TABLE I

REDUCTION OF CARBON DIOXIDE

Run	$LiAlH_4$ concn., % by wt.	$LiAlH_4$, mmoles.	CO_2, mmoles.	Ratio, CO_2 to $LiAlH_4$	HCO_2H yield, %	HCHO yield, %
1[a]	0.44	3.84	15.6	4.1	81	6.3
2[a]	0.38	3.36	13.69	4.1	87	[c]
3[a]	3.53	10.10	36.90	3.6	43	9.7
4[b]	0.41	3.04	12.32	4.1	79	5.2
5[b]	0.53	4.20	16.80	4.0	88	[c]
6[b]	2.79	10.70	33.40	3.1	41	17.7

[a] Solvent was diethyl ether. [b] Solvent was diethylene glycol diethyl ether. [c] Product was oxidized with BaO_2 prior to isolation of acid.

to air. Dissolving the deteriorated hydride in ether at room temperature followed by filtration eliminated insoluble oxides or hydroxides but the resulting solution often still gave low yields of formic acid. Evaporation of such a hydride solution to dryness *in vacuo* at 70–80° gave a dark colored solid. Pure lithium aluminum hydride at 80° remains white. The low decomposition temperature suggests that the more unstable aluminum hydride may in some way have been formed by the action of light or air on lithium hydride. Aluminum hydride does react with carbon dioxide, but the highest yield of formic acid which could be obtained was 52%. Thus any binary hydride present as an impurity in the lithium aluminum hydride could cause the above-mentioned irregularities in yield. Lithium aluminum hydride was purified by refluxing an ether solution, a technique which would precipitate aluminum hydride as an insoluble etherate.[6]

Formaldehyde was identified as a by-product in all of the reductions. The yield was determined by weighing the dimedon derivative. In experiments using the more highly concentrated solutions, methanol was also isolated and identified by its vapor pressure at 0° and the characteristic refractive index. In several runs reported in Table I, the overall yield of formic acid was raised to 87–88% by oxidation of the formaldehyde with barium peroxide prior to the final isolation of the acid by distillation.

Several attempts were made to direct the reduction of carbon dioxide according to equation (2) by control of the ratio of reagents. The highest yield of formaldehyde was 23% based on the carbon dioxide which reacted.

The ratio of carbon dioxide to lithium aluminum hydride in many runs was over four. This may possibly be explained by incomplete recovery of carbon dioxide although care was taken to avoid loss of unreacted reagent.

Experimental

Apparatus.—Standard high vacuum techniques were used.

Materials.—A diethyl ether solution of commercial lithium aluminum hydride (Metal Hydrides, Inc.) was refluxed for three hours, filtered under nitrogen through a sintered glass filter and the filtrate evaporated to dryness *in vacuo* at 80°. The solid product was over 98% pure by hydrogen analysis.[5] Solutions of the hydride were made by dissolving the solid in the solvent and filtering *in vacuo* into a reaction vessel just before use. The concentration of hydride was determined by hydrogen analysis of an aliquot which was removed from the reaction vessel with a glass syringe under dry nitrogen.

Reduction in Diethyl Ether.—A solution of 0.145 g. (3.84 mmoles) of lithium aluminum hydride in 33.24 g. of diethyl ether was placed in a 100-ml. reaction vessel which was attached to the vacuum system through a ground joint. The solution was cooled with liquid nitrogen and the flask was evacuated. Carbon dioxide, 838 cc. (37.3 mmoles), was condensed into the reaction vessel. The mixture was warmed slowly to room temperature with constant agitation by a magnetic stirrer. As the hydride solution warmed, a reaction took place with the formation of a white precipitate. The volume of the vacuum system was such that the carbon dioxide pressure during the reaction never dropped below 300 mm. After stirring the mixture for one hour at room temperature, the excess carbon dioxide was removed and was separated from ether by fractionation in the vacuum line. The carbon dioxide recovered was 488 cc. indicating that 350 cc. (15.6 mmoles) had reacted.

Ether was removed from the reaction product by adding water and then bubbling nitrogen through the mixture.[5] After addition of 5 ml. of 85% phosphoric acid, a high vacuum distillation brought over water and formic acid. Two more 20-ml. portions of water were added and distilled to ensure complete removal of the formic acid. Titration of the distillate with sodium hydroxide showed 12.6 mmoles (81%) of formic acid had been formed. The acid was identified by the S-benzylthiuronium salt, m.p. 150–151°. Correction for traces of phosphoric acid were made with blank runs. Confirmation of the yield with $HgCl_2$ gave a slightly higher value than 81%.

The dimedon test of the distillate indicated that 6.3% of the carbon dioxide formed formaldehyde. Only a trace of the aldehyde was found in the residue.

Runs with diethylene glycol diethyl ether were made in the same way as with diethyl ether except that the solvent was not removed before the high vacuum distillation of formic acid.

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[6] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

The Decomposition by Heat of *d*-Camphoryl Diesters[1]

BY TORSTEN HASSELSTROM, CLIFFORD E. BALMER AND HAROLD W. COLES

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The instability of *d*-camphoric diesters to heat has been reported in the literature but, excepting *d*-camphoric anhydride, no decomposition products have been described.[2]

The decomposition by heat of di-*n*-hexyl *d*-camphorate and diisobornyl *d*-camphorate was investigated. *d*-Camphoric anhydride was the main product. The reaction as to the alcohol part proceeds substantially in the same manner as described for the ester decomposition in the aliphatic monocarboxylic series, since 1-unsaturated hydrocarbons were isolated.[3]

The camphorates are not homogeneous stereochemically but are mixtures of the respective *d*-camphoric and isocamphoric acid esters.[2a,b,c] This was confirmed in case of the di-*n*-hexylcamphorate

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[1] Paper presented at the XIIth International Congress of Pure and Applied Chemistry, September 13, 1951, New York, N. Y.

[2] (a) O. Aschan, *Ber.*, **27**, 2005 (1894); (b) *Ann.*, **316**, 221 (1901); (c) *Acta Soc. Sc. Fenn.*, **21**, No. 5, 102, 145 (1898); (d) J. W. Brühl, *Ber.*, **24**, 3408 (1891); (e) T. Hasselstrom, C. E. Balmer, N. E. Kennedy and H. W. Coles, *TAPPI*, **33**, 538 (1950).

[3] F. Kraft, *Ber.*, **16**, 3019 (1883).

which, by following the procedure of Aschan (ref. 2a) was saponified, the acid regenerated and treated with acetyl chloride. The camphoric acid forms camphoric anhydride, whereas the isocamphoric acid is left intact and can be separated from the mixture by extraction with an aqueous sodium carbonate solution.

On heating at temperatures above 130° di-*n*-hexylcamphorate decomposes into *d*-camphoric anhydride, water and 1-hexene along with minute quantities of the 2- and 3-*n*-hexene isomers and with unidentified small amounts of high boiling products. The physical constants of the 1-hexene agreed with the figures given in the literature.[4]

The 1-hexene was oxidized with aqueous alkaline potassium permanganate to *n*-valeric acid, identified through the anilide.

The di-*l*-isobornyl *d*-camphorate yielded a camphoric anhydride, water and camphene. This was confirmed in the same manner as previously described.[5]

The possible hydrocarbons which may be formed on dehydration of isoborneol are bornylene, camphene and cyclene. The results reveal the presence only of camphene, showing that the alcohol part of the di-*l*-isobornyl D-camphorate had undergone the Wagner–Meerwein rearrangement.[6]

Experimental

Di-*n*-hexyl *d*-Camphorate.—2.5 moles of *d*-camphoric acid [m.p. 186° (uncor.), $[\alpha]^{22.5}\mathrm{D}$ +47.1° (in ethanol)], 5.5 moles of *n*-hexyl alcohol and 0.1% of benzenesulfonic acid together with toluene used as the water carrying-off reagent, were refluxed at 135–145° until the calculated amount of water was collected in a Dean–Stark water-trap. This took about 100 hours. After cooling, the brown solution was washed with aqueous sodium carbonate and then with water. Toluene and excess *n*-hexyl alcohol were removed by distillation at ordinary pressure. The residue was then fractionated in high vacuum and the main fraction repeatedly refractionated, each fractionation yielding a fore-run of a small quantity of *d*-camphoric anhydride; yield of di-*n*-hexyl camphorate, 58%; b.p. 159–161.5° (65 μ); $n^{20}\mathrm{D}$ 1.4597; $d^{20}{}_4$ 0.96468; $[\alpha]^{19.5}\mathrm{D}$ +18.85° (in ethanol).

Anal. Calcd. for $C_{22}H_{40}O_4$: C, 71.69; H, 10.94; *MR*, 104.47. Found: C, 70.60, 70.29; H, 10.37, 10.37[7]; *MR*, 104.46.

One hundred grams of *d*-camphoric acid was suspended in 500 ml. of water and made alkaline to phenolphthalein with a 10% solution of sodium hydroxide. To the clear solution was added an aqueous solution of 190 g. silver nitrate with good stirring. The disilver salt separated as a finely divided brownish powder. It was filtered off, washed with water and dried in vacuum. The salt was then covered with a 10% excess of *n*-hexyl iodide and the flask cooled with water to prevent the exothermic reaction from becoming violent. After the main reaction had taken place, the mixture was heated for 22 hours at 75°. The silver iodide was filtered off and washed with ethanol and the filtrate was distilled with steam to remove excess *n*-hexyl iodide and ethanol. The residue was dissolved in ether and the ether solution left standing overnight with aluminum amalgam made from 2 g. of aluminum foil. The mixture was then filtered free from aluminum hydroxide, the ether solution washed with dilute sulfuric acid and dried with anhydrous sodium sulfate and the ether distilled off. The ester was halogen-free and was fractionated in high vacuum. After separating, the first fraction contained *d*-camphoric anhydride, and the main portion, 54 g., showed the following properties: b.p. 170–171° (125 μ); $n^{20}\mathrm{D}$ 0.96923; calcd. for $C_{22}H_{40}O_4$ *MR* 104.47; found *MR*, 109.62.

In repeating this procedure the observation was made that fluctuations in density were considerable. This is attributed to the varying amounts of *d*-camphoric anhydride present in the rectified product.

The solid material observed in the fore-runs of both preparations was filtered off, washed with ether and sublimed, melting point 223–224° (uncor.). It did not depress the melting point of an authentic sample of *d*-camphoric anhydride in the mixed melting point test.

Pyrolysis of Di-*n*-hexyl *d*-Camphorate.—Eighty grams of di-*n*-hexyl *d*-camphorate was heated for approximately 100 hours at 240–275°, yielding 16.3 g. of distillate containing water and hydrocarbon, of which 12 g. boiled at 54–64°. Refractionated over sodium in a small Vigreux column, the boiling point of the 1-hexene was 63.5–64.5°; $n^{20}\mathrm{D}$ 1.3907; $d^{20}{}_4$ 0.6730.

Anal. Calcd. for C_6H_{12}: C, 85.71; H, 14.29. Found: C, 85.88, 85.91; H, 14.17, 14.22.

In comparison, the corresponding figures by Brooks and Humphrey[4] are b.p. 60.5–61.5° (756 mm.); $n^{25}\mathrm{D}$ 1.3821; $d^{20}{}_0$ 0.6830.

Fifteen grams of the 1-hexene was oxidized with 3000 ml. of a 2% potassium permanganate solution made alkaline with 5 g. of potassium hydroxide. After 5 hours the solution was decolorized with sodium bisulfite. The solution was then heated to boiling, the manganese dioxide filtered off and the filtrate evaporated to about 50 ml. It was acidified with dilute sulfuric acid and extracted with ether. The ether extract was fractionated at ordinary pressure, yielding 11.5 g. of *n*-valeric acid boiling at 174–178°. It was converted into the anilide in the usual manner. Recrystallized from aqueous ethanol it melted at 62–63° (uncor.) and did not lower the melting point of an authentic sample of *n*-valeroylanilide in the mixed melting point test.

The infrared spectrum revealed the presence of minute quantities of the 2- and 3-hexene isomers in the 1-hexene isolated.

The residue obtained in the pyrolysis reaction, 34.2 g., was saponified with 240 g. of an alcoholic potassium hydroxide solution containing 40 g. of potassium hydroxide by refluxing for eight hours. The ethanol was distilled off, the residue dissolved in water and the water solution extracted with ether to remove the *n*-hexyl alcohol. The alkaline solution was acidified with dilute sulfuric acid and extracted with ether. After drying with anhydrous sodium sulfate the ether was distilled off and the solid residue covered with acetyl chloride. On standing for 24 hours the excess acetyl chloride had evaporated. The semi-solid residue was dissolved in ether and the ether solution washed with aqueous sodium bicarbonate, which dissolved the *l*-isocamphoric acid, leaving the *d*-camphoric anhydride in the ether solution. Yield of camphoric anhydride—9.6 g., m.p. 223–224.5° (uncor.), which was not lowered in the mixed melting point test with an authentic sample. The aqueous sodium bicarbonate solution was acidified with dilute sulfuric acid and extracted with ether; yield of *l*-isocamphoric acid, 8.5 g. It was recrystallized from water and ethanol; m.p. 170–172°; $[\alpha]^{27}\mathrm{D}$ −53.6° (in ethanol); calcd. for $C_{10}H_{16}O_4$ neut. equiv., 200.22; found neut. equiv., 199.58.

The figures given by Aschan[8] for the same compound are: m.p. 171–172°; $[\alpha]^{14}\mathrm{D}$ −47.1° (ethanol).

Di-*l*-isobornyl *d*-Camphorate.—0.5 mole of *d*-camphoric acid, 1 mole of *l*-isoborneol (b.p. 208–211°), and 0.1% benzenesulfonic acid, together with xylene, were treated in the same manner as described for the preparation of di-*n*-hexyl *d*-camphorate. The reaction product was steam distilled to remove xylene and excess isoborneol. The camphorate was then dissolved in ether and the ether solution washed with aqueous sodium carbonate and water. After drying with anhydrous sodium sulfate the ether was evaporated and the solid ester, waxy in nature, recrystallized from pentane, after chromatographic purification on activated alumina. It melted at 49–55° (uncor.); yield of crude ester, 26.5%. *Anal.* Calcd. for $C_{30}H_{48}O_4$: C, 76.22; H, 10.23 Found: C, 76.43, 76.25; H, 10.21, 10.19.[9]

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[4] B. T. Brooks and I. W. Humphrey, THIS JOURNAL, **40**, 832 (1918).

[5] (a) T. Hasselstrom, *Ann. Acad. Sci. Fenn.*, Ser. A, Tome **XX**, No. 2 (1923); (b) T. Hasselstrom and G. Komppa, *Ann.*, **498**, 116 (1932).

[6] (a) H. Meerwein and L. Gerard, *ibid.*, **435**, 174 (1923); (b) H. Meerwein, O. Hammel, A. Serini and J. Vorster, *ibid.*, **453**, 16 (1927).

[7] Analyses by P. Sadtler & Son, Philadelphia, Pennsylvania.

[8] O. Aschan, *Acta. Soc. Sc. Fenn.*, **21**, No. 5, 52, 158 (1898).

[9] Analyses by Micro-Tech Laboratories, Skokie, Illinois.

Pyrolysis of Di-*l*-isobornyl *d*-Camphorate.—Di-*l*-isobornyl *d*-camphorate, 37.7 g., was heated for 5 hours at 235–260°, whereby 11.7 g. of distillate containing water and a dark semi-solid residue, 23.2 g., were obtained.

After separating the water, the distillate was refractionated over sodium. The main fraction, 7.5 g., was a solid, boiling at 157–159° and melting at 40°. It was made liquid with a few drops of benzene and oxidized with 1250 ml. of an aqueous solution containing 26 g. of potassium permanganate and 3 g. of potassium hydroxide by efficient stirring for 24 hours at room temperature. The solution was then decolorized with sodium bisulfite and steam distilled. The ether extract of the steam distillate yielded a minute residue with a strong camphor odor, but the quantity was too small to permit the identification of tricyclene. The residue from the steam distillation was filtered free from manganese dioxide, evaporated to about 50 ml. in a stream of nitrogen, acidified with dilute sulfuric acid, extracted with ether and the ether layer evaporated after drying with anhydrous sodium sulfate. The residue, 5.3 g., was treated with acetyl chloride in the same manner as described above for the separation of *d*-camphoric acid from *l*-isocamphoric acid, since camphenic acid does not form an anhydride.

Four grams of camphenic acid was obtained. It was recrystallized from water, m.p. 135.5–136.5° (uncor.); calcd. for $C_{10}H_{16}O_2$, neut. equiv., 200.23; found neut. equiv., 200.62, 199.48. It did not lower the melting point of an authentic sample in the mixed melting point test. This result establishes the presence of camphene.

The ether solution from the acetyl chloride treatment yielded no residue upon evaporation, showing the absence of camphoric anhydride, hence of bornylene.

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Thermodynamic Functions of Adsorbed Molecules from Surface Tension Measurements: Toluene, Benzene and *n*-Heptane on Mercury[1]

BY TERRELL L. HILL AND CHARLES KEMBALL

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Methods of calculating thermodynamic functions of adsorbed molecules from adsorption isotherm measurements[2] or calorimetric measurements[3,4] have been discussed recently. In order to obtain the molar internal energy E_S and entropy S_S of the adsorbed molecules it is necessary, using the above methods, to calculate first the surface pressure φ. This calculation requires, unfortunately, an extrapolation of the adsorption isotherm to zero pressure.

However, in some systems it is possible to measure φ directly, as the difference between the surface tension of the pure adsorbent (*e.g.*, liquid mercury) and the surface tension of the adsorbent with adsorbed molecules on it.[5–7] In the present note, which is intended to be primarily thermodynamic rather than interpretive in nature, we calculate the energy, entropy and surface concentration of toluene, benzene and *n*-heptane adsorbed on liquid mercury, using the data of Kemball and Rideal.[5] These calculations are to be regarded as supplementary to the analysis given by Kemball and Rideal.[5]

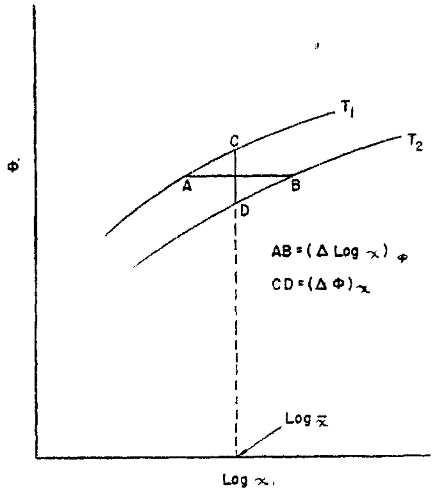

Fig. 1.—Schematic φ *versus* log x curves showing how Eq. (3) is applied.

We make the approximation throughout that the mercury surface is "unperturbed" by the adsorbed molecules. The thermodynamic calculations themselves are of course independent of any such assumption[8]; the approximation is introduced when one attributes the computed energy, entropy, etc., changes entirely to the adsorbed molecules.

Calculations

The two authors made independent calculations (circles and squares in the figures) starting with the same experimental data.[5] The procedure was as follows for each adsorbate.

Smooth curves are drawn through the experimental points of φ *versus* log x, where $x = p/p_0$, at 25 and 50°. For convenient values of φ, Δ log x is obtained from the smooth curves. We then calculate $H'_L - \mathcal{H}_S$ from[8]

$$H'_L - \mathcal{H}_S = -R\left(\frac{\partial \ln x}{\partial(1/T)}\right)_{\varphi} \qquad (1)$$

where $\mathcal{H}_S = E_S + (\varphi/\Gamma)$, Γ is the surface concentration, and L' refers to the liquid state in equilibrium with vapor. Using average values[2] $\bar{x}$ and $\bar{T}$, the molar entropy relative to the liquid state is

$$S_S - S'_L = \frac{\mathcal{H}_S - H'_L}{\bar{T}} - R \ln \bar{x} \qquad (2)$$

To calculate the surface concentration we employ

$$\Gamma = \frac{1}{RT}\left(\frac{\partial\varphi}{\partial \ln x}\right)_T = -\frac{1}{RT}\frac{(\partial\varphi/\partial T)_x}{(\partial \ln x/\partial T)_{\varphi}}$$
$$\cong -\frac{1}{RT}\frac{(\Delta\varphi)_x}{(\Delta \ln x)_{\varphi}} \qquad (3)$$

For each value of log $\bar{x}$, $\varphi_{25°}$ and $\varphi_{50°}$ are read off the smooth φ *versus* log x curves (Fig. 1), giving $(\Delta\varphi)_x$. $(\Delta \log x)_{\varphi}$ is already available (Eq. (1)), so Γ may now be calculated from Eq. (3) for each $\bar{x}$ (and φ originally chosen). Finally, the molar

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(1) Presented at the American Chemical Society Meeting, New York, September, 1951.

(2) T. L. Hill, P. H. Emmett and L. G. Joyner, THIS JOURNAL, **73**, 5102, 5933 (1951).

(3) L. E. Drain and J. A. Morrison, American Chemical Society Meeting, New York, September, 1951.

(4) G. Jura and T. L. Hill, THIS JOURNAL, **74**, 1598 (1952).

(5) C. Kemball and E. K. Rideal, *Proc. Roy. Soc.* (*London*), **187A**, 53 (1946). References to earlier work of this type are given by Kemball and Rideal.

(6) C. Kemball, *ibid.*, **187A**, 73 (1946).

(7) C. Kemball, *ibid.*, **190A**, 117 (1947).

(8) T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949); **18**, 246 (1950).