

filtrate saturated with hydrogen sulfide. The precipitated silver sulfide was removed by filtering through a charcoal mat and the filtrate concentrated to a sirup under reduced pressure. To the residue was added 200 ml. of toluene and the solvent removed under reduced pressure. The residue was dissolved in 100 ml. of boiling isopropyl ether, and on cooling the trimethylglucose crystallized out. After twenty-four hours the crystals were filtered off and the filtrate concentrated and cooled in the refrigerator to obtain a second crop. Further concentration and cooling yielded a third crop. The total crystalline material was 8 g. (71.8%). The product was recrystallized by dissolving in 100 ml. of boiling isopropyl ether, charcoaling, and filtering the hot solution. On cooling to room temperature crystals of trimethylglucose soon formed and were filtered off. Four grams of colorless crystals (thick plates) was obtained. The compound sintered at 94° and melted at 97–98° (cor.);  $[\alpha]^{25}_D +41.1^\circ$  (*c*, 1.6; *l*, 4; H<sub>2</sub>O). The specific rotation increased to +78° at equilibrium. The data on mutarotation are given in Table I. A sample of this material was dissolved in water containing a trace of ammonia and the rotation determined,  $[\alpha]^{25}_D +77.5^\circ$  (*c*, 2; H<sub>2</sub>O).

*Anal.* Calcd. for C<sub>9</sub>H<sub>18</sub>O<sub>6</sub>: CH<sub>2</sub>O, 41.89. Found: 41.64.

On cooling the filtrate from the first crystallization in the refrigerator, 2.5 g. of colorless needles was obtained; m. p. 64–67° (cor.);  $[\alpha]^{25}_D +91.9^\circ$  (*c*, 2; *l*, 4; H<sub>2</sub>O). The specific rotation decreased to +77.4° at equilibrium. Data on mutarotation are given in Table I. A sample was recrystallized several times from isopropyl ether with cooling. Melting point of final product, 76–77° (cor.).

The following procedure was used in the preparation of the first sample of 3,4,6-trimethyl-*D*-glucose which crystallized. Five grams of methyl 3,4,6-trimethyl- $\beta$ -*D*-glucoside was dissolved in 150 ml. of 5% aqueous hydrochloric acid and the solution refluxed for two and one-half hours. The solution was then filtered and treated with an excess of barium carbonate. A small amount of charcoal was added and the mixture filtered. The filtrate was evaporated to dryness *in vacuo* and the residue extracted with boiling chloroform. A little charcoal was added and the mixture filtered. The solvent was evaporated and the residue sirup placed in a vacuum oven overnight at 60°. The yield of thick sirup was 4 g. (84%);  $[\alpha]^{25}_D +74.2^\circ$  (*c*, 1.66; H<sub>2</sub>O).

After standing at room temperature for two months, this product was found to have partially crystallized. It was recrystallized from isopropyl ether with cooling, re-

serving a sample for seed crystals. The compound crystallized in the form of fine colorless needles, m. p. 77–79.5°. After another recrystallization the melting point was 78–80°. Further recrystallization produced no change in melting point.

TABLE I

MUTAROTATION OF 3,4,6-TRIMETHYL-*D*-GLUCOSE AT 25°<sup>a</sup>

Time in minutes	Rotation observed, °	Specific rotation, °
A. Alpha form (needles), weight of compound 0.4989 g.		
2.5	7.33	91.9
5	7.18	90.0
10	7.12	89.3
25	6.91	86.6
90	6.42	80.5
300	6.16	77.4
1050	6.16	77.4
B. Beta form (plates), weight of compound 0.4031 g.		
2.5	2.65	41.1
3.5	2.72	42.2
5	2.75	42.6
10	2.95	45.8
15	3.14	48.7
35	3.64	56.5
65	4.13	64.0
155	4.69	72.8
210	4.79	74.4
1050	5.03	78.0
1260	5.03	78.0

<sup>a</sup> Solvent, water; volume of solution, 25 ml.; length of tube, 4 dm.

### Summary

3,4,6-Trimethyl- $\beta$ -*D*-glucose and 3,4,6-trimethyl- $\alpha$ -*D*-glucose have been obtained in crystalline form.

A new synthesis of methyl 3,4,6-trimethyl- $\beta$ -*D*-glucoside has been carried out.

IOWA CITY, IOWA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## Equilibrium in the Dehydrogenation of Secondary Propyl and Butyl Alcohols

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### Introduction

Equilibrium has been studied in the dehydrogenation of but one secondary alcohol, *i*-propyl alcohol.<sup>2</sup> It appeared profitable to re-investigate this reaction with other techniques and to extend the study to other secondary alcohols. This paper reports the results of such investigation in the cases of *i*-propyl and *s*-butyl alcohols. The study of other secondary alcohols will be continued when circumstances permit.

(1) Present address. Naval Research Laboratory, Washington, D. C.

(2) Parks and Kelley, *J. Phys. Chem.*, **32**, 740 (1928).

### Experimental

**Materials.**—Mono-*i*-propyl phthalate was twice recrystallized from ligroin and saponified. After drying with lime, the alcohol was fractionated in a 50-plate Stedman column;  $d^{24.82}_4$ , 0.78106.<sup>3</sup>

*s*-Butyl alcohol (Eastman Kodak Company) was fractionated in a 150-plate Podbielniak Heli-Grid column at a reflux ratio of 100 to 1 and a take-off rate of 5 ml. per hour;  $d^{25}_4$ , 0.80250,  $n^{25}_D$  1.3948.<sup>4</sup>

(3)  $d^{25}_4$  0.78099 interpolated from the data of Timmermans and Delcourt, *J. chim. phys.*, **31**, 105 (1934). Brunel, *This Journal*, **45**, 1337 (1923), gives 0.78084. Correcting our value to 25° by the temperature coefficient of Timmermans, one gets 0.78091.

(4) Brunel<sup>3</sup> reports  $d^{25}_4$  0.80235;  $n^{25}_D$  1.39495; Timmermans and Martin, *J. chim. phys.*, **25**, 431 (1928), report  $d^{25}_4$  0.80299.

As catalyst for the dehydrogenation of 2-propanol, 20–40 mesh granular copper oxide was reduced with hydrogen *in situ* at 185°. Spectroscopic analysis showed traces of barium, calcium, iron, nickel and magnesium.

The copper catalyst employed for 2-butanol contained 0.5% nickel. Mixed carbonates coprecipitated from nitrates by ammonium carbonate were heated to 250°, briquetted by hydraulic pressure after mixing with 6% of graphite, broken and sieved to 20–40 mesh. This oxide was reduced by a 5–1 nitrogen–hydrogen mixture at 185° in the equipment of the Ipatieff Laboratory through the kindness of Professor H. Pines.

Other catalysts showed either too little activity (as the first mentioned catalyst) or interfering side reactions (as copper chromite). The addition of nickel promoted the activity of copper considerably without, in the dehydrogenation of *s*-butyl alcohol, introducing side reactions.<sup>5</sup>

**Apparatus.**—Equilibrium constants were determined in an apparatus shown in part by Fig. 1. Purified alcohol was drawn from a storage system attached at A to the reservoir of a feed system connected at C. The feed system provided a controllable and very uniform flow of alcohol to the pre-reactor, D, which was packed with catalyst. Here, the alcohol was volatilized and partially transformed to ketone and hydrogen. The resulting vapor mixture passed through the catalyst tube of the main reactor, E. Provision was made for analyzing the equilibrium mixtures produced in E in two ways. Condensables (alcohol and ketone) were removed by the water-cooled condenser, F, supplemented by the trap, G, which was cooled with liquid air or Dry Ice. Determining the ratio of alcohol to ketone in the condensate allowed calculation of the composition of the reaction mixture. The composition could also be found by measuring the quantity of hydrogen passing through trap, G, in combination with that of the amount of alcohol fed. The unit, K, served as a manostat and delivered the hydrogen to a system of known volume, the increase in pressure in which during a run gave the amount of hydrogen evolved. Analyses by the hydrogen evolution method were always performed and were supplemented in sample cases by the other.

Initially the apparatus was permitted to run until a steady state was reached. Four cc. of alcohol was passed through the catalyst chamber at the rate of about 1.5 cc. per hour. The first run was usually made with the temperature of the pre-reactor set somewhat below that of the main reactor thus providing an approach from the alcohol side of the equilibrium position. The process was then repeated with the pre-reactor heated 20–50° above the reactor thus providing an approach from the other side of the equilibrium position. Permanganate was added to the condensate to test for unsaturation from side reactions. None was found for either alcohol.

Using the 0.5% nickel catalyst, runs were made with pentanol-3 and cyclopentanol. From permanganate test and polarographic analysis, pentene and cyclopentylidene-cyclopentanone, respectively, were found in concentrations high enough to prevent reliable determinations of equilibrium constants.

**Storage and Feed System.**—Alcohol was delivered from a glass-helix packed column of the Fenske type into a storage flask sealed to the apparatus at A. The contents of this were boiled to eliminate air while alcohol was being drawn into the feed system at C. Necessary valves were provided by B and by the loop beyond C. The latter was "closed" by congealing entrained alcohol slugs with liquid air; the former was of the type of sintered glass disk with mercury closure.

The feed system has been described.<sup>6</sup> It consisted of a long 25-cc. calibrated buret which could be read to 0.01 cc. Water from a thermostat kept at 25° was circulated through its water jacket. Alcohol was displaced by mercury which was forced into the bottom of the buret by gas evolved in an electrolytic cell. Flow rates varied less than 1% during a run.

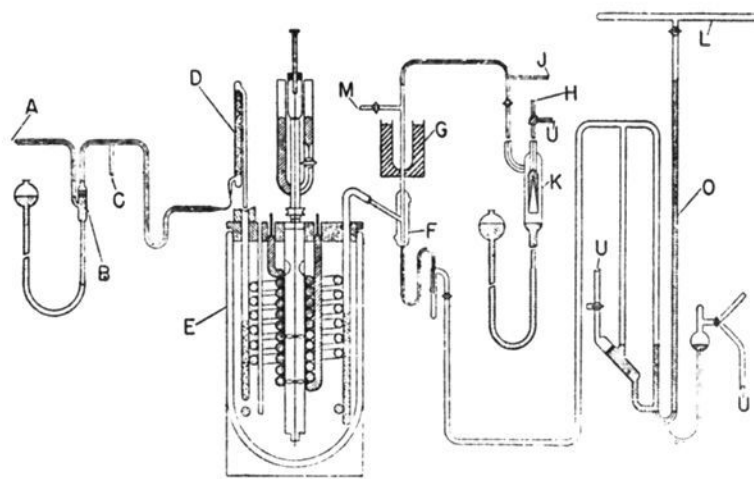


Fig. 1.—Apparatus.

**Reactors.**—Alcohol was volatilized into the pre-reactor by a small flame at the capillary constriction. The pre-reactor contained 10 cc. of catalyst and was heated by a tube furnace. The main reactor (double scale in Fig. 1) consisted of a two-quart Pyrex Dewar flask provided with a stirrer at the center, about which in concentric helices were placed a tubular heating element (Aminco "Lo-Lag," copper jacketed), the mercury reservoir of the mercury thermoregulator, and the catalyst tube. The latter, a helix of a turn and a half, contained 5 cc. of catalyst and exposed a large surface to the bath fluid, mineral oil. This arrangement provided temperatures constant to within  $\pm 0.1^\circ$  during a run in the range of 140–250°. Temperatures were measured with a copper–constantan thermocouple which was frequently compared *in situ* at 25° intervals with a set of thermometers calibrated by the Bureau of Standards and also with the steam point. An accuracy in temperature measurement within  $\pm 0.5^\circ$  would make the effect of temperature errors on the equilibrium constant smaller than the estimated errors from other sources. Judging from comparisons with the standard thermometers, the precision in temperature measurement was distinctly better than 0.5°.

To obtain samples of the condensate for analysis, the stopcock was opened to manostat, O, which was kept at a pressure just below that of the reaction system. The sample was thus drawn into the collection tube. Upon closing the stopcock and congealing condensate slugs in the U-tube by means of liquid air, the collection tube was removed. After replacing a tube, the stopcock was opened and closed and the liquid air removed.

**Hydrogen Collection System.**—A manometer sealed to the line at J indicated the total pressure in the reactor. Section K (double scale) served as the pressure control. A section of capillary tubing was blown out to yield a conical portion. This was sealed off at the wide end and cut on a saw along the axis. The glass on one side of the cut was removed and in its place was cemented an equivalent planar portion of unglazed pottery. Any desired portion of the pottery could be covered by mercury so that there resulted a leak which could be adjusted over a wide range by adjustment of the mercury level. With rise in pressure, the mercury level was forced down with a resulting faster removal of hydrogen. A small change in mercury level and consequently in pressure accommodated a large change in hydrogen evolution. In our runs, because of the constant rate of alcohol feed, the mercury level after an initial setting remained at a constant level.

The manostat, O, operated similarly. A porous "Celas" plate was sealed in a tube inclined at an angle of 45°. By adjustment of the mercury level in the tube adjacent to O, any desired pressure could be maintained.

A hydrogen collection system consisted of four 2-liter flasks sealed together and connected to the three-way stopcock at H, and immersed in a thermostat at 25°. It was evacuated before each run. With a cathetometer, the manometer of large bore tubing could be read to  $\pm 0.05$  mm. The other sections of the apparatus were: the high vacuum line, L, also connected to the hydrogen collection

(5) Ipatieff and Corson, *J. Phys. Chem.*, **45**, 431 (1941).

(6) Burwell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 681 (1940).

system; the electrolytic hydrogen generator, M; and the water-aspirated manifold connected at points, U.

### Experimental Results

The quantity of alcohol passed over the catalyst combined with that of the hydrogen liberated allowed the calculation of  $\alpha$ , the fraction dissociated, and thence the value of the equilibrium constant

$$K_p = \alpha^2 P / (1 - \alpha^2) \quad (1)$$

where  $P$  is the total pressure. Results are given in Table I.

TABLE I

#### EQUILIBRIUM CONSTANTS IN THE DEHYDROGENATION OF SECONDARY PROPYL AND BUTYL ALCOHOLS

a = approach from ketone-hydrogen side of equilibrium.  
b = approach from alcohol side of equilibrium.

$T$ , °K.	$P$ , mm.	$\alpha$	Approach	$K_p$
<i>i</i> -Propyl alcohol				
416.7	731	0.338	b	0.124
417.8	729	.348	a	.132
422.7	718	.374	b	.154
		.377	a	.156
433.4	729	.443	a	.234
436.4	737	.471	b	.276
444.8	718	.523	b	.356
452.2	720	.561	b	.435
		.569	a	.454
455.7	739	.592	b	.525
464.3	729	.645	b	.683
		.662	a	.748
472.8	717	.710	b	.959
		.713	a	.975
491.6	715	.791	b	1.57
		.793	a	1.59
<i>s</i> -Butyl alcohol				
419.7	707	0.369	b	0.146
		.373	a	.150
419.6	285	.535	b	.150
		.540	a	.154
428.0	720	.416	b	.198
		.428	a	.212
434.9	721	.481	b	.285
		.481	a	.285
438.2	521	.561	b	.315
		.558	a	.309
444.2	724	.522	b	.357
		.543	a	.384
453.3	484	.684	b	.560
		.659	a	.489
454.6	721	.601	b	.536
		.611	a	.565
456.1	733	.611	b	.574
		.598	a	.537
472.2	308	.849	b	1.046
		.843	a	0.995

The precision of the measurement of  $\alpha$  depends upon the precision of the measurement of the alcohol volume and the hydrogen pressure and is about  $\pm 0.005$ . The corresponding uncertainty in  $\log K_p$  is about  $\pm 0.01$  save at small and large

values of  $\alpha$  in which cases the uncertainty increases. The smoothed values of  $\log K_p$  are probably accurate to within 0.02.

In certain cases, the fractions of alcohol dissociated were determined by analysis of the condensate and compared with the values obtained by simultaneous measurement of the hydrogen evolution. A number of runs were made by an adaptation to small samples of the *i*-propyl alcohol determination of Cassar<sup>7</sup> which involves the oxidation of the alcohol with potassium dichromate. Differences in values of  $\alpha$  so determined were within about 0.02, the limit of error of the oxidation method.

The analytical method as employed by Parks and Kelley<sup>2</sup> which depends upon index of refraction measurements was also employed, although the indices of *i*-propyl alcohol and acetone being, respectively,  $n_D^{20}$  1.3743 and 1.3555, the presence of small amounts of by-products could lead to large errors in  $\alpha$ . Agreement to within 0.01 in  $\alpha$  with the hydrogen evolution method was, however, obtained.

### Discussion

In the case of *s*-butyl alcohol, which, owing to its higher boiling point, would be expected to exhibit the greater departure from ideality, several runs were made at two-thirds and one-third atmospheres. Since fugacities approach partial pressures as the pressure is reduced, extrapolation to zero pressure will yield the true equilibrium constant. However, it developed that the measured value of  $K_p$  was independent of pressure. To within the experimental error, the measured values must, therefore, correspond both to the true and to the ideal ones.

This effect must arise from the negligible departure from unity of the fugacity coefficient of hydrogen and from the cancelling of the fugacity coefficients of ketone and alcohol, which are nearly equal since the critical constants are probably about the same. This is the case with acetone and *i*-propyl alcohol,  $t_c = 236^\circ$ ,  $P_c = 53$  atm., approximately.<sup>8</sup>

In Fig. 2, the values of  $\log K_p$  are plotted against the reciprocal of the absolute temperature. The data for both systems are adequately represented by the simple van't Hoff equation

$$\log K_p = A - \frac{\overline{\Delta H}}{2.303RT} \quad (2)$$

where  $\overline{\Delta H}$  is the average enthalpy increase in the temperature range under consideration. From the slopes of the best straight lines for the acetone, hydrogen, *i*-propyl alcohol equilibrium

$$\overline{\Delta H} (T_{av.}, 454^\circ\text{K.}) = 13,980 \text{ cal.}$$

for the butanone, *s*-butyl alcohol, hydrogen equilibrium

$$\overline{\Delta H} (T_{av.}, 446^\circ\text{K.}) = 14,110 \text{ cal.}$$

(7) Cassar, *Ind. Eng. Chem.*, **19**, 1061 (1927).

(8) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Vol. 1, 5th ed., J. Springer, Berlin, 1923, pp. 253, 260.

The probable errors are of the order of 200 cal.

The only modern experimental value of  $C_p$  for acetone is that of Bennewitz and Rossner<sup>9</sup> at but one temperature, 410°K., 22.5 cal. per deg. The others are very old.<sup>10</sup>

Aston and co-workers<sup>11</sup> have established partition functions which allow the determination of the heat capacities of acetone and 2-propanol. In disagreement with the latter are the experimental values of Parks and Shomate<sup>12</sup> which seem to have too high a temperature coefficient.

It seems best to employ the values of Bennewitz and Rossner<sup>9</sup> who have measured on the same apparatus  $C_p$  for *i*-propyl alcohol at 410°K., 26.5. These coupled with 7.0 as the  $C_p$  for hydrogen, give  $\Delta C_p = 3.0$ . This value will be used as independent of temperature, though since *i*-propyl alcohol has the higher heat capacity its temperature coefficient should be greater and  $\Delta C_p$  should decline with temperature. An error of as much as 3 cal. per deg. in the temperature range under consideration may result from this assumption.

Bennewitz and Rossner report  $C_p$  for methyl ethyl ketone to be 29.8 at 410°K. No values for the heat capacities of *s*-butyl alcohol have been published. However, Bennewitz and Rossner report  $C_p$  at 410°K. for *n*-butyl alcohol to be 32.9 and for *i*-butyl alcohol to be 33.3. One would then expect  $\Delta C_p$  for the dehydrogenation of *s*-butyl alcohol to be about the same as that of *i*-propyl alcohol.

Parks and Kelley<sup>2</sup> used 4.0 for  $\Delta C_p$  for the *i*-propyl alcohol reaction. Kistiakowsky<sup>13</sup> has employed 4.0 for dehydrogenation reactions in general.

Using 3.0 for  $\Delta C_p$ , the values of  $\overline{\Delta H}$  obtained from Fig. 2, and the values of  $K_p$  read from the best straight line at the values of  $T_{av}$  appropriate to the  $\overline{\Delta H}$ 's, the following equations have been established:

For *i*-propyl alcohol

$$\log K_p = -2758/T + 1.510 \log T + 1.759 \quad (3)$$

$$\Delta H_T^0 = 12,620 + 3.0T \quad (4)$$

$$\Delta S_T^0 = 11.05 + 6.908 \log T \quad (5)$$

For *s*-butyl alcohol

$$\log K_p = -2790/T + 1.510 \log T + 1.865 \quad (6)$$

$$\Delta H_T^0 = 12,770 + 3.0T \quad (7)$$

$$\Delta S_T^0 = 11.54 + 6.908 \log T \quad (8)$$

The average departure of the experimental values of  $\log K_p$  from the equations given above is 0.015.

Subtracting equations of types (3) and (2), one obtains

(9) Bennewitz and Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

(10) Wiedemann, *Wied. Ann.*, **2**, 195 (1877); Regnault, *Mem. de l'Acad.*, **26**, 1 (1862).

(11) Aston, Isserow, Szasz and Kennedy, *J. Chem. Phys.*, **12**, 336 (1944); and Aston and Schumann, *ibid.*, **6**, 485 (1938).

(12) Parks and Shomate, *ibid.*, **8**, 429 (1940).

(13) Dolliver, Gresham, Kistiakowsky, Smith and Vaughan, *This Journal*, **60**, 440 (1938).

$$\log K_p - \log \bar{K}_p = \frac{\Delta C_p}{2.303R} \left[ \ln \frac{T}{T_a} + \frac{T_a - T}{T} \right] - \frac{\Delta C_p}{2.303R} \left[ \frac{(T - T_a)^2}{T_a T} \right] \quad (9)$$

where the last relation holds for small values of  $(T_a - T)$ . At  $T_a$ , the average temperature of the range on which  $\overline{\Delta H}$  is evaluated,  $\log K_p = \log \bar{K}_p$ . In the plot of  $\log K_p$  vs.  $1/T$ , one would draw the straight line to split its deviation from equation (3) thus halving that given by equation (9). With  $\Delta C_p = 4$ ,  $T_a = 460^\circ\text{K.}$ ,  $\log K_p - \log \bar{K}_p \approx 0.0033$  at 420 or 500°K. Thus, deviation of our data from equation (2) would be detectable only over a much greater temperature range.

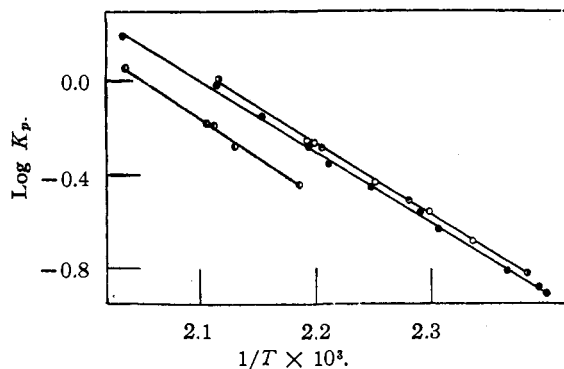


Fig. 2.—Plot of  $\log K_p$  vs.  $1/T$ :  $\bullet$ , values of Parks and Kelley for *i*-propyl alcohol;  $\bullet$ , this investigation for *i*-propyl alcohol, 1 atm.;  $\circ$ , for *s*-butyl alcohol, 1 atm.;  $\odot$ , for *s*-butyl alcohol,  $2/3$  atm.;  $\ominus$ , for *s*-butyl alcohol,  $1/3$  atm.

Acetone and methyl ethyl ketone are among the compounds the heats of hydrogenation of which have been measured by Kistiakowsky and his co-workers.<sup>13</sup> In the case of acetone, they report that a colorimetric test indicated about 0.6% acetone in the hydrogenation product, a value not far from that predicted by the extrapolation of our values of  $K_p$ , about 0.8%. However, their estimate of the quantity of methyl ethyl ketone left unhydrogenated is 0.2% while our results predict 0.8–0.9%. Their averaged value of  $\Delta H$  in this case would be increased from 13,193 to 13,277 cal. The value for acetone was 13,426 cal.

Considering the estimated error in the measurements of Kistiakowsky, 100 cal., the possible error in the slope of our plot of  $\log K_p$  vs.  $1/T$  and the uncertain errors involved in our extrapolation, the agreement between Kistiakowsky's results and ours, 13,690 cal. by equation (4), is quite satisfactory in the case of the hydrogenation of acetone. The agreement in the case of methyl ethyl ketone is less good, where, by equation (7), our results lead to a value of 13,840 cal.

In Fig. 2, the results of Parks and Kelley<sup>2</sup> are also plotted. Their values of  $K_p$  are throughout substantially smaller than ours. Their values of  $\Delta F_T^0$  are about 350 cal. greater than ours. The

origin of the difference between their results and ours is not clear. It should be noted that the presence of side reactions could lead, with their analytical method, to substantial errors.

From considerations of a statistical mechanical nature, Aston, Isserow, Szasz and Kennedy<sup>11</sup> have calculated the equilibrium constants for the dehydrogenation of *i*-propyl alcohol and compared these with those of Parks and Kelley.<sup>2</sup> These statistically calculated values of  $\log K_p$  and those calculated from equation (3) are, respectively, at 355.5, 450 and 500°K.: -2.09, -2.14, -0.38, -0.36, +0.28, +0.32.

## Summary

1. Equilibrium constants for the reactions of *i*-propyl and *s*-butyl alcohols to form the corresponding ketones and hydrogen have been measured in the temperature range of 416 to 491°K. The degree of dissociation of the latter alcohol is very slightly the greater of the two.

2. The equilibrium constants in terms of partial pressures are independent of pressure at pressures between one-third and one atmosphere.

EVANSTON, ILL.

RECEIVED AUGUST 10, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Coördination Compounds of Boron Trichloride. II.<sup>1</sup> Systems with Sulfur Dioxide and Hydrogen Sulfide

BY DONALD RAY MARTIN

Since the boron atom of boron trichloride has only six electrons, it acts as an acceptor in the formation of coördination compounds.<sup>1</sup> The donor atoms of these compounds have been found to be limited to the non-metals nitrogen, phosphorus, arsenic, oxygen, sulfur, fluorine and chlorine.

In studying the formation of coördination compounds of a gas like boron trichloride, the method of thermal analysis offers many advantages. The object of this investigation was to extend the knowledge of the coördination compounds of boron trichloride with gaseous sulfur compounds by means of thermal analysis.

### Apparatus and Procedure

The apparatus and procedure used for this investigation were very similar to those previously described<sup>2,3,4</sup>

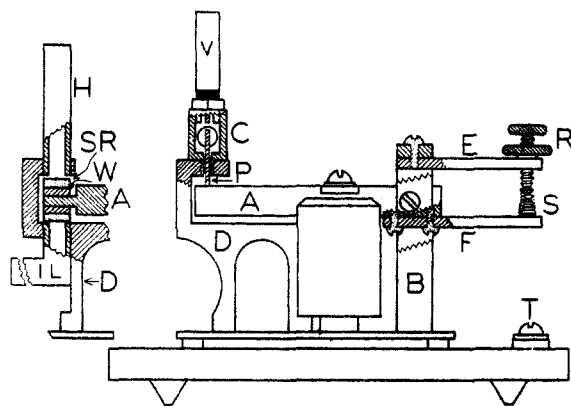


Fig. 1.

- (1) D. R. Martin, *Chem. Rev.*, **34**, 461-473 (1944).
- (2) H. S. Booth and D. R. Martin, *THIS JOURNAL*, **64**, 2198-2205 (1942).
- (3) H. S. Booth and D. R. Martin, *Chem. Rev.*, **33**, 57-88 (1943).
- (4) A. P. O. Germann and H. S. Booth, *J. Phys. Chem.*, **30**, 369-377 (1926).

except for four modifications. First, the fractionating column using liquid air as the head refrigerant was modified to give better control of the fractionation as suggested by Booth and McNabney.<sup>5</sup>

Second, in order to have more positive action in the opening and closing of the automatic stopcock on the fractionating column, the 20-ohm telegraph sounder described by Booth and Bozarth<sup>6</sup> was modified as shown in Fig. 1. The compressed air bleed-off line is connected to the bicycle tire valve V which is attached to the sounder base D by a brass adapter C. When electrical contact is made by the mercury in the control manometer of the fractionating column, the sounder is actuated causing its arm A to be lowered toward the base D. As a result the iron pin P drops thus allowing the bicycle tire valve stem to close. All of the compressed air is then forced into the automatic stopcock mechanism. Due to the strength of the spring in the bicycle tire valve stem, the sounder spring S has to be located at a greater distance from the fulcrum than on an unmodified sounder. This is achieved by attaching brass strips E and F.

The modified sounder is unsatisfactory as the control valve for the injection of liquid air into the head of the fractionating column because the narrow opening through the bicycle tire valve V affords too much resistance to the escaping air thus producing a pressure of sufficient magnitude to cause the injection of liquid air. This difficulty was obviated by modifying the sounder as shown by the section at the left in Fig. 1. The liquid air injector is connected to the brass tubing IL which is soldered into the special brass base D. This replaces the regular base differing from it in being one-half inch in width. This affords room for the brass tubing which is  $\frac{5}{32}$  inch in diameter. The exit tube from the head of the fractionating column is connected to the brass tubing H. The arm A of the sounder is modified as shown to accommodate the valve seats made from brass washers W and spongy-rubber pads SR. With this arrangement one of the valves is always open while the other is closed with the result that liquid air can be injected only when the sounder is actuated by the control manometer.

The third modification deals with the use of cooled acetone as the refrigerant for the head of the fractionating column. As previously described,<sup>6</sup> the acetone is circulated by a small centrifugal pump from a pint size Dewar

(5) H. S. Booth and Ralph McNabney, *Ind. Eng. Chem., Anal. Ed.*, **16**, 131-133 (1944).

(6) H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470-475 (1937).