Table I

Decomposition of Mercurials by Aqueous Hydrochloric Acid

	Compound mg.	Compound mmole	Acid ml.	Acid N	Time, hr.	Decomp., %
	37	0.10	100	0.01	230	16
	37	.10	100	.07	4	3
					7	7
					24	20
					66	50
					188	76
					316	90
I	370	1.0	100	.07	168	11
II	66.8	0.20	200	.01	0.5	51
					24	48
II	33.4	.10	100	.07	0.5	85
					1	100
III	48.7	.10	100	.07	312	0
III	120	.25	10	1.0	24	18
					136	63
					312	68
III	120	.25	10	6.0	16	90

Decomposition of 0.00025 mole of III by 10 ml. of 6 N hydrochloric acid was close to 100% within 16 hours. With 1 N hydrochloric acid decomposition was relatively slow and equilibrium appeared to have been reached after 312 hours. Because of difficulty in determining the solubility of III and of allyldiphenylacetic acid in water, an equilibrium constant was not calculated for this reaction.

The percentages of decomposition of 2-chloromercurimethyl-2,3-dihydrobenzofuran (I), determined after vigorous shaking with hydrochloric acid appear in Table I. From these studies and a solubility of I in water at room temperature of *ca.* 0.0001 M, values of K for the reaction of mercuric chloride and *o*-allylphenol were found to lie in a range from 0.4 to 1.0. The value of 1.0 calculated from the 90% decomposition of 0.0001 mole of I by 0.07 N hydrochloric acid is the least reliable; in this case a variation of 5% in the measurement of mercuric chloride could lower the value of K to 0.45. When the equilibrium was approached from the opposite direction by the reaction of 0.0001 M mercuric chloride with 0.0001 M *o*-allylphenol in 0.001 N hydrochloric acid, the reaction was 87% complete; the value of K as determined by this experiment was 0.55.

The rate of reaction of I with acid, similar to the rate of reaction of III with acid, would appear to be limited by the rate of solution of I.

Polarographic study of the decomposition in alcoholic solution was not possible by the technique which we attempted which involved dilution with water prior to analysis. The equilibria were indicated, however, by the yields of I and III produced in ethyl alcohol by reaction of mercuric chloride with *o*-allylphenol and with allyldiphenylacetic acid.

Although the results of this investigation suggest a study of the rate of reaction of mercuric chloride with allylacetic acid and with *o*-allylphenol, as well as a more complete study of the decomposition by mineral acid of olefin–mercury addition compounds, we are unable at the present time to devote further attention to these problems.

Experimental

Mercuric ion was determined polarographically using the standard addition technique[6] at zero potential with a saturated calomel anode. The analyses gave high results which were corrected by a factor determined using known concentrations of mercuric chloride. Although the inherent error may be relatively large, this method appeared suitable for the purpose of this investigation. Prior to study of their decomposition the mercurials were crystallized to constant melting point as previously described.[1,2]

Equilibria in Alcohol.—Polarographic study of the reaction of III with hydrochloric acid in ethyl alcohol was hindered, presumably owing to the shifting of the reaction by the addition of aqueous hydrochloric acid prior to the polarographic determination. Thus addition of 3.1 ml. of 2.2 N ethanolic hydrogen chloride to a boiling mixture of ethyl alcohol and 0.22 g. of III followed by dilution with ethyl alcohol to a volume of 100 ml. resulted in complete solution of III. No precipitation occurred upon cooling to room temperature although the solubility of III in ethyl alcohol is only *ca.* 0.5 mg./ml. In contrast to this indication of decomposition of 75% or more, polarographic analysis after dilution with aqueous acid showed no mercuric chloride present. Moreover, from concentration at room temperature of a mixture of 1.0 g. of III, 125 ml. of boiling methyl alcohol and 0.5 ml. of concentrated hydrochloric acid, was isolated 0.2 g. (40%) of a solid melting at 142–143° which did not depress the melting point of allyldiphenylacetic acid.

By reaction of a solution of 1.26 g. of allyldiphenylacetic acid in 20 ml. of ethyl alcohol with a solution of 1.36 g. of mercuric chloride in 20 ml. of ethyl alcohol, a precipitate of III was obtained which weighed 0.89 g. Allowing for the solubility of the mercurial, the mercuration proceeded to the extent of 37%.

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[6] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 251–252, 257.

Chemical Research Div.
Lakeside Laboratories, Inc.
Milwaukee 1, Wisc.

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The Heat of Formation of Aluminum Borohydride[1,2]

By Richard M. Rulon and L. S. Mason

The present investigation is a continuation[3,4] of studies of the thermochemical and thermodynamic properties of certain metallo-borohydrides and related compounds. The reactions of aluminum borohydride with a number of substances were examined in order to select reactions which would be most suitable for determinations of the changes of heat content for the reactions in a bomb calorimeter. The heat of formation of the aluminum borohydride could then be calculated from the heats of reaction and the known heats of formation of all other reactants and products. The direct hydrolysis of liquid aluminum borohydride with liquid water in the bomb produced dark colored residues, strong odors and variation in the extent of completion of the reaction. The reaction of the liquid with oxygen in a combustion bomb offered similar complications. Aluminum borohydride vapor reacted with chlorine and with hydrogen chloride to give white products and apparently

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[1] This report is part of a thesis presented by Richard M. Rulon to the Faculty of the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

[2] The Office of Naval Research supported the major part of this work.

[3] W. D. Davis, L. S. Mason and G. Stegeman, This Journal, **71**, 2775 (1949).

[4] Joe Smisko and L. S. Mason, *ibid.*, **72**, 3679 (1950).

complete reactions in glass bulbs at low pressures, but yielded dark residues at concentrations great enough to evolve sufficient heat for calorimetric measurement. When aluminum borohydride vapor reacted in the bomb with (a) water vapor in the presence of a small excess of liquid water, with (b) the vapors over a small excess of dilute aqueous ammonia, and with (c) moist oxygen (these reactions were all "damped" with three to five atmospheres of argon) white reaction products and absence of odor occurred in some but not in all cases. The results of colorimetric measurements were reasonably consistent in all cases when white products were found and no odors were observed. Conversely, the measured heat effects scattered widely and indicated quite incomplete reactions when there were dark residues and strong odors. Heats of formation therefore were calculated only for what were believed to be complete reactions with definite end products.

Experimental

The aluminum borohydride was supplied by Dr. H. I. Schlesinger, University of Chicago, and by Dr. R. R. Miller, Naval Research Laboratory, Washington, D. C. The material had been prepared, purified and "stabilized" according to the methods of Schlesinger[5]; the methods produce a material which is at least 99% pure. The material was stored in the vapor state in a vacuum system equipped with mercury-sealed cut-off valves. The vapor is stable at room temperature for a long time.[6] Each sample taken was subjected to fractional distillation immediately before use. Gases or vapors resulting from any decomposition during storage were removed from the system before any samples were taken. This material was assumed to be of satisfactory purity for the calorimetric determinations. However, a check was made on the boron[7] and aluminum[8] content to confirm the identity of the material. The results agreed with the theoretical composition within 2%. For the calorimetric determinations, samples of approximately 200 mg. of vapor were taken in 125-ml. spherical glass bulbs, weighed against tare bulbs matched for mass and volume with each sample bulb, and used immediately.

The heats of reaction were measured in an Emerson combustion bomb[3] containing a mechanical device for breaking the sample bulbs at the desired instant. The heat capacity of the calorimetric system (2800.0 cal./deg., mean square deviation, 0.05%) was determined by combustion of benzoic acid (National Bureau of Standards standard sample #39f). Temperatures were measured with a Leeds and Northrup platinum resistance thermometer and a Leeds and Northrup Muller resistance bridge.

For reactions of type (a), a bulb containing the sample was placed in the bomb with 3 ml. of water. The bomb was flushed with argon to remove all the air and then filled with argon at 3 atmospheres pressure. The bulb was broken and the heat effect of the reaction (between aluminum borohydride vapor and water vapor) was measured. In reactions of type (b) the water was replaced by dilute aqueous ammonia. In type (c) the bomb contained the sample, a trace of moisture, argon at 3 atmospheres and oxygen at 1 atmosphere pressure.

Results and Conclusions

It has been reported[5] that aluminum borohydride hydrolyzes according to

$$Al(BH_4)_3 + 12H_2O = Al(OH)_3 + 3H_3BO_3 + 12H_2$$

From the heats evolved by the reactions in the bomb, the standard heats of reaction for (a) and (b) were calculated for the substances in the following standard states at 298.2°K. and 1 atm. pressure

$$Al(BH_4)_3(l) + 12H_2O(l) = Al(OH)_3(amorph) + 3H_3BO_3(cryst) + 12H_2(g)$$

and for reaction (c)

$$Al(BH_4)_3(l) + 6O_2(g) = {}^1/_2Al_2O_3(cryst.\ corundum) + {}^3/_2\ B_2O_3(cryst) + 6H_2O(l)$$

Petrographic[9] and X-ray[9] examinations were made of some of the reaction products. The particle size was such as to make petrographic examination difficult. The work was limited largely to index of refraction tests. There was no material in reactions (a) and (b) which had an index of refraction as great as that of aluminum oxide. A large amount of water soluble material matched samples of boric acid very closely. The index of refraction of the insoluble material matched that of aluminum hydroxide. A sample of reaction (c) showed an appreciable amount of material corresponding to aluminum oxide and a small amount to boric acid. Tests for boron trioxide were inconclusive. X-Ray examination of reactions (a) and (b) confirmed the presence of boric acid. It was believed that in the case of reaction (c) because of the probable high temperature of the combustion (the reaction occurs as a detonation)[5] the solid products were primarily anhydrous alumina and boric oxide. The boric oxide probably hydrated slowly after the reaction, but the extent of this was indeterminable. Solution of boric acid in reactions (a) and (b) was considered negligible since the solid reaction products were found on the inner surfaces of the shattered sample bulb and on the walls and top of the bomb, out of contact with the small amount of water remaining on the bottom of the bomb.

The results of the few successful experiments are shown in the following table, where $\Delta H°$ is the heat content change for the reaction at 298.2°K. with all reactants and products in their standard states and $\Delta H_f^{298.2}$ is the standard heat of formation of $Al(BH_4)_3(l)$. In the case of five other reactions in which strong odors and dark reaction products were produced, the calculated heats of formation ranged from about −150 to −250 kcal./mole. No known differences in operating procedure existed between these and the "clean" reactions.

Reaction	ΔH^0, kcal./mole	$\Delta H^{289.2}$, kcal./mole
a	−196.0	−71.4
	−195.1	−72.3
b	−197.5	−69.9
c	−989.1	−74.8
Average		−72.1

Standard heats of formation, in kcal./mole, for the following compounds were used in the calculation of the heat of formation of the aluminum borohydride

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(5) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, THIS JOURNAL, **62**, 3421 (1940).

(6) H. I. Schlesinger, R. T. Sanderson and A. B. Burg, *ibid.*, **61**, 536 (1939).

(7) W. F. Hillebrand, "Analysis of Silicate and Carbonate Rocks," Bulletin 700, U. S. Geological Survey, 1919, pp. 234-241.

(8) I. M. Kolthoff and E. B. Sandell, "A Textbook of Quantitative Analysis," The Macmillan Company, New York, N. Y., 1943.

(9) The assistance of Mr. Daniel Bode and Mr. Donald Edwards is acknowledged.

$H_2O(l)$[10] $= -68.3174$; $Al(OH)_3$(amorph)[10] $= -304.2$; H_3BO_3(cryst)[4] $= -261$; Al_2O_3(cryst, corundum)[10] $= -399.09$; B_2O_3(cryst)[11] $= -303$

The heat of vaporization of aluminum borohydride is 7.2 kcal./mole.[5]

It was believed that ±4 kcal./mole was a reasonable estimate of the experimental errors of determination of the heats of reaction. In the case of reactions (a) and (b), 0.5% of inert impurity in the sample would produce a difference of about 1 kcal. in $\Delta H_f(Al(BH_4)_3)$. One per cent. error in measuring the energy change of the reaction would result in an additional 2 kcal. error in $\Delta H_f(Al(BH_4)_3)$. In reaction (c), however, 0.5% impurity would cause about 5 kcal. error in $\Delta H_f(Al(BH_4)_3)$, and 1% error in $\Delta H°$ would result in 10 kcal. error in $\Delta H_f(Al(BH_4)_3)$. No assignment of error due to uncertainties in the heats of formation of the other participants in the reactions has been made, but it may be noted that a 2% error in $\Delta H_f(B_2O_3)$ (which is quite possible) would alter $\Delta H_f(H_3BO_3)$ by 3 kcal. and this would be reflected as 9 kcal. error in $\Delta H_f(Al(BH_4)_3)$ calculated from $\Delta H°$ for (a) and (b). Two per cent. error in $\Delta H_f(B_2O_3)$ would produce 10 kcal. error in $\Delta H_f(Al(BH_4)_3)$ from (c).

The value for $\Delta H°$ of -989.1 from (c) is in good agreement with a value of -984 kcal. obtained earlier in this Laboratory for the heat of combustion of aluminum borohydride in the liquid state.[12]

(10) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," 1949.

(11) E. J. Prosen, W. H. Johnson and F. A. Yenchius, National Bureau of Standards Technical Report on Project Na-onr-8-49, 1948. C. C. Nathan, Thesis, University of Pittsburgh, 1948.

(12) W. E. Wallace and G. Stegeman, unpublished results, 1945.

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The Reduction of 1,3-Dichloroacetone with Lithium Aluminum Hydride[1,2]

BY HERMANN SCHLENK AND BEVERLY LAMP

The selective reduction of carbonyl groups of α-monohaloketones by $LiAlH_4$ was reported for several compounds in the recent literature.[3] In developing synthetic methods for preparation of glycerol containing radioactive carbon we were interested in the reduction of 1,3-dichloroacetone to 1,3-dichlorohydrin. Using aluminum isopropylate for this reaction the yields were between 20 and 25%, being unacceptably low. We found it possible, however, to obtain 1,3-dichlorohydrin in yields of 70–80% by $LiAlH_4$. These results are in accordance with, and an extension of the observations of the previous authors to include an α,α′-dihaloketone.

Experimental

Dichloroacetone was prepared following the procedure of Arndt and Eistert[4] in a yield of 71.8% based upon chloroacetyl chloride. The product, 7.41 g. or 0.0583 mole (boiling point 168–172°), was dissolved in 100 ml. of absolute ether and was added to 0.022 mole of $LiAlH_4$ in 25 ml. of absolute ether during one hour. The reaction was carried out at −2° under nitrogen, using a mechanical stirrer and a reflux condenser. After continuing the stirring for ten more minutes the Fehling test for dichloroacetone was negative. The solution was poured into 100 ml. of ice-cold 2 *N* HCl and the aqueous phase was twice extracted with ether. The combined ether solutions were dried over Drierite and the solvent then was evaporated. In distilling the product, the main fraction was 1,3-dichlorohydrin boiling at 69–70° at 16 mm. pressure, having a refractive index n^{34} 1.4729 comparing well with that of authentic dichlorohydrin n^{34} 1.4743. The yield was 5.79 g. or 77% based upon dichloroacetone. Hydrolysis of this product gave the same yield of glycerol (n^{25} 1.4738) as authentic samples of dichlorohydrin.

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[1] This investigation was supported in part by a grant from the United States Atomic Energy Commission.

[2] Presented at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

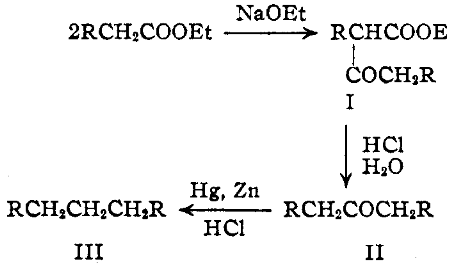
[3] R. E. Lutz, R. L. Wayland, Jr., and H. G. France, THIS JOURNAL, **72**, 5511 (1950).

[4] F. Arndt and B. Eistert, *Ber.*, **61**, 1124 (1938).

Clemmensen Reduction of a Long Chain β-Ketoester[1]

BY DAVID A. SHIRLEY AND GUSTAV A. SCHMIDT[2]

In connection with a study of the synthesis of certain long chain fatty acids containing twenty-six carbon atoms, we evaluated a route to these types which involved a Claisen condensation of a long chain carboxylic ester followed by a Clemmensen reduction of the resulting β-ketoester. The reduction of ethyl 2-tridecanoyltridecanoate (I), from Claisen condensation of ethyl tridecanoate, with amalgamated zinc, absolute ethanol and dry hydrogen chloride gave an 87% yield of pentacosane (III) rather than the expected ethyl 2-tridecyltridecanoate. The formation of the hydrocarbon was apparently due to the hydrolysis and decarboxylation of the β-ketoester under conditions of the Clemmensen reduction to give 13-pentacosanone followed by normal reduction of this ketone to the corresponding hydrocarbon. These transformations are shown in the accompanying diagram (R = $CH_3(CH_2)_{10}$−).



Connor and Adkins[3] have shown that in the action of absolute alcohol and dry hydrogen chloride on β-ketoesters there is no alcoholysis or removal of carbethoxy group. The apparent removal of the carbethoxy group during the Clemmensen reduction under our conditions must have occurred as a result of the action of water formed by the reaction of ethanol and hydrogen chloride. The presence of the zinc chloride in the reaction mixture would have aided this latter process.

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[1] This work was carried out as a part of a project supported by a F. G. Cottrell grant from the Research Corporation.

[2] Department of Chemistry, University of Texas, Austin.

[3] R. Connor and H. Adkins, THIS JOURNAL, **54**, 3420 (1932).