the heat of formation of boron carbide. Thus

$$\Delta Hf^0_{298} = -603.5 - 94.05 + 683.8 = -13.8 \pm 2.7 \text{ kcal./mole}$$

The entropies of boron, carbon and boron carbide have been tabulated by the Bureau of Standards[5] and from them one calculates that the standard entropy of formation of boron carbide is $\Delta Sf^0_{298} = -0.53$ eu. Combination of this value with that for heat of formation leads to the standard free energy of formation

$$\Delta Ff^0_{298} = -13.6 \pm 2.7 \text{ kcal./mole}$$

The results presented in this paper may be combined with other thermochemical data to give the heat of reaction for atomization of boron carbide.[7] One obtains

$$B_4C(c) = 4B(g) + C(g);\ \Delta H^0_{298} = 748.3 \text{ kcal.} \quad (2)$$

The lattice energy (average) per atom will be one-fifth of this value, or 149.7 kcal. It is interesting to observe that this value lies between those of boron and graphite as shown in Table II.

TABLE II

LATTICE ENERGIES PER GRAM ATOM AT 25°, IN KCAL.

B	140.9	Ref. 7
B_4C	149.7	This work
BN	157.3	Calcd. from ref. 2 using $D(N_2)$ = 225.93[8]
C	170.9	Ref. 8

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[7] The other values taken were: heat of sublimation of carbon to monatomic vapor, 170.9 kcal./mole (ref. 8); heat of vaporization of boron to monatomic vapor, 140.9 kcal./mole (Searcy and Myers, presented A.C.S. Meeting, Los Angeles, 1953).

[8] L. Brewer, private communication.

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A Survey of the Effects of Changes in *p*H, Solvent and Salt Concentration upon the Rate of the Periodate–Glycol Reaction[1]

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RECEIVED DECEMBER 3, 1954

A quantitative study of the effect of the periodate–glycol complex upon the rate of the periodate–glycol reaction was made in an earlier paper.[3] The data for the present paper were taken before those of the previously published paper and, for the most part, before the importance of the periodate–glycol complex had been recognized.[4] It has not been possible therefore to interpret the present data with the degree of thoroughness of the earlier paper. However, certain very interesting conclusions can be made.

The Effect of Variation of *p*H.—The inhibiting effect of base upon the reaction of ethylene glycol, and *cis*- and *trans*-cyclohexandiol with periodic acid was first observed by Price and co-workers.[5,6] A more complete survey of the effect of *p*H upon the reaction of 0.0025 *M* periodic acid and ethylene glycol has shown that at 25° there is a broad maximum in the *p*H–rate curve between *p*H 2.5 and 6.0 and as either acid or base is added the rate decrease (see Fig. 1). Periodic acid is known to be dibasic and may form the monovalent ion ($IO_4^- + H_4IO_6^-$) or the divalent ion ($H_3IO_6^{=}$). If the observed *p*H–rate curve is compared with a calculated curve in which the average maximum value for the rate constant is multiplied by the ratio of the monovalent ion to total periodate at the given *p*H, good agreement between the curves is obtained in acid solution, but only fair agreement may be observed in basic solution. The reason for the latter discrepancy appears to be extensive periodate–glycol complex formation in basic solution.[7,8] Thus, it may be concluded that at 25.1° the monovalent ion is the sole reactive form of periodic acid and that the undissociated acid or the divalent ion must first be transformed to this ion before reaction can occur. This differs in part from the conclusions of Buist and Bunton[8] based on recent work at 0°. Their work will be analyzed in detail in a later paper.

For pinacol[9] and certain carbohydrates[10] the effects of *p*H change do not correlate with the observations for glycol.

Effect of Changes in Solvent.—The addition of ethanol to a reaction mixture of ethylene glycol and periodic acid in 0.0025 *M* concentrations causes a marked lowering of the rate of reaction. The data which show these trends are graphed in Fig. 2.

The decrease in rate is accompanied by a variation in activation energy. The activation energy (0.3–25.1°) decreases from 12 kcal. in pure water to 8 kcal. in 28% alcohol concentration. As the alcohol concentration is further increased the activation energy then increases to 10 kcal. in 45% alcohol. It is quite possible that this minimum in activation energy may be the result of decreased hydration of the periodate ion and decreased periodate–glycol complex formation. Both of these factors make a positive contribution to the observed activation energy.[3]

The Effects of Certain Salts.—In concentration above 0.1 *M* neutral salts of the alkali metals effect an observable increase of the rate of the periodate–glycol reaction. For any individual salt this increase is proportional to the concentration of the salt. For example, the rate of reaction of 0.0025 *M* periodic acid with 0.0025 *M* glycol is increased by a factor of 1.20 upon adding 1 *M* $NaNO_3$ at *p*H 3.5 at 24.9°.

The effect of the presence of small quantities (0.003 *M* or less) of cobalt(II) nitrate or copper(II) sulfate upon the reaction of 0.0025 *M* periodic acid and glycol at 25.1° may be well explained upon assuming the precipitation or complexing of part of the periodic acid. The acid is thereby made unavailable for reaction with the glycol. The observed rate is essentially first order with respect to the periodic acid, and upon extrapolating the apparent concentration of periodic acid back to zero

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[1] From the Ph.D. Thesis of B. Soldano, University of Wisconsin, 1949.

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[3] J. E. Taylor, THIS JOURNAL, **75**, 3912 (1953).

[4] F. R. Duke, *ibid.*, **69**, 3054 (1947).

[5] C. C. Price and H. Kroll, *ibid.*, **60**, 2726 (1938).

[6] C. C. Price and M. Knell, *ibid.*, **64**, 552 (1942).

[7] J. E. Taylor, unpublished work.

[8] G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 1406 (1954).

[9] F. R. Duke and V. C. Bulgrin, THIS JOURNAL, **76**, 3803 (1954).

[10] G. Neumuller and E. Vasseur, *Arkiv Kemi*, **5**, 235 (1953).

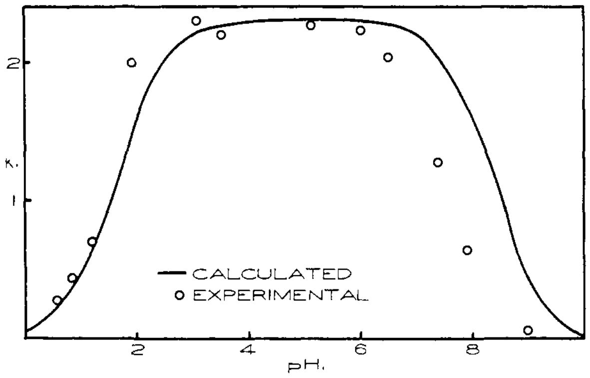

Fig. 1.—The effect of the variation of *p*H upon the second-order reaction rate constant for the reaction of 0.0025 *M* periodic acid with 0.0025 *M* glycol at 25.1°. The solutions were unbuffered in the region *p*H 0.5 to 7. In the basic solutions either phosphate or borate buffers were used. The ionization constants of periodic acid used to determine the values for the calculated curve were K_a = 0.023 and $K_b = 4.35 \times 10^{-9}$.

time it was found to be equal to the original concentration of periodic acid less one-half the molarity of the copper or cobalt ion. It is known that the insoluble salt Cu_2HIO_6 readily forms in aqueous solutions, and similarly cobalt nitrate forms a brown precipitate upon treatment with potassium periodate. It was further observed that when periodic acid is titrated by the arsenite method in the presence of either copper(II) or cobalt(II) salts an amount of the periodate, equal to one-half of the molarity of the added metal ion, is not titrable.

Some work was done on the oxidation of 2,3-butandione with periodic acid. A rapid initial reaction precedes a slower reaction. The slow part of the reaction appears to have a negative salt effect and a low activation energy. A possible explanation of the rapid and slow reactions is that there are hydrated and unhydrated forms of the butandione in solution and that these are interconverted only at a slow rate. The periodate ion may react at markedly different rates with each of the two forms or may react with only one of the two forms. Another possibility is that the periodate ion and butandione react at a fast rate and that this reaction is accompanied by the formation (at a similar or somewhat faster rate) of an inactive periodate–butandione complex. The resulting changes in the states of the reactants could account for the final slow rate of reaction.

An extensive study of *p*H and salt effects upon this reaction is to be reported soon and more detailed studies of certain other phases of this reaction have been started.

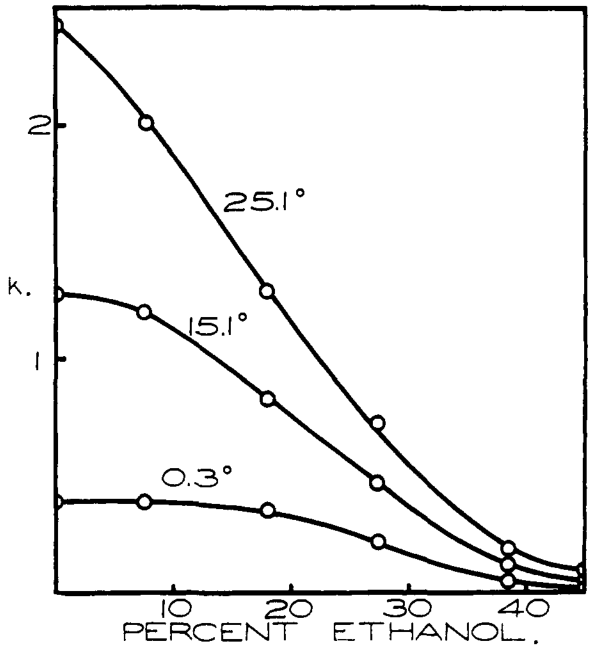

Fig. 2.—The effect of ethanol in percentage by weight upon the second-order reaction rate constant for the reaction of 0.0025 *M* periodic acid with 0.0025 *M* glycol.

Experimental

Solutions of periodic acid were made up from the dihydrate and these were standardized against standard sodium arsenite. The glycol and butandione were purified by distillation. Conductivity water was used to make up all solutions to be used in the kinetic reaction mixtures. The glycol solutions were standardized against periodic acid.

To make a typical run 75 ml. of periodic acid was placed in a 1-l. French beaker which was set into a constant temperature bath. A round dipper had previously been made by cutting off the top of a 200-ml. round bottom flask, enlarging the opening and attaching a handle. This container was then placed into the French beaker and 75 ml. of the glycol solution was added. After the solutions had come to thermal equilibrium, the solutions were mixed by inverting the dipper and quickly stirring. At appropriate times samples of the reaction mixture of about 10 ml. were removed using a small glass dipper and each sample was poured into a previously tared glass-stoppered erlenmeyer containing standard sodium arsenite, sodium bicarbonate and potassium iodide. The volume of the solution was found by reweighing the flask, and the concentration of periodic acid was determined by titrating the excess arsenite with standard iodine. The time of sampling could be determined to the nearest second or better. The accuracy of the data is of the order ±10%, which is much less satisfactory than that obtained in reference 3. Mainly the difference in accuracy was due to the use of the less reliable (for kinetic work) arsenite method of analysis.

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