glutamic acid originate, respectively, from the δ and carboxyl carbons of its precursor histidine. Thus our results are consistent with the proposed pathway[2-4] for histidine metabolism and confirm the findings of Tabor, et al.[1]

TABLE I

Experiment No.	Specific activity of glutamic acid, counts per min. per mM.	Specific activity of ninhydrin-liberated CO_2 (α-COOH), counts per min. per mM.	C^{14} in α-COOH carbon of glutamic acid, %
1A	4100	170	4.2
1B	4100	188	4.6
2A	5220	125	2.4
2B	5220	133	2.6

Experimental

Radioactive Histidine.—DL-Histidine dihydrochloride labeled with C^{14} on the carboxyl carbon position was synthesized.[5] Its activity was measured with the use of a thin mica window tube and corresponded to approximately 1100 counts per minute per mg.

Incubation of Liver Homogenates in Presence of Labeled Histidine.—Cell-free homogenates of rat liver were prepared.[6] Into each of 50-ml. conical flasks were added 25 mg. of DL-histidine (C^{14}OOH)·2HCl, 1 ml. of 0.22 N NaOH to neutralize the hydrochloric acidity, 5-ml. aliquots of fresh homogenate and finally 10 mg. of normal L-glutamic acid as trapping agent, in the case of experiments 2A and 2B. The flasks were stoppered with cotton plugs and then agitated for 6 hours in a 38° water-bath.

Isolation and Purification of Glutamic Acid.—At the end of the incubation period, the contents of each flask were mixed with 10 volumes of absolute alcohol and heated to boiling for 10 minutes. The coagulated protein was separated by centrifugation and washed twice with alcohol. The clear alcohol solutions and washings of each preparation were evaporated to about 1 ml. and the volume brought to 10 ml. with distilled water. Into each solution was added as carrier 300 mg. of L-glutamic acid. Glutamic acid was precipitated as the calcium salt, recrystallized three times in water and alcohol, and regenerated according to the method of Foreman.[7] The aqueous solutions were each concentrated to about 4 ml. to which was added 10 ml. of absolute alcohol. Glutamic acid was allowed to crystallize slowly in an ice-box. Quantities of the purified radioactive amino acid as large as 150 mg. were recovered.

Decarboxylation of Glutamic Acid and Radioactivity Measurements.—Fifty-mg. portions of isotopic glutamic acid were decarboxylated by means of ninhydrin[8] and the evolved carbon dioxide was collected as barium carbonate. The radioactivity of the glutamic acid and the barium carbonate (40-mg. samples each) was measured with a thin mica window Geiger counter, corrected for background and self-absorption.[9] The final values were expressed as counts per minute per millimole.

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Solubility of Diborane- and Boron-containing Lithium Salts[1]

BY J. R. ELLIOTT, W. L. ROTH, G. F. ROEDEL AND E. M. BOLDEBUCK

As part of a program for studying the preparation of diborane from lithium hydride and boron trihalides in ether type solvents, it became necessary for us to determine the approximate solubility of diborane and several boron-containing lithium salts in the two solvents, diethyl ether and tetrahydrofuran.

The solubility of diborane gas was calculated from measurements of the pressure of the vapor in equilibrium with a solution of diborane at various temperatures. The temperature–pressure data listed in Tables I and II were interpreted by assuming perfect gas laws and estimating the vapor

TABLE I

EQUILIBRIUM PRESSURES FOR DIBORANE IN DIETHYL ETHER

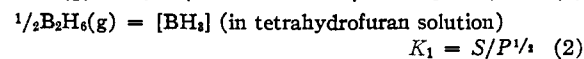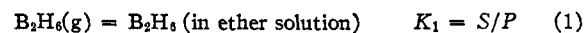Weight diethyl ether, 20.24 g.; volume of cylinder, 79.3 cc.

Series A 0.395 g. diborane		Series B 0.617 g. diborane		Series C 1.032 g. diborane	
	Obsd.		Obsd.		Obsd.
Temp., °C.	press., p.s.i. abs.	Temp., °C.	press., p.s.i. abs.	Temp., °C.	press., p.s.i. abs.
0.5	21.7	0.6	28.7	0.8	54.7
11.3	27.7	12.0	41.2	13.0	60.7
27.2	37.7	24.5	51.2	25.5	74.7
40.3	49.2	40.0	67.7	40.0	94.7
58.3	69.7	60.0	95.7	50.0	111.7
27.0	38.2				

TABLE II

EQUILIBRIUM PRESSURES FOR DIBORANE IN TETRAHYDROFURAN

Wt. diborane, g.	0.540	1.008	1.721	0.993	1.704	2.172
Wt. tetrahydrofuran, g.	25.01	25.01	25.01	24.18	24.18	24.18
Vol. of cylinder, cc.	79.3	79.3	79.3	76.3	76.3	76.3
T, °C.			Observed pressure, p.s.i. abs.			
7	2.9	3.2	4.9	2.9	5.9	13.2
20	3.9	5.6	9.8	5.4	12.2	26.7
30	5.9	9.1	16.7	9.3	21.7	42.7
40	8.3	15.2	27.7	14.2	32.7	66.7
50	...	21.5	42.2	...	49.7	93.7

pressure of the solvent on the basis of Raoult's law. The equilibrium partial pressures of solute were obtained by difference, using successive approximations for the lowering of the vapor pressure of the solvent by the solute. Calculations are summarized in Tables III and IV in terms of the equilibria

$$B_2H_6(g) = B_2H_6 \text{ (in ether solution)} \qquad K_1 = S/P \qquad (1)$$

$$^1/_2B_2H_6(g) = [BH_3] \text{ (in tetrahydrofuran solution)}$$
$$K_1 = S/P^{1/2} \qquad (2)$$

where P is the equilibrium pressure of diborane in atmospheres and S is the solubility expressed as moles diborane in 100 g. of solvent.

TABLE III

SOLUBILITY OF DIBORANE IN DIETHYL ETHER

$T°$, K	Initial B_2H_6, moles/100 g. solvent	0.706	0.110	0.184	K_1,[a] average
273	Total press., atm.	1.47	1.90	3.70	
	B_2H_6 press.	1.24	1.68	3.49	
	K_1	0.055	0.064	0.051	0.057
283	Total press., atm.	1.82	2.16	4.02	
	B_2H_6 press.	1.46	1.81	3.68	
	K_1	0.047	0.059	0.049	.052
293	Total press., atm.	2.22	3.22	4.64	
	B_2H_6 press.	1.67	2.68	4.13	
	K_1	0.041	0.040	0.043	.041
303	Total press., atm.	2.70	3.85	5.48	
	B_2H_6 press.	1.89	3.06	4.73	
	K_1	0.036	0.035	0.038	.036
313	Total press., atm.	3.33	4.63	6.48	
	B_2H_6 press.	2.17	3.50	5.40	
	K_1	0.032	0.031	0.033	.032
323	Total press., atm.	4.07	5.52	7.60	
	B_2H_6 press.	2.48	3.96	6.11	
	K_1	0.028	0.027	0.029	.028

[a] $K_1 = S/P$ (moles B_2H_6/100 g. ether—atm.).

This suggests that diborane is present in tetrahydrofuran solution as the complex $C_4H_8O:BH_3$. Heats of solution of -2800 cal./mole in ether and -4900 cal./mole in tetrahydrofuran were obtained from the change in equilibrium constants with temperature. These values should be given only qualitative significance.

The unusual solvent properties of tetrahydrofuran on boron-containing salts are shown in Table V. Solubility of the salts was roughly determined by evaporation of solvent from saturated solutions.

Experimental

Determination of Diborane Solubility.—A tared stainless steel cylinder, equipped with a pressure gage, was filled to approximately one-third capacity with dry solvent and was degassed by repeated freezing and evacuation. The cylinder was reweighed and connected by flexible metal tubing to a steel storage tank containing diborane of purity greater than 99%. Connecting lines were evacuated and small portions of diborane were admitted to the cylinder until the desired equilibrium pressure registered on the gage. The cylinder was again weighed, then submerged in a water-bath of known temperature until an equilibrium pressure was established. After a series of pressure-temperature values had been obtained, the cylinder was placed in a bell jar and dried under vacuum until constant weight had been reached.

TABLE IV

SOLUBILITY OF DIBORANE IN TETRAHYDROFURAN

$T°$, K	Initial B_2H_6 moles/100 g. solvent	0.0779	0.148	0.145	0.248	0.255	0.324	K_2[a] average
280	Total press., atm.		0.198	0.218	0.333	0.401	0.899	
	B_2H_6 press.		.113	.133	.250	.325	.828	
	K_2		.44	.40	.49	.44	.35	0.42
293	Total press., atm.	0.266	0.368	0.381	0.667	0.830	1.819	
	B_2H_6 press.	.100	.215	.227	.530	.694	1.691	
	K_2	.25	.32	.30	.33	.30	0.24	.29
303	Total press., atm.	0.402	0.619	0.633	1.137	1.477	2.910	
	B_2H_6 press.	.147	.388	.398	0.931	1.272	2.716	
	K_2	.20	.23	.23	0.25	0.22	0.18	.22
313	Total press., atm.	0.566	0.967	1.033	1.885	2.230	4.545	
	B_2H_6 press.	.196	.626	0.691	1.579	1.925	4.255	
	K_2	.18	.18	0.17	0.19	0.18	0.14	.17
323	Total press., atm.			1.461	2.874	3.386	6.380	
	B_2H_6 press.			0.967	2.429	2.942	5.967	
	K_2			0.14	0.15	0.14	0.12	.14

[a] $K_2 = S/P^{1/2}$ (moles B_2H_6/100 g. tetrahydrofuran—atm.$^{1/2}$).

The solubility of diborane in diethyl ether is slightly greater than predicted by Raoult's law but is proportional to pressure. In tetrahydrofuran the solubility of diborane is much greater than perfect solution predictions, and solubility increases as the square root of diborane pressure.

TABLE V

COMPARISON OF SOLVENT PROPERTIES OF DIETHYL ETHER AND TETRAHYDROFURAN AT 25°

	Solubility in ether, g. solute/100 g. solvent	Solubility in tetrahydrofuran, g. solute/100 g. solvent
B_2H_6	1.1[a]	8.1[a]
$LiBF_4$	1.9	71
$LiBH_4$	3[a]	28
LiF	0.05	0.6

[a] Calcd. from Tables III and IV. Diborane at 1 atm., 20°.

(2) H. I. Schlesinger, et al., Final Report, Navy Contracts No. N173 S-9058 and N173 S-9820.

A second portion of diborane was then introduced and the above procedure repeated.

Solutions of diborane in ether showed no change in pressure after several days storage. In two weeks, a pressure increase from 2 to 14 lb. and from 28 to 118 lb. had occurred in the two diborane-tetrahydrofuran cylinders.

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Separation of Mixtures with Triethylamine–Sulfur Trioxide

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In an earlier paper[1] we have reported that the action of triethylamine–sulfur trioxide on anthrahydroquinones leads to the formation of anthranol sulfuric esters in addition to the expected disulfuric

(1) M. Scalera, W. B. Hardy, E. M. Hardy and A. W. Joyce, THIS JOURNAL, 73, 3094 (1951).