

at room temperature and at the reflux temperature.

3. The scission of the octyl group of 4-(1,1,3,3-tetramethobutyl)-phenol has been demonstrated.

4. *t*-Butylbenzene has been prepared from 4-*t*-butylphenol and from 4-(1,1,3,3-tetramethobutyl)-phenol. *t*-Amylbenzene has been pre-

pared from 4-*t*-amylphenol.

5. Further studies of this type of migration are being made. Systems now under investigation include migrations from phenol nuclei of different types of alkyl groups to simple and substituted (phenol, phenyl ether and naphthol) aromatic nuclei.

NEW YORK, N. Y.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Equilibria of the Reactions between Acetylene and Heavy Water at 0 and 100° and the Heats of Reaction¹

BY L. H. REYERSON AND BRUCE GILLESPIE

In a previous communication² the equilibrium constants for the reactions between acetylene and heavy water at 25° were given. At equilibrium six different molecular species were involved in seven possible reactions and the constants for five of them were calculated from the experimental results. The experimental technique involved the accurate determination of the deuterium content of the heavy water before and after exchange. This investigation has been extended and the equilibria of the reactions have been determined at 0 and 100°.

The experimental methods with some small refinements remained much the same as in the previously reported study, except that a heavily insulated constant temperature air thermostat was substituted for the water-bath used in the earlier investigations. At 100° the normal alkaline solutions attacked the Pyrex glass bulbs so strongly that several of them broke during the time required for equilibrium. As a result quarter normal solutions of sodium hydroxide were used in the experiments run at 100° and half normal solutions were used at 0°. Because of the high partial pressure of water vapor at 100° the partial pressure of the acetylene was kept at about half an atmosphere to reduce the hazard of explosions. In all cases the bulbs containing the acetylene and heavy water solutions were made up and run at room temperature for several days, after which they were run at either 100 or 0° for from forty-eight to sixty hours. At the conclusion of a given

run the heavy water was recovered from the bulbs and its density determined in the same manner as previously reported.² From the changes in the density of the heavy water solutions and a knowledge of the equilibrium constants K_6 for the reaction $D_2O + H_2O \rightleftharpoons 2HDO$ and K_7 for the reaction $C_2D_2 + C_2H_2 \rightleftharpoons 2C_2HD$ it was possible to calculate the number of moles of each of the six reacting molecules at equilibrium. According to Topley and Eyring³ K_6 has a value of 3.118 at 0° and 3.374 at 100°. Glockler and Morrell⁴ gave the value of K_7 at 0° as 1.373 and at 100° as 1.584. Tables I and II give the results of these calculations at 0 and 100°.

Using the values given in Tables I and II the equilibrium constants for the following exchange reactions were calculated.

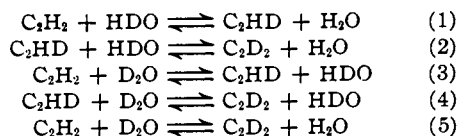


Table III gives the equilibrium constants for the exchanges at 0° and Table IV gives the values at 100°. The equilibrium constants at 100° are all higher than those previously reported at 25° and the values at 0° are all lower than at 25°.

It is of interest to note that Hiroto and Okamoto⁵ calculated the equilibrium constant K_1 at 25° from spectroscopic data. They obtained a value of 0.59 where our experimentally determined value was 0.599. The agreement is excellent and

(1) This investigation was made possible by a grant from the Graduate School of the University of Minnesota.

(2) L. H. Reyerson and Bruce Gillespie, *THIS JOURNAL*, **58**, 282 (1936).

(3) Topley and Eyring, *J. Chem. Phys.*, **2**, 217-230 (1934).

(4) Glockler and Morrell, *ibid.*, **4**, 15 (1936).

(5) Hiroto and Okamoto, *Bull. Chem. Soc. Japan*, **11**, 349-351 (1936).

TABLE I

Initial percentage of D in water	Pressure C ₂ H ₂ , mm.	Moles of reactants in equilibrium at 0°					
		H ₂ O	HDO	D ₂ O	C ₂ H ₂	C ₂ HD	C ₂ D ₂
99	642	0.009229	0.04323	0.06495	0.004426	0.01209	0.02407
99	354	.003929	.03116	.07928	.001141	.005049	.01628
44	730	.05883	.05179	.01462	.02805	.01348	.004715
44	366	.04989	.050095	.01613	.01254	.007486	.003255
25	610	.07624	.03379	.004803	.03045	.007745	.001435

TABLE II

Initial percentage of D in water	Pressure C ₂ H ₂ , mm.	Moles of reactants in equilibrium at 100°					
		H ₂ O	HDO	D ₂ O	C ₂ H ₂	C ₂ HD	C ₂ D ₂
98	286	0.003154	0.02840	0.07580	0.0005849	0.003567	0.01374
55	310	.03420	.05131	.02282	.007337	.007325	.004616
28	374	.06554	.03671	.006095	.01556	.005981	.001452
28	322	.06443	.03725	.006382	.01331	.005125	.001246

TABLE III

Initial percentage of D in water	Pressure C ₂ H ₂ , mm.	Equilibrium constants at 0°				
		K ₁	K ₂	K ₃	K ₄	K ₅
99	642	0.583	0.425	1.819	1.325	0.773
99	354	.558	.406	1.740	1.267	.707
44	730	.546	.397	1.701	1.239	.676
44	366	.595	.433	1.854	1.350	.803
25	610	.574	.418	1.790	1.303	.748
Average		0.571	0.416	1.781	1.297	0.741

TABLE IV

Initial percentage of D in water	Pressure C ₂ H ₂ , mm.	Equilibrium constants at 100°				
		K ₁	K ₂	K ₃	K ₄	K ₅
98	286	0.677	0.428	2.286	1.443	0.977
55	310	.665	.419	2.245	1.417	.943
28	374	.685	.433	2.316	1.462	1.003
28	322	.666	.421	2.248	1.419	.946
Average		0.674	0.425	2.274	1.435	0.967

offers additional confirmation of the fact that equilibrium was reached by our method of investigation.

The values reported in Tables III and IV are given just as they came out in the calculation. No significance is attached to any figure beyond the second decimal place and it may not be correct. Taking the average value to two decimal places we have for the constants at 0° K₁ = 0.57, K₂ = 0.42, K₃ = 1.78, K₄ = 1.30 and K₅ = 0.74. At 100° the values would be K₁ = 0.67, K₂ = 0.43, K₃ = 2.27, K₄ = 1.44 and K₅ = 0.97.

Using these values together with those previously reported² it is possible to determine the heats of reaction for these isotopic exchanges. From the well-known equation of van't Hoff it is evident that the heats of reaction, ΔH, may be determined by plotting -R ln K (equilibrium constant) against 1/T (T in absolute temperature). The slopes of the curves so obtained give the values of ΔH. In Fig. 1 the values of log K are plotted against 1/T. The resulting curves are practically

straight lines. Using the slope of these curves and multiplying by -4.5787 to convert to -R ln K the values of ΔH in calories are obtained.

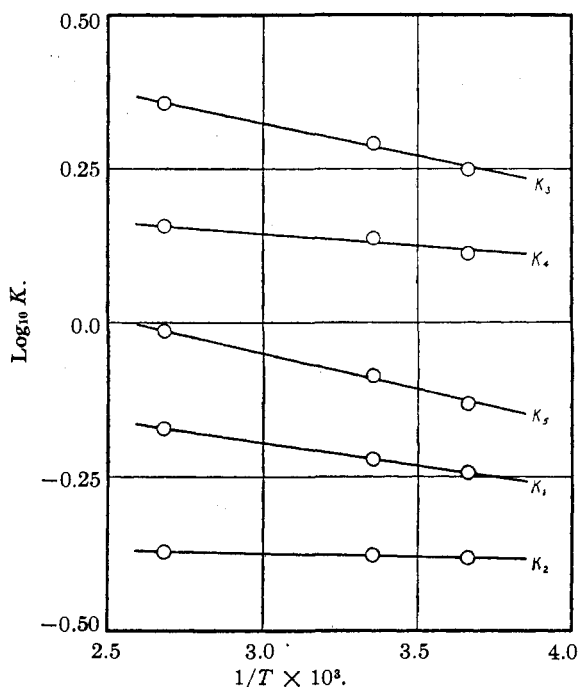


Fig. 1.—Variation of exchange equilibrium constants with temperature.

These values are given in Table V together with all of the equilibrium constants for the five reactions. As might well be expected the heats of reaction for these isotopic exchanges are very small.

TABLE V

Reactions	Equilibrium Constants			ΔH
	0°	25°	100°	
1	0.57	0.60	0.67	275
2	.42	.42	.43	35
3	1.78	1.95	2.27	480
4	1.30	1.37	1.44	175
5	0.74	0.82	0.97	530

Summary

1. The equilibrium constants for the reactions between H_2O , HDO , D_2O , C_2H_2 , C_2HD and C_2D_2 have been determined experimentally at 0 and 100° .
2. From a knowledge of the change of the

equilibrium constants of isotopic exchange reactions with the temperature (in the range 0 to 100°), the heats of reaction of these exchanges have been calculated.

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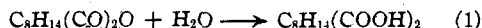
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[CONTRIBUTION FROM THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

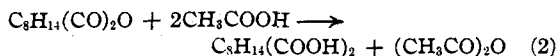
A Polarimetric Method for the Determination of Water in Acetic Acid¹

BY GERRIT TOENNIES AND MARGARET ELLIOTT

Some recently proposed methods for the determination of water in organic media are based on the acidimetric determination of acetic acid formed from acetyl chloride² or from acetic anhydride.³ Application of these methods to the determination of water in acetic acid or similar liquids, although possible in principle, is obviously limited in accuracy and sensitivity by the large acidimetric blank value of the acetic acid. This limitation would be abolished if in the method of Toennies and Elliott³ the acetic anhydride could be replaced by an optically active anhydride the hydration of which is measurable by an accompanying change in optical rotation. *d*-Camphoric acid and the corresponding anhydride differ widely in their effect on polarized light, but the hydration of camphoric anhydride



in acetic acid solution, although susceptible to acid catalysis,⁴ was found to be too slow, with tolerably low acid concentrations (in presence of $0.1 M \text{HClO}_4$ $k_{25} \cong 10^{-3}$), to be of practical promise. On the other hand, the complete absence of a conceivable⁵ interfering reaction



—in spite of the large excess of one of the potential

(1) Aided by the Robert McNeil Fellowship maintained by McNeil Laboratories, Inc.

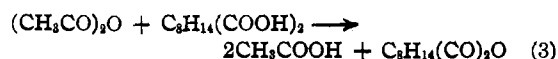
(2) D. M. Smith and W. M. D. Bryant, *THIS JOURNAL*, **57**, 841 (1935).

(3) G. Toennies and M. Elliott, *ibid.*, **57**, 2136 (1935).

(4) The catalysis of the hydration of organic anhydrides by strong acids in non-aqueous media, first suggested by observations of Orton and Jones [*J. Chem. Soc.*, **101**, 1708 (1912)] on acetic anhydride and confirmed by observations made in this Laboratory [Toennies and Lavine, *J. Biol. Chem.*, **100**, 474 (1933); Lavine and Toennies, *ibid.*, **101**, 732 (1933); ref. 3], has been studied by us on a number of anhydrides of different types, and widely differing rates of catalysis have been found (results to be published).

(5) The analogous reaction $(\text{C}_6\text{H}_5\text{CO})_2\text{O} + 2\text{CH}_3\text{COOH} \longrightarrow 2\text{C}_6\text{H}_5\text{COOH} + (\text{CH}_3\text{CO})_2\text{O}$ has been described: R. Kremann and W. Rösler, *Monatsh.*, **43**, 358 (1925); *C. A.*, **17**, 1426 (1923).

reactants (CH_3COOH)—suggested the probability of a strong thermodynamic tendency for the opposite of reaction (2)



This was found to exist: the bimolecular constant⁶ of this reaction in acetic acid is directly proportional to the amount of strong acid present⁷ and is, in the presence of $0.001 M$ perchloric acid and at about 25° , of the order of 10^{-1} ; *i. e.*, with equal amounts of catalyst, reaction (3) is estimated to be 10^4 times as fast as reaction (1). Therefore, and since the acid-catalyzed reaction of acetic anhydride with moderate amounts of water in acetic acid is even more rapid than reaction (3), the following principle for the determination of water in glacial acetic acid suggests itself.

In the presence of a suitable small concentration of a strong acid (perchloric acid) the acetic acid solution of water is allowed to react with a measured quantity of acetic anhydride, and the unused amount of acetic anhydride is determined by the decrease in optical rotation coincident with its reaction with a measured amount of *d*-camphoric acid.

The experimental investigation of the method has been confined to a demonstration of its practicability and its minimum accuracy, while it has not been extended either to a quantitative study of various factors that might add to its refinement (such as temperature, concentration or mutual effects on the specific rotations of *d*-camphoric acid and *d*-camphoric anhydride) nor to a consideration of possible interfering substances (such as might conceivably be formic acid or

(6) All velocity constants are expressed in moles per liter per minute.

(7) G. Toennies and M. Elliott, abstracts of papers to be presented before the Division of Physical and Inorganic Chemistry at the Meeting of the American Chemical Society, Chapel Hill, N. C., April, 1937.