

## The Relative Values of the Four ButaneButeneHydrogen Equilibrium Constants

Louis S. Kassel

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## LETTERS TO THE EDITOR

*This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor*

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### The Relative Values of the Four Butane-Butene-Hydrogen Equilibrium Constants<sup>1</sup>

Eidinoff and Aston<sup>2</sup> have given a very convenient method for calculating the rotational entropy of molecules with internal rotating groups. This method, after some further development, has been used to calculate the following values for the translational plus rotational entropies at 25°C.

<i>n</i> -butane	75.366	2-butene, <i>cis</i>	68.225
isobutane	71.249	2-butene, <i>trans</i>	67.800
1-butene	72.98	isobutene	68.215

The value given for 1-butene is an estimate which should be reliable, but which will subsequently be replaced by an exact value. An accurate calculation of vibrational entropies for these molecules is not yet possible. It is probably a good approximation to assume that the vibrational contributions for *n*- and isobutane are the same, and also that the contributions for the four butenes differ only in the part coming from torsion about the C=C bond. This part may be estimated by taking the fairly reliable figure of 790 cm<sup>-1</sup> for the torsion frequency in ethylene to determine the force constant, and by using the ratio 21.5 : 1 for the moments of CH<sub>3</sub> and H about the C=C axis. A simple calculation gives 572 cm<sup>-1</sup> for the torsion frequency in 1-butene and isobutene, 244 cm<sup>-1</sup> in both 2-butenes. The entropies calculated in this way may be combined with heats of hydrogenation determined by Kistiakowsky, Ruhoff, Smith and Vaughan.<sup>3</sup> The most direct calculation is that of the *cis-trans* equilibrium, since here the torsion cancels out. The equilibrium constant is  $[cis]/[trans] = \exp[-949/RT + 0.425/R]$  or 0.61 at 400°C. The experimental value of Frey and Huppke<sup>4</sup> is 0.64. The 1-butene, transbutene calculation is more involved; the rotational entropy of 1-butene is 5.179 e.u. higher than that of transbutene; the torsion correction of 1.67 e.u. lowers this to 3.509 e.u. The heat content of 1-butene is 2720 cal. higher at 82°C; the torsion correction gives 2617 cal. at 400°C. Hence  $[1\text{-butene}]/[\text{transbutene}] = 0.49$ , against the experimental value of 0.56. The ratio of the dissociation constant for isobutane to isobutene against that of *n*-butane to transbutene depends upon the rotational entropy differences between *n*- and isobutane, and between *trans*- and isobutene, the same calculated torsional entropy and heat content differences as in the preceding example, and the hydrogenation heats. The isobutane dissociation involves a 2.862 e.u. greater entropy

increase and a 695 cal. greater heat input at 400°C. Hence  $K_{iso}/K_{trans} = 2.51$ , in somewhat fortuitous agreement with 2.56, the experimental value of Frey and Huppke. The experimental determination of  $[1\text{-butene}]/[\text{transbutene}]$  varies less with temperature, and that of  $K_{iso}/K_{trans}$  varies more, than the theoretical values. Frey and Huppke have stated, however, that the accuracy of their data would not justify a calculation of  $\Delta H$  from the temperature coefficient. The agreement of calculated and observed values is thus as good as could be expected.

It is of interest to note the extremely simple basis of these calculations. The bond distances and angles are semispectroscopic in origin, but might have been determined entirely from x-ray diffraction. The individual translation-rotation entropies depend upon the quantum constant  $h$ , but the entropy differences actually used are ratios of purely classical phase-space volumes. The treatment of the torsional vibration is the only part of the calculation that Gibbs or Boltzmann would have been unable to make.

A more complete account of this work is contained in two papers, of which one has been, and the other shortly will be, submitted to the *Journal of Chemical Physics*.

LOUIS S. KASSEL<sup>5</sup>

Physical Chemistry Section, Pittsburgh Experiment Station,  
U. S. Bureau of Mines, Pittsburgh, Pennsylvania,  
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<sup>2</sup> Eidinoff and Aston, *J. Chem. Phys.* **3**, 379 (1935).

<sup>3</sup> Kistiakowsky, Ruhoff, Smith and Vaughan, *J. Am. Chem. Soc.* **57**, 876 (1935).

<sup>4</sup> Frey and Huppke, *Ind. Eng. Chem.* **25**, 54 (1933).

<sup>5</sup> Physical chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

### The Mutarotation of Glucose in H<sub>2</sub>O - D<sub>2</sub>O Mixtures

In an earlier communication<sup>1</sup> it was shown that the dependence of the specific velocity constant for the mutarotation of  $\alpha$ -D-glucose could be described satisfactorily by the equation

$$k_{obs} = k_{H_2O}CH_2O + k_{HDO}CHDO + k_{D_2O}CD_2O. \quad (1)$$

Eq. (1) furnishes evidence for the kinetic influence of the decrease in basicity of the solvent with increase in D content but implicitly denies any influence of the isotopic exchange which takes place in the substrate.

TABLE I.

$P_w$	$k(10)^5$	(H <sub>2</sub> O)	(HDO)	$R_w$	$R_g$	$K$	$P_g$
0.050	976	50.03	5.20	9.61	0.090	0.87	0.08
0.056	979	49.91	5.78	8.54	0.086	.73	0.09
0.112	925	43.82	10.76	4.07	0.174	.71	0.17
0.142	891	40.96	13.14	3.11	0.238	.74	0.21
0.145	869	40.69	13.36	3.05	0.284	.87	0.22
0.179	826	37.61	15.74	2.39	0.382	.91	0.26
0.190	829	36.64	16.46	2.23	0.375	.84	0.27
0.265	762	30.38	20.68	1.469	0.561	.82	0.36
0.369	677	22.70	24.52	0.925	0.885	.82	0.47
0.384	653	21.69	24.88	0.868	1.003	.87	0.49
0.404	654	20.35	25.34	0.803	0.987	.79	0.51
0.416	644	19.57	25.56	0.765	1.050	.80	0.52
0.507	560	14.17	26.23	0.540	1.638	.89	0.61
0.575	526	10.68	25.74	0.414	1.984	.82	0.67
0.624	496	8.50	24.66	0.345	2.38	.82	0.71
0.652	467	7.31	23.94	0.303	2.87	.87	0.73
0.663	452	6.88	23.58	0.292	3.18	.93	0.74
0.831	356	1.81	15.06	0.120	7.68	.92	0.87
0.890	324	0.79	10.62	0.073	12.1	.88	0.92
0.895	328	0.71	10.14	0.070	11.67	.82	0.92
0.960	293			0.025			0.97
0.960	293			0.025			0.97
Av. 0.83							

$$R_g \text{ (Col. 6)} = \frac{(P_g \text{ Eq. 2})}{1 - P_g \text{ (Eq. 2)}}; P_g \text{ (Eq. 2)} = (1040 - k_{\text{obs}})/(1040 - 273);$$

$$P_g \text{ (Col. 8)} = \frac{0.83/R_w}{1 + 0.83/R_w}.$$

If one adopts as a working hypothesis the alternate view that the decrease in velocity is due only to replacement of H by D in that position in the glucose molecule which is involved in the mutarotation and does not depend kinetically upon the relative abundance of H<sub>2</sub>O, HDO, and D<sub>2</sub>O, we may write

$$k_{\text{obs}} = k_{\text{H}_2\text{O}} - (k_{\text{H}_2\text{O}} - k_{\text{D}_2\text{O}})P_g. \quad (2)$$

$P_g$  denotes the fraction of  $\alpha$ -D-glucose in which the OH on the terminal carbon atom has become OD. This ex-

change may be assumed as more rapid than mutarotation. This hypothesis may be tested readily by calculating from Eq. (2), values of  $P_g$  over the range H<sub>2</sub>O–D<sub>2</sub>O, using the experimental values of the  $k$ 's.  $P_g$  is readily converted into  $R_g$ , the ratio of the concentrations of heavy glucose and light glucose, which may be combined with  $R_w = (\text{HOH})/(\text{HOD})$  to give the exchange constant

$$R_g R_w = \frac{(D - G)(\text{HOH})}{(H - G)(\text{HOD})} = K. \quad (3)$$

The earlier data<sup>1</sup> together with more recent results have been combined in Table I.  $P_w = \Delta s/0.1079$  is the excess specific gravity ratio. The  $K$ 's are constant within experimental error. The average  $K = 0.83$  agrees exactly with that for tetramethyl glucose found directly from exchange experiments<sup>2</sup> but disagrees with the value for glucose (0.69). This is to be expected since the exchanging hydrogen atom in tetramethyl glucose is the only one which is involved in mutarotation catalyzed by bases while the constant reported for glucose is an averaged constant  $(K_1 K_2 K_3 K_4 K_6)^{1/5}$ , where subscripts refer to the positions of the five exchangeable hydrogens in the glucose molecule.

When  $k_{\text{obs}}$  is plotted against  $P_g$  as calculated from  $K = 0.83$ , Eq. (2) is obeyed within the experimental error. The single experimental value for the isotopic exchange with tetramethyl glucose must be confirmed before the hypothesis advanced may be accepted as conclusive. The correct explanation may lie between the two extreme views.

W. H. HAMILL  
V. K. LA MER

Fordham University,  
New York City.

Columbia University,  
New York City.

<sup>1</sup> Hamill and La Mer, J. Chem. Phys. 2, 891 (1934).

<sup>2</sup> Hamill and Freudenberg, J. Am. Chem. Soc. 57, 1427 (1935).