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

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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.

$$CrCl_3(c) + 2KI(c) = CrI_2(c) + 2KCl(c) \quad \Delta H = 5.0 \text{ kcal.} \quad (1)$$

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

TABLE I

MOLAR HEATS OF SOLUTION

Solute, millimoles	ΔH soln., kcal.	Solute, millimoles	ΔH 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_2	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

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

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*.

From the heats of formation, an enthalpy change of 10 kcal. is predicted for the reaction

$$CrI_3(c) = CrI_2(c) + {}^1/_2I_2(c) \qquad (3)$$

3 kcal. less than previously estimated by extrapolation of thermal dissociation equilibrium data at 570°.[5] The heat of reaction (3) at 25° has been determined by comparison of the heats of solution of CrI_3 and CrI_2 with excess solid iodine in 750 ml. of 0.02 N HCl solution. Known mixtures of CrI_3 and CrI_2 were dissolved and iodine was subsequently introduced. The heat of solution of pure CrI_2 was determined under similar conditions and the contribution of each component in the mixtures calculated. Inasmuch as iodine readily oxidizes chromium(II) to chromium(III), the final state of chromium after dissolving CrI_2 is the same as that with CrI_3. The results for the mixtures are somewhat less consistent than those for the pure substances; however, the difference between the mean values, 11 kcal. (Table I), agrees with the predicted result within experimental uncertainty.

Experimental Procedure

A description of the simple adiabatic calorimeter and its operation[6] and the preparation of CrI_3[7] have been given previously. Heats of solution were measured at 25 ± 1°. CrI_2 was prepared by thermal decomposition of CrI_3 in vacuum (400–500°), followed by sublimation in vacuum at 700°. The chromium chlorides were also purified by sublimation. The composition of these substances was checked by analysis; deviation from theoretical values did not exceed 0.5%. Samples were introduced into the calorimeter in sealed thin glass capsules, previously filled in a dry-box.

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The Stability of Hydroxystreptomycin

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An unknown antibiotic isolated in the antibiotic screening program carried out at these laboratories was found to be identical with hydroxystreptomycin.[1–4] In the course of our degradation studies, it was found remarkably resistant to hydrolytic inactivation, compared to streptomycin.[5]

The stability of hydroxystreptomycin in water and methanol solutions is shown in Table I. Solutions initially contained 10 mg./ml. of hydroxystreptomycin base and were followed by bioassays.

TABLE I

Solvent	pH	Time, days	Temp., °C.	Activity remaining, %
Water	2	8	20	>95
Water	6.5	8	20	>95
Water	12	8	20	>95
Water	2	1	100	56
Water	6.5	1	100	58
Methanol	2	4	65	72
Methanol	6.5	1	65	83

Hydroxystreptomycin is much more stable to acid hydrolysis under mild conditions than is streptomycin. Table II shows the results obtained from stability studies on streptomycin and hydroxystreptomycin in 2 N hydrochloric acid at 20°. Initial concentrations were 4 mg. of antibiotic base/ml. The figures are taken from the best line fitted to the plot of the logarithm of concentration against time.

TABLE II

	Activity remaining, %			
	1 day	2 days	7 days	21 days
Streptomycin	50	19	<1	
Hydroxystreptomycin	93	85	58	20

The hydrogenated derivatives are very similar to the unreduced compounds with respect to stability in hydrochloric acid.

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The Reaction of Esters with Phenylhydrazine in the Presence of Phosphoric Acid[1]

BY T. O. JONES, R. E. HALTER AND W. L. MYERS

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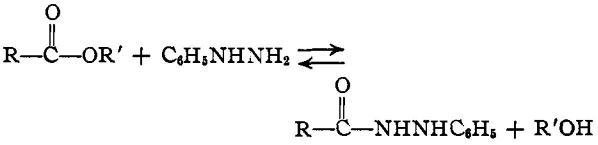
The reactions of esters with ammonia, hydroxylamine and hydrazine to produce the corresponding amide, hydroxamic acid or hydrazide are well known. Cohn[2] and Meyer[3] reported a reaction between methyl salicylate and phenylhydrazine to produce the corresponding phenylhydrazide, and Baidakowski, Reformatski and Slepak[4] prepared a few phenylhydrazides by heating the ester and phenylhydrazine in a sealed tube at 210°, but no other examples of this reaction have since been reported.

Various modifications and adaptations of earlier procedures for carrying out similar reactions were tried for the reaction



$$R{-}\overset{\overset{\large O}{\|}}{C}{-}OR' + C_6H_5NHNH_2 \rightleftarrows R{-}\overset{\overset{\large O}{\|}}{C}{-}NHNHC_6H_5 + R'OH$$

using the ester and the free base in various solvents or using the ester and the hydrochloride or sulfate salts, all without results. It was noted that when the phenylhydrazine salts were used, they remained unchanged during the trials so the phenylhydrazine

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(1) Supported in part by a grant from the Research Corporation, 405 Lexington Ave., New York 17, N. Y.

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