] *vs.* time, log [IO_3^-] *vs.* {1-exp($-K_Ht$)}/K_H, the corrected time.

Rate Experiments.—No significant specific ion effects were observed. It was demonstrated that the rate of the reaction was independent of initial concentration of the reduction product, iodide, by varying the ratio of initial concentrations of iodide to iodate from zero to eight. The order of mixing the reactants, illumination under conditions that reaction was normally studied, and oxygen were shown to be kinetically unimportant.

Data from one typical experiment, treated by equation 7, are shown in Fig. 1. The borohydride and iodate concentrations are shown as a function of time. According to equation 7, a plot of {1-exp(-K_Ht)} ,K_H, called "corrected time", against log [IO_3^-] should be linear if the reaction is first order in iodate. From the slope of the straight line shown in Fig. 1, the specific rate constant, K_I, was evaluated.

Plots of the values of log K_I and log K_H against pH showed no indication of deviation from linearity and both had the same slope of minus one. Therefore, a pH independent rate constant k can be defined, $\log k = (\log K + \text{pH})$. At 25° the value of the third order iodate rate constant k_I is $7.4 \times 10^{-7}\ M^{-2}$ sec.$^{-1}$ and the value of the second order hydrolysis rate constant k_H is $1.6 \times 10^6 M^{-1}$ sec.$^{-1}$.

The initial concentrations of iodate varied from 3 to 100 mM and for borohydride from 10 to 500 mM. The ratio of initial concentrations of borohydride to iodate varied from 0.5 to 150. The concentrations of reactants in each mixture were determined until 90% of the reaction was completed. No experimentally significant deviation from first order in each H^+, BH_4^- and IO_3^- was found.

The rates for the hydrolysis and the iodate reactions were measured in the temperature range from 10 to 40°. Carbonate-bicarbonate buffers adjusted to pH = 10.2, measured at the reaction temperature, were used. The activation energy for the hydrolysis reaction was calculated to be 9.9 kcal., and for the iodate reaction 7.9 kcal. Since no significant specific ion effects were observed at 25°, it was considered proper to assume that these activation energies describe the reaction at other *p*H values adequately.

Qualitative Experiments.—The reduction of iodate ion (oxidation state +5) to iodide (oxidation state-1) may proceed by several elementary reactions involving various intermediate oxidation states of iodine. No evidence could be found for the build up of an iodine (+1) species, iodine or tri-iodide by ultraviolet and visible spectrophotometric investigation of the reacting solutions. Recent[15] careful studies of iodine (O) and +1) indicate that (+1) should not be stable at the hydrogen ion concentrations used in our investigations.

Qualitative experiments indicate that I (+1), stabilized by chloride ion, reacts extremely rapidly with borohydride ion.

Qualitative experiments also established that tri-iodide reacts many orders of magnitude faster than iodate with borohydride.

It was also shown that the rate of reaction of tri-iodide with borohydride is not very much faster than the rate of hydrolysis. When we added a basic borohydride solution to an acid solution containing twice the number of equivalents of I_3^-, we found that only about $^3/_4$ of the borohydride reacts with the iodine; the rest of borohydride hydrolyzes. Care was taken to insure that the resulting solution would be more than 0.1 M in acid.

It was also shown that a hydrolytic path for the borohydride ion was still important in very acid solutions containing iodate. When we added an alkaline borohydride solution to an acid solution containing twice the number of equivalents of IO_3^-, we found that no more than $^5/_8$ of the borohydride reacts with the iodate; the rest of the borohydride hydrolyzes. The iodate solution was initially 0.08 M in acid and after completion of the addition of the borohydride solution the reaction mixture was at least 0.07 M in acid.

Discussion

The only mechanistic conclusion that can be drawn from the rate law for the reaction of borohydride with iodate is that the transition state for the rate determining step involves three ions, H^+, BH_4^-, IO_3^-, or species in equilibrium with these ions. Necessarily, the reactions subsequent to this rate determining step are faster.

However, certain other experiments (carried out by us and others) give considerable information concerning the reactions subsequent to the rate determining step. Discussions of the Jensen iodometric procedure, and reaction of borohydride with zero valent iodine, with IO^+, and with IO^-, are presented below.

In Jensen iodometric procedure one starts with an alkaline solution containing iodide, iodate and borohydride ions. Upon acidification it is found that all the borohydride reacts with the iodate and none of the borohydride hydrolyzes. The iodide must play an important role in this procedure since we have shown that in acid solutions containing

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(15) R. E. Connick, E. E. Genser and Y. T. Chia, 140th American Chemical Society Meeting, Chicago, September, 1961.

only iodate and borohydride, a large fraction of the borohydride undergoes hydrolysis.

It has been reasonable to assume that the mechanism of the Jensen titration is described by reaction 10 followed by reaction 11

$$IO_3^- + 8I^- + 6H^+ = 3I_3^- + 3H_2O \quad (10)$$

$$4I_3^- + BH_4^- + 2H_2O = 12I^- + HBO_2 + 7H^+ \quad (11)$$

Our experiments have shown that the rate of reaction of tri-iodide in acid solution is not much faster than hydrolysis. Hence, the mechanism of the Jensen titration can not be reaction 10 followed by reaction 11, since this would lead to a titration error due to hydrolysis. Intermediate oxidation states of iodine such as +3 or ±1 must be formed and one or more of these must react faster than the zero valent state.

Furthermore, the rate of *generation* of tri-iodide in the Jensen procedure is not fast enough to compete with the rate of hydrolysis of borohydride. This deduction is based on the assumption that the reported rate laws for the hydrolysis of borohydride, and for the generation of tri-iodide[16] from iodate and iodide, both hold at high acidities.

Therefore, it seems likely that borohydride in the Jensen procedure reacts with an intermediate oxidation state of iodine such as IO^+ or IO^- to yield iodide. Jensen has shown that nearly a 100% excess of IO_3^- (2.67 moles iodate per mole borohydride) is required in order to get a quantitative titration. One possible explanation for this requirement is that rapid reactions involving iodate and iodide generate one mole of +3 iodine per mole of iodate. The +3 iodine, such as IO^+, then reacts with boron-containing reducing species to yield I^- at a rate which can successfully compete with the hydrolysis of borohydride. It is presumed that the other oxidation states of iodine do not react rapidly with boron-containing reducing species but rather with iodine-containing species which ultimately result in the formation of I_3^-. Such a scheme requires at least 2 moles of iodate in the Jensen titration.

Additional support for the above mechanism can be found from the suggestion[17] that one mole of IO^+ is produced per mole of iodate in acid solutions containing iodide.

Finally, in preliminary experiments we have found that hypobromite reacts faster than hypochlorite with borohydride in basic solutions. We expect that hypoiodite will react at an even faster rate. We plan to commence a detailed study of the reactions of borohydride with +1 halogens.

It should be pointed out that the kinetic rate law for the iodate reaction stands in contrast to the rate laws found for other oxidants with borohydride. No other system, yet investigated, has shown first order in all three species: oxidant, hydrogen ion and borohydride ion. The order with respect to oxidants has been reported to be zero for ferricyanide[7,8] and one for ketones[5,6,18] and permanganate.[9] The order with respect to hydrogen ion is zero for permanganate[9] and acetone[18] and one for water[2-5] and ferricyanide.[7,8] Like the iodate reaction, all the reactions which have been reported are first order in borohydride.

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[CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS]

Basicities of the Methyl Benzenes. II. Induction in the L.C.A.O.–M.O. Framework

BY S. EHRENSON[1]

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The quantum chemical examination of the methylbenzene-methylbenzenium ion equilibria previously described has been extended to evaluate the importance of methyl inductive effects upon these equilibria. Employing the same semi-empirical M.O. methods as used in evaluating the methyl hyperconjugative effects, one finds that an unrealistically large inductomesomeric effect must be assigned to methyl to reproduce the relative experimental basicities, if the latter is assumed to be the sole effect. A combined model, however, where hyperconjugation accounts for two-thirds of the total effect is found to better correlate with these basicities than does either single model alone. Realistic parameter choices are used with this combination model. The theoretical results are also presented and discussed in terms comparable with the Taft $\rho\sigma$ equation where resonance and inductive effects have been separated. Some comparisons are drawn with n.m.r. results recently obtained for a number of aromatic carbonium ions.

Introduction

The conclusion was reached in an earlier paper[2] that the equilibrium basicity order of the methyl benzenes could be satisfactorily explained in terms of hyperconjugative stabilization of the product cations. The appropriate (linear combination atomic orbitals–molecular orbitals) semi-empirical self-consistent energy differences (cation minus neutral aromatic) could be quantitatively correlated with two sets of experimental data on the protonation reactions in HF media.[3,4] The results of a later, independent and more careful study of six of the thirteen aromatics[5] while qualitatively in agreement with the previous work indicated a generally greater spread between the equilibrium constants ($K_{eq.}$). Comparison of these latter results with those of the theory suggested an addi-

(1) This work was assisted by the Office of Naval Research. Computations carried out at Wright Air Force Development, Dayton, Ohio.

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