and $x$ = amount of borohydride reacted at time $t$. This expression may be integrated to

$$\log [(A - x)/(B - 4x)] = (4A - B)kt/2.303 - \log (B/A)$$

The typical bimolecular plot for this equation is given in Fig. 1 for the data of run no. 2. The linearity is consistent with this postulated mechanism which is further substantiated by the fact that variation of the initial borohydride concentration does not significantly affect the rate constant (Table I, runs 3 and 5).

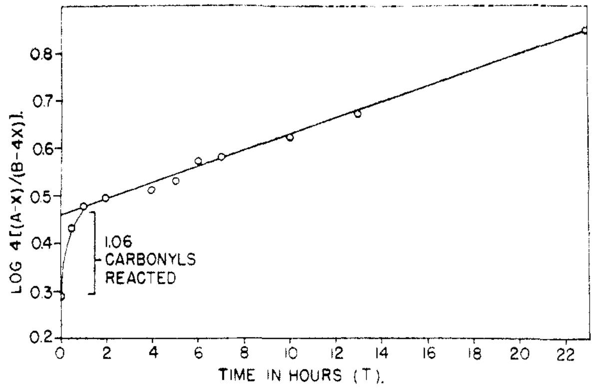

Fig. 1.—Bimolecular plot of log $4[(A - x)/(B - 4x)]$ against time ($t$) in hours at 25° in 68.5% dioxane for the reduction of the initial reducible carbonyl concentration ($B$) by the initial sodium borohydride concentration ($A$), where $x$ is the amount of borohydride reacted at time ($t$): $A$ = 0.0502 $M$ $NaBH_4$; $B/2$ = 0.0517 $M$ 11α-acetoxypregnane-3,20-dione and the initial solution is 0.0564 $M$ in NaOH.

These kinetics are also consistent with an alternative mechanism, one that does not postulate a large tetrasteroid complex with borohydride in aqueous solution or does not necessitate borohydride–steroid adducts reacting with carbonyls at faster rates than borohydride alone. This alternative mechanism would involve the rate-determining formation of a 1:1 steroid–borohydride complex which undergoes hydrolysis to a corresponding carbinol and an oxidized borohydride moiety. This moiety may subsequently react quickly in non-rate-determining steps with other molecules of carbonyl. The presence of alkali may assist in their stabilization. The sequence of equations may be written

$$R_2C{=}O + NaBH_4 \xrightarrow{k_1} (R_2CHO)NaBH_3 \quad (1)$$

$$(R_2CHO)NaBH_3 + HOH \xrightarrow{k_1'} R_2CHOH + NaBH_3(OH) \quad (2)$$

$$R_2C{=}O + NaBH_3(OH) \xrightarrow{k_2} (R_2CHO)NaBH_2OH \quad (3)$$

$$(R_2CHO)NaB(OH)_3 + HOH \xrightarrow{k_4'} R_2CHOH + NaBO_2 + 2HOH \quad (8)$$

where the rate constant $k_1$ (and/or $k_1'$) is very much smaller than the rate constants $k_2$, $k_3$, $k_4$ and the hydrolysis constants $k_2'$, $k_3'$, $k_4'$.

The wide discrepancy in reactivities of the 3- and 20-keto groups is shown in Fig. 2 for runs no. 3 and 6. The open circles represent the reduction of the diketo compound, 11α-acetoxypregnane-3,20 dione (I). The solid circles represent the reduction of the monoketo compound, 3α-hydroxy-11α-acetoxypregnan-20-one (II). The conditions at the start of this latter reaction were chosen to be exactly the same as those of the former on the assumption of instantaneous reduction of the 3-keto groups. The agreement of the data with the common line drawn through the points is confirmatory.

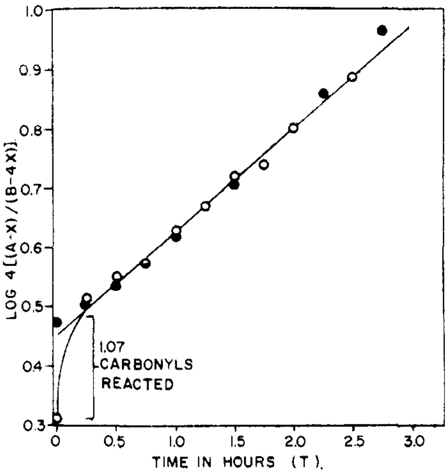

Fig. 2.—Bimolecular plot of log $4[(A - x)/(B - 4x)]$ against time ($t$) in hours at 56° in 68.5% dioxane for the reduction of the initial carbonyl concentration ($B$) by the initial sodium borohydride concentration ($A$), where $x$ is the amount of borohydride reacted at time ($t$). For the solid circles, $A$ = 0.0389 $M$ $NaBH_4$, $B$ = 0.0517 $M$ 3α-hydroxy-11α-acetoxypregnan-20-one. For the open circles, $A$ = 0.0533 $M$ $NaBH_4$, $B/2$ = 0.0517 $M$ 11α-acetoxypregnane-3,20-dione. Both reaction solutions were initially 0.0552 $M$ in NaOH.

Variation in alkali concentration has no mechanistic effect on the reduction rate as per the rate constants for runs no. 3 and 4. Run no. 4 did show an apparent rate increase near completion of the reduction of the 20-keto group which can readily be accounted for by concomitant decomposition of borohydride in a more acidic media.[5] It is indicated that alkali concentration, above the necessary minimum to stabilize the borohydride, is not kinetically significant.

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## Metal–Water Reactions. I. The Reaction between Calcium and Water Vapor*

BY DALE S. GIBBS AND HARRY J. SVEC

RECEIVED APRIL 20, 1953

During the development of an analytical method for determining the oxygen content of Ca metal, the reaction between water vapor and Ca metal was studied. In the temperature range 177 to 369° a series of distinct reactions was found. In order of occurrence these are

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* Work was performed in the Ames Laboratory of the Atomic Energy Commission.

$$2Ca + H_2O \longrightarrow CaO + CaH_2 \qquad (I)$$

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2 \qquad (II)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (III)$$

Step I takes place exclusively as long as Ca metal is present. An investigation of the reaction shown in step I indicated that the equation correctly describes the stoichiometry involved.

The solid products of the reaction maintained the shape of the original metal specimens with no spalling occurring until hydrogen began to evolve with the onset of step II. Examination of the cross sections of the reaction product specimens showed a definite band structure. When the reaction was stopped before all the Ca was consumed, five bands were observed. The compositions of these as determined by X-ray methods were: (1) pure CaO, (2) mixture of CaO and $CaH_2$, (3) pure $CaH_2$, (4) mixture of $CaH_2$ and Ca, (5) pure Ca. When the reaction was allowed to proceed until all the metal was consumed, bands (4) and (5) disappeared.

This band structure can be explained on the basis of known physicochemical properties of all the substances involved in reaction I. CaO is insoluble or very slightly soluble in Ca metal.[1] As CaO forms in the initial stages of the reaction, it is deposited on the metal surface. Johnson, *et al.*,[2] have shown that $CaH_2$ is 19 to 35% soluble in $\gamma$-Ca and liquid Ca in the temperature range 778–894°. It is impossible to extrapolate these data to the temperature range covered in this paper due to the transition[3] in Ca at 440°: however, it is probable that a limited solubility of $CaH_2$ in $\beta$-Ca exists. Hence any $CaH_2$ formed in the initial stage of the reaction dissolves in the metal and does not deposit along with CaO until local saturation is reached. The CaO deposited during the time in which saturation of Ca with $CaH_2$ is occurring constitutes band (1). Band (2) consists of the mixed Ca and $CaH_2$ and increases in width as the reaction proceeds. As $CaH_2$ is precipitated from solution in the metal, an extremely thin band, band (3), appears. The boundary between band (4) and the metal is very diffuse. Pilling and Bedworth[4] have shown that the CaO film will be cracked because of the great difference between the molecular volumes of oxide and metal. It is assumed, therefore, that water vapor diffuses through the relatively loose structure of the reaction products and that the reaction between water molecules and Ca takes place on the receding metal surface.

The experimental facts were consistent with the above theory. Band (1) was always thin and of relatively constant thickness in all specimens examined. From a consideration of the dimensions of band (1) the solubility of $CaH_2$ in Ca at 369° was estimated to be 14.2 ± 4.0%. Band (2) reached its maximum width when all the Ca metal had been consumed in the reaction. Band (3) was so thin that positive identification of its composition as pure $CaH_2$ was very difficult to determine experimentally. Since the boundary between bonds (4) and (5) was very diffuse, etching with air passed through hot water was required to develop any evidence for its existence.

A detailed consideration of the composition of band (2) is of interest. It might be expected that because of the nature of its boundaries a concentration gradient of $CaH_2$ should exist. Both X-ray and $H_2$ evolution experiments supported this contention. The concentration of $CaH_2$ was greater near the center of the reaction product specimens than near the surface.

### Experimental

**Apparatus.**—The apparatus consisted of a reaction tube, recording manometer,[5] a means of introducing water vapor into the system and appropriate high vacuum equipment to evacuate the entire system thoroughly. By means of a special furnace which could be slid over the reaction tube, the reaction temperature was controlled to ±0.1°. The vacuum tight port through which water was introduced into the apparatus consisted of a serum bottle rubber stopper placed in a constricted tube and covered with mercury. Below this stopper was a well into which liquid water was introduced by means of a hypodermic syringe. Throughout the experiments liquid water always remained in this well and was maintained at 25 ± 1°.

**Procedure.**—Cylinders of redistilled Ca metal (Ca distilled in the Ames Laboratory) were prepared by machining under sodium-dried turbine oil. The oil-covered cylinders were suspended at two points in a special stainless steel frame. After four rinses in sodium-dried petroleum ether and one rinse in sodium-dried diethyl ether the cylinders and frame were placed in the reaction tube. The entire apparatus was rapidly evacuated and as soon as the pressure was reduced to less than 0.1 $\mu$ of Hg the preheated furnace was slid into place. When temperature equilibrium was reached the reaction was initiated by introducing degassed liquid water into the water well.

Great care was taken to prevent manual handling of the Ca metal even under oil. This precaution was necessary to prevent fingerprinting which introduces active centers on the metal surface and obviates a uniform reaction product. Neoprene-tipped forceps or rubber gloves previously dipped in dry oil or solvent were used for handling the metal samples.

During the course of some of the experimental runs a small increase in pressure (about 25 to 35 mm. of Hg partial pressure of $H_2$) was observed. This $H_2$ pressure, after rising to a maximum, rapidly diminished, and after two or three hours no detectable amount of $H_2$ remained in the apparatus. In most runs, however, no initial $H_2$ pressure was observed nor could $H_2$ be detected in the apparatus. All gas analyses were made by means of a mass spectrometer having a sensitivity for $H_2$ of 1 part in 40,000.

**Weight Gained by the Sample.**—In one representative trial a Ca cylinder weighing 20.718 g. was allowed to react with $H_2O$ vapor until the gas pressure within the apparatus began to rise when $H_2$ formed. The reaction was stopped, and the weight of the cylinder was found to be 25.210 g. Assuming the product mixture to be CaO and $CaH_2$ in equimolar quantities, the calculated weight was 25.38 g. A small residual core of metal in the cylinder of reaction products could very easily account for the difference between observed and calculated weights.

**Analysis of Solid Reaction Products.**—Two types of reaction product specimens were examined. Type A was obtained from experimental runs in which the reaction had consumed about half the Ca. In type B specimens all the Ca was consumed. Longitudinal sections of the specimens were examined by means of a recording X-ray diffractometer. The bands have already been identified above. It is significant, however, that in type B specimens where a more detailed examination of band (2) was made, a reversion of peak heights (due to principal reflections of CaO and $CaH_2$)

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[1] From experiences in the Ames Laboratory of the Atomic Energy Commission during years of handling Ca. No quantitative data are available at this time.

[2] W. C. Johnson, M. F. Stubbs, A. E. Sidwell and A. Pechukas, THIS JOURNAL, **61**, 318 (1939).

[3] O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys," Academic Press, Inc., New York, N. Y., 1953, p. 6.

[4] N. B. Pilling and R. E. Bedworth, *J. Inst. Metals (London)*, **29**, 529 (1923).

[5] H. J. Svec and D. S. Gibbs, *Rev. Sci. Instruments*, **24**, 202 (1953).

was observed as sections deeper within the specimens were examined. The $H_2$ evolution experiments corroborated these results. Table I shows the results of some typical experiments on one of the reaction product specimens obtained at 369°.

TABLE I

COMPOSITION OF CaO–$CaH_2$ MIXTURES FROM DIFFERENT REGIONS OF THE REACTION PRODUCT SPECIMENS

| Sample no. | Sample description | Wt. of sample, g. | $H_2$ pressure, cm. of Hg | $CaH_2$, %[a] calcd. |
|---|---|---|---|---|
| 1 | Center | 0.4947 | 30.5 | 84.5 |
| 2 | Center | .7228 | 43.4 | 82.3 |
| 3 | Center | .5178 | 31.2 | 87.5 |
| 4 | Center | .7258 | 47.6 | 88.7 |
| 5[b] | Near outer surface | .8339 | 34.4 | 41.8 |

[a] Volume of apparatus was 1250 ml. [b] Gas evolution experiments were performed at 35 ± 0.02°, except this one which was at 47 ± 02°.

In all the X-ray experiments, peaks due to X-ray reflections were not as sharp as would be expected in well-defined crystalline materials, thus indicating crystallites of short range. Although the gross appearance of the reaction product specimens was solid, the specimens appeared granular when broken to expose their cross sections, indicating that ample paths for the diffusion of water vapor through the reaction product coat were available.

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# Heats of Formation of Chromium(III) and Chromium(II) Iodides

BY N. W. GREGORY AND T. R. BURTON

RECEIVED AUGUST 6, 1953

The heat of formation of $CrI_3$ has not been determined previously; the reported value for $CrI_2$ (−54.2 kcal./mole)[1] is based on a heat of solution determined by Mosnier[2] and is not consistent with properties observed in this Laboratory. From heats of solution of $CrI_3$ and $CrI_2$ and related substances, we find the heats of formation[3] at 25° to be −47.8 and −37.8 kcal./mole, respectively, with an uncertainty of ±3%.

Heats of solution of millimole quantities of $CrCl_2$, $CrCl_3$, $CrI_2$, $CrI_3$, KCl and KI in 750 ml. of an aqueous solution 1 molal in KCl and approximately 0.001 *M* in chromium(II) chloride were measured. $Cr^{+2}$ is necessary to effect solution of the chromium(III) halides.[4] It has been assumed that the final state of chromium in the solution after dissolution of $CrCl_3$ is the same as that when $CrI_3$ is dissolved (similarly for the chromium(II) halides), *i.e.*, that the concentration of iodine complexes is negligible in the presence of the comparatively high concentration of chloride ions. Hence the mean values of the heats of solution (Table I) have been combined to determine heats of the reactions.

$$\mathrm{CrCl_2(c) + 2KI(c) = CrI_2(c) + 2KCl(c)} \qquad \Delta H = 5.0\ \mathrm{kcal.} \quad (1)$$

$$\mathrm{CrCl_3(c) + 3KI(c) = CrI_3(c) + 3KCl(c)} \qquad \Delta H = 9.2\ \mathrm{kcal.} \quad (2)$$

TABLE I

MOLAR HEATS OF SOLUTION

| Solute, millimoles | $\Delta H$ soln., kcal. | Solute, millimoles | $\Delta H$ soln. kcal. |
|---|---|---|---|
| $CrCl_3$ | | $CrI_3$ | |
| 1.184 | −32.3 | 0.7798 | −41.1 |
| 1.277 | −33.0 | 0.9215 | −41.6 |
| 1.502 | −32.9 | 2.563 | −41.3 |
| 2.065 | −32.7 | | −41.3 |
| | −32.7 | $CrI_2$ | |
| $CrCl_2$ | | 2.198 | −22.6 |
| 0.8525 | −18.1 | 2.221 | −22.8 |
| 1.426 | −17.9 | 2.389 | −22.5 |
| 5.216 | −17.9 | 2.907 | −22.6 |
| | −18.0 | | −22.6 |
| KCl | | KI | |
| 29.02 | 4.0 | 11.00 | 4.3 |
| 36.50 | 3.9 | 12.74 | 4.2 |
| 41.61 | 4.1 | 14.96 | 4.4 |
| 42.95 | 4.0 | 16.12 | 4.0 |
| | 4.0 | | 4.2 |

HEATS OF SOLUTION OF CHROMIUM IODIDES AND EXCESS IODINE IN 0.02 *N* HCl

| | | $CrI_2$–$CrI_3$ mixtures | | |
|---|---|---|---|---|
| | | $CrI_3$ | $CrI_3$ | Contribution of $CrI_3$ |
| $CrI_2$ | | | | |
| 1.141 | −54.8 | 0.4809 | 1.149 | −44.0 |
| 1.700 | −54.8 | .2272 | 1.445 | −42.3 |
| 2.075 | −54.8 | .4829 | 1.709 | −44.6 |
| 2.861 | −54.4 | .4047 | 1.990 | −44.4 |
| | −54.7 | 1.571 | 3.260 | −43.2 |
| | | | | −43.7 |

Using standard heats of formation for the chromium chlorides and potassium halides, values are obtained for the chromium iodides. The sensitivity of the calorimeter was not sufficient to detect any variation in the molar heats of solution with the slightly differing quantities dissolved. Somewhat larger samples (than required by reactions 1 and 2) of the potassium halides were used to obtain a sufficiently large thermal effect for accurate measurement. The relatively small difference in the change of heats of solution with concentration for these substances indicates that this does not introduce a significant error.

The combined heats of chromium(II) and halogen ions in the KCl solution is essentially the same as the sum of the standard values for these ions; the observed heat of solution, if assigned to the simple reaction

$$\mathrm{CrI_2(c) = Cr^{+2}(aq) + 2I^-(aq)}$$

gives −37.3 kcal. for the heat of formation of $CrI_2$ (using −33.2 kcal. for $Cr^{+2}$ (aq)[1] and −13.37 kcal. for $I^-$ (aq)[1]). A similar treatment with $CrCl_2$ leads to a heat of formation of −95.2 kcal. (accepted value[1] −94.6).

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(1) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Pr. Office, Washington, D. C., 1952.

(2) M. A. Mosnier, *Ann. chim. phys.*, **12**, 374 (1897).

(3) $I_2$(c) taken as the standard state for iodine.

(4) The concentration of $Cr^{+2}$ is not critical. In a series of experiments with $CrCl_3$, no dependence of the heat of solution with concentration of $Cr^{+2}$ was observed as the latter was varied between 0.001 and 0.0035 *m*.