and trimethylethylene in nitric acid solutions is striking and apparently unusual.[18]

(18) Ref. 16, p. 151.

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Thermodynamic Properties for the System Isobutene-*t*-Butyl Alcohol[1]

BY ROBERT W. TAFT, JR., AND PETER RIESZ

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In order to compare the rates, equilibria and their thermodynamic properties for the hydration of 4- and 5-membered ring olefins with those of isobutene, we have measured[2] over the temperature interval 50–70° the equilibrium constant, K_p, for reaction (1)

$$\text{isobutene(g)} + H_2O(l) = t\text{-butyl alcohol(aq)} \quad (1)$$

The aqueous phase is 0.0973 molar in perchloric acid and one-tenth to two-tenths molar in *t*-butyl alcohol. The apparatus and procedures are those which have previously been used to study rates of olefin hydration and carbinol dehydration.[3,4]

Equilibrium has been attained starting from the carbinol. We have also obtained directly the dehydration rate and its temperature coefficient. These in combination with earlier results on the hydration rate and its temperature coefficient[3] serve as a check on the measurements.

Standard thermodynamic properties have been derived for the hydration reaction by combining present and earlier data. In a similar manner the free energy and enthalpy of formation of liquid *t*-butyl alcohol at 25° have been obtained.

Experimental

A sample of *t*-butyl alcohol was fractionated over calcium hydride. A center cut, m.p. 25.0°, was retained for the present work.

The apparatus and procedure used were essentially those reported earlier.[4] Experiments were carried out in 0.0973 *M* perchloric acid. At 60 and 70° preliminary work indicated that 0.973 *M* nitric acid (the solvent used in a number of previous experiments[4]) led to decomposition of the carbinol.

Solutions either one-tenth or two-tenths molar in *t*-butyl alcohol were made up in the acid solution, a measured volume of the solution added to the apparatus, and the system degassed as described in procedure B reference 4b. At room temperature and below (at which the solutions were kept during the above operation) the rate of dehydration at this acidity is so small that no measurable loss of olefin occurs. The closed and evacuated systems were completely submerged in a thermostat at the desired temperature and rapid shaking was begun within 2 or 3 minutes.

TABLE I

SUMMARY OF EXPERIMENTAL DATA

Temp., °C.	50.07	50.07	60.05	60.05	69.95	69.95
$10^{3r}/RT$	73.1	95.9	70.9	119.5	68.8	116.0
C^{e}_{a}, *M*	0.2014	0.2006	0.1986	0.1951	0.0970	0.0940
P^{e}_{o}, cm.	2.77	2.74	5.86	5.67	5.58	5.29
K_p	5.53	5.56	2.58	2.61	1.322	1.351
$10^{3} S$	....	....	5.42	3.16	12.57	7.97

Pressure readings were taken at one-minute intervals. The time at which the system reached thermal equilibrium with the thermostat was that at which the time derivative of pressure became constant (about four minutes were generally required). The vapor pressure of the acidified carbinol solution was obtained from the initial pressure reading obtained at the desired temperature. At 60 and 70° this pressure was obtained by extrapolation of the initial dehydration rate to the time shaking was begun. This extrapolation procedure introduced no errors out-side of those involved in the reading of pressure (±0.03 cm.), for the dehydration rates were relatively slow (the smallest half-life of the total pressure increase was about one hour).

Duplicate experiments were carried out at each temperature and the average equilibrium constant is reported. At 60 and 70° the dehydration rates, *S*, were observed directly over at least 50% of the reaction ($S = -d \ln (P^{e} - P)/dt$. The results are summarized in Table I. The equilibrium constant, K_p, is given by C^{e}_{a}/P^{e}_{o}, where C^{e}_{a} is the equilibrium carbinol concentration in moles $l.^{-1}$ and P^{e}_{o} is equilibrium partial pressure of olefin in atm.

Results

The equilibrium constants, K_p, are tabulated in Table II along with their probable errors.

TABLE II

EQUILIBRIUM CONSTANT, K_p, FOR THE HYDRATION OF GASEOUS ISOBUTENE TO DILUTE AQUEOUS TERTIARY BUTYL ALCOHOL IN UNITS OF MOLES $L.^{-1}$-ATM.$^{-1}$

Temp., °C.	50.07	60.05	69.95
K_p	5.54	2.59	1.336
P.e.	0.02	0.02	0.014

A plot of K_p against $1/T$ is linear within the precision of measurement. Thus the value of K_p at 60.05° computed on the basis of this linearity is 2.65 ± 0.04 compared with the experimental value of 2.59 ± 0.02. Accordingly, the best values of the enthalpy and entropy changes accompanying reaction 1 are obtained by the Van't Hoff equation from the slope of the $1/T$ plot as defined by the points for the extreme temperatures. In this manner the enthalpy change, ΔH_p, is found to be -15.76 ± 0.12 kcal. mole^{-1}, and the entropy change. ΔS_p, is -45.3 ± 0.3 cal. deg.$^{-1}$ mole^{-1} for the interval 50–70°.

The rates of dehydration of *t*-butyl alcohol at unit concentration, k_{-1}, by 0.0973 *M* perchloric acid at 60 and 70 have been calculated from the rate data of Table I by equation 4 of reference 4a using distribution constants of isobutene between gas and liquid phases obtained by extrapolation of the data of Purlee, Taft and DeFazio.[3,5] The

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(1) The work herein reported was carried out on Project NRO55-295 between the Office of Naval Research and the Pennsylvania State University.

(2) *Cf.* P. Riesz and R. W. Taft, Jr., THIS JOURNAL, **77**, in press (1955).

(3) *Cf.* E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *ibid.*, **77**, 837 (1955), and previous references cited there.

(4) (a) R. W. Taft, Jr., J. B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952); (b) J. B. Levy, R. W. Taft, Jr., D. Aaron, L. P. Hammett, *ibid.*, **73**, 3792 (1951).

(5) The value of the distribution constant makes little contribution under these conditions to the value of k_{-1} calculated. Thus complete neglect of the distribution constant would in the worst case decrease the value of k_{-1} by 3%. Any error introduced in the extrapolation will therefore not affect the value of k_{-1} obtained.

average rate constants together with their probable errors are listed in Table III.

TABLE III

DEHYDRATION RATES, k_{-1}, FOR *t*-BUTYL ALCOHOL IN 0.0973 *M* PERCHLORIC ACID IN UNITS OF 10^4 MIN.$^{-1}$

Temp., °C.	60.05	69.95
k_{-1}	1.46	6.33
P.e.	0.04	0.03

From the data of Table III and eq. 8 and 9 of reference 4b are obtained values of $+33.0 \pm 0.7$ kcal. mole^{-1} and $+15.7 \pm 2.1$ cal. deg.$^{-1}$ mole^{-1} for the enthalpy of activation, $\Delta H^{\ddagger}_{-1}$, and the entropy of activation, $\Delta S^{\ddagger}_{-1}$, of the dehydration reaction, respectively.

Discussion

From the values of the enthalpy change, ΔH_p, for reaction 1 and the enthalpy of activation, $\Delta H^{\ddagger}_{-1}$, given above for the 50–70° temperature interval, one obtains for the enthalpy of activation, $\Delta H^{\ddagger}_p$, for the hydration of gaseous isobutene by 0.0973 *M* perchloric acid in dilute *t*-butyl alcohol solution the value 17.2 ± 0.7 kcal. mole^{-1}. This may be compared to the figure 17.27 ± 0.12 kcal. mole^{-1} obtained by direct measurements in 0.0909 *M* nitric acid (infinitely dilute in *t*-butyl alcohol) for the temperature interval 35–55.[4b] In view of the indetectable temperature dependence of $\Delta H^{\ddagger}_p$ for this interval,[4b] and of ΔH_p for the present 50–70° interval, and the reasonable result that the rather small change in media has no measurable effect on the enthalpy changes, the agreement between the two values serves as an excellent check on the measurements.

Eberz and Lucas have measured the equilibrium constant for reaction 2 at two temperatures, 25 and 35°, in solutions 0.1 to 0.2 *M* in nitric acid and 0.250 molal in *t*-butyl alcohol.[6]

$$\text{isobutene(aq)} + \text{H}_2\text{O(l)} = t\text{-butyl alcohol(aq)} \quad (2)$$

From these measurements are derived for the enthalpy change, ΔH_c, accompanying reaction 2, the value -11.6 kcal. mole^{-1}, and for the entropy change, ΔS_c, the value -21.0 cal. deg.$^{-1}$ mole^{-1}. In view of the virtual equivalence of the media, the enthalpy of vaporization of isobutene from the solution may be obtained by subtracting ΔH_p from ΔH_c (assuming temperature independence of these values for the interval 25–70°). There results the figure 4.16 kcal. mole^{-1}, which is in quite reasonable accord (particularly considering the fact that ΔH_c is based upon measurements only 10° apart) with the value of $+3.87 \pm 0.04$ obtained by Purlee, Taft and DeFazio for the heat of vaporization of isobutene from its saturated aqueous solution for the temperature interval 25–50.[3]

The standard thermodynamic property changes for reaction 3 may be obtained from the present results in combination with data from the literature.

$$\text{isobutene(g, 1 atm.)} + \text{H}_2\text{O(l)} = t\text{-butyl alcohol(l)} \quad (3)$$

Assuming the value of ΔH_p obtained above to apply at 25°, this, together with the enthalpies of vaporization at 25° of *t*-butyl alcohol from dilute acidic alcohol solution and from the pure liquid state, gives the standard enthalpy change, ΔH°_{298}, accompanying reaction 3. The second of these quantities has not been obtained directly, but Everz and Lucas measured the partial pressure of *t*-butyl alcohol over its 0.25 molal solution containing 0.2 *M* KNO_3 at 25 and 35°.[6] The enthalpy of vaporization obtained from these data is 14.4 kcal. mole^{-1}. Butler has reported the same figure for the enthalpy of vaporization of *t*-butyl alcohol from its dilute aqueous solution.[7] It therefore appears that this value may be applied to the above conditions without introducing appreciable error. The enthalpy of vaporization of *t*-butyl alcohol(l) at 25° is 11.20 kcal.-mole^{-1}.[8] We are thus led to the result

$$\Delta H^{\circ}_{298} = -12.6 \text{ kcal. mole}^{-1} \qquad \text{(reaction 3)}$$

Eberz and Lucas previously reported on the basis of several indirect measurements at 25 and 35° the value -12.8 kcal. mole^{-1} for ΔH°_{298}.[6]

The standard free energy change, ΔF°_{298}, accompanying reaction 3 may be obtained in the following manner. Taking the value of ΔH_p given above to apply at 25°, we calculate from the data of Table II, $K_p^{298} = 41.0$ moles l.$^{-1}$ atm.$^{-1}$, and thus $\Delta F_p^{298} = -2.2$ kcal. mole^{-1}. Proceeding in a manner analogous to the above calculation of ΔH°_{298}, ΔF°_{298} may be obtained from this value of ΔF_p and the free energy changes accompanying vaporization of *t*-butyl alcohol from its dilute aqueous acidified solution and from the pure liquid state at 25°. The first of these two quantities can be estimated from Eberz and Lucas' data which indicate that the partial pressure of *t*-butyl alcohol over its 0.15 *M* solution containing 0.2 *M* KNO_3 is 1.43 mm. at 25°.[6] From the known regularities of salt effect orders (KNO_3 "salts-out" and HClO_4 usually "salts-in")[9] we estimate the value 1.40 mm. would apply to a solution 0.15 *M* in alcohol and 0.0973 *M* in perchloric acid. The vapor pressure of *t*-butyl alcohol(l) at 25° is 42.0 mm.[10] These figures indicate the free energy change accompanying the transfer of one mole of alcohol from the acidic 0.15 *M* solution to the pure liquid state is $-2.303(R)(298.2) \log [1.40/(42.0)(0.15)]$ or $+0.9$ kcal. mole^{-1}. Thus the standard energy change is ΔF_p^{298} $+0.9$ kcal., or

$$\Delta F^{\circ}_{298} = -1.3 \text{ kcal. mole}^{-1} \qquad \text{(reaction 3)}$$

This is the same result as given earlier by Eberz and Lucas.[6] Parks and Huffman calculated from unpublished gas phase measurements (of a "rather crude" nature) by Francis the standard free energy change, ΔF°_{298}, to be -2.0 kcal. mole^{-1}.[10] The difference between this and the value we now report is well within the error of "one or two thousand calories" estimated by Parks and Huffman.

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(6) W. F. Eberz and H. J. Lucas, THIS JOURNAL, **56**, 1230 (1934).

(7) J. A. V. Butler, *Trans. Faraday Soc.*, **33**, 2291 (1937); the value is calculated from data given in the I.C.T. based on original measurements by de Forcrand.

(8) J. A. V. Butler, *et al.*, *J. Chem. Soc.*, 280 (1935).

(9) F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

(10) G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., New York, N. Y., 1932, p. 124.

Based upon an early heat of combustion for *t*-butyl alcohol obtained by Zubow-Swietoslawski, Parks and Huffman give for the enthalpy and free energy of formation of *t*-butyl alcohol(l) at 25° the values −89,410 and −47,500 cal. mole^{-1}, respectively.[11] From the enthalpies of formation of isobutene(g) (−4.04 kcal.)[12] and water(l) (−68.32 kcal.)[13] which must certainly be reliable, one obtains for the standard enthalpy change of reaction 3, ΔH°_{298}, the value −17.05 kcal. mole^{-1}. This result is 4.5 kcal. less than the value of ΔH°_{298} reported above, and indicates that the heat of combustion of *t*-butyl alcohol is too low (*ca.* 0.7%) by about this amount. On the basis of the data presented above, the enthalpy of formation of *t*-butyl alcohol(l) is −85.0 kcal. mole^{-1} at 25°. This value is 5.4 kcal. more negative than the value given by Parks and Huffman for *n*-butyl alcohol.[11]

From the free energies of formation of isobutene(l) (+13.88 kcal.)[12] and of water(l) (−56.69 kcal.),[13] and ΔF°_{298} of reaction 3, one obtains for the free energy of formation of *t*-butyl alcohol(l) at 25° the value −44.1 kcal. mole^{-1}. This is 3.8 kcal. more negative than the value for the free energy of formation at 25° of *n*-butyl alcohol given by Parks and Huffman.[11]

The standard entropy change accompanying reaction 3 may be obtained from the values of ΔF°_{298} and ΔH°_{298} given above. The result (which is unlikely to be in error more than 1.5 e.u.) is

$$\Delta S^\circ_{298} = -37.9 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad \text{(reaction 3)}$$

Third Law entropies may also be used to calculate ΔS°_{298}. From the entropies of the substances involved (isobutene(g)S°_{298} = 70.2 e.u.[12]; water(l), ΔS°_{298} = 16.7[13] e.u.; *t*-butyl alcohol(l), S°_{298} = 45.3 e.u.[11]), one obtains for ΔS°_{298} the figure −41.7 cal. deg.$^{-1}$ mole^{-1}. The agreement between the two values for ΔS°_{298} is rather disappointing.[14]

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(11) Ref. 10, p. 109.

(12) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Penna., 1953, p. 475.

(13) Ref. 12, p. 464.

(14) The two values may be brought into agreement if we take ΔS°_{298} = −39.4 e.u., and use for isobutene the experimental value of S°_{298} = 69.0 e.u. given by S. S. Todd and G. S. Parks, THIS JOURNAL, **58**, 134 (1936), and the value 46.3 e.u. for S°_{298} for *t*-butyl alcohol(l), which is within the limits of error given by Parks for the value quoted above.

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The Formation of Silicon Monosulfide[1]

BY WALTER C. SCHUMB AND WALTER J. BERNARD[2]

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During the course of the preparation of silicon disulfide by direct synthesis, as described by Gabriel and Alvarez-Tostado,[3] it was found that a major product of the reaction was silicon monosulfide. Similar results were obtained, but to a lesser extent, by the use of Malatesta's[4] method. In both cases the initial reaction product was white to gray, indicating the presence of SiS_2, whereas the sublimed product was yellow, and red to black, these being known modifications of SiS. The composition of this colored sublimate was confirmed by chemical analysis. The failure to observe the characteristic color of SiS in the crude reaction mixture suggested that the formation of the monosulfide was due to subsequent reaction between SiS_2 and excess Si, analogous to the formation of SiO from SiO_2 and Si. The possibility of this reaction occurring has been suggested by Kohlmeyer and Retzlaff.[5]

In order to demonstrate that SiS may be formed in this way, pure SiS_2 was intimately mixed with excess Si and heated under vacuum to 850°. The reaction was quantitative and the product consisted entirely of SiS. It was further shown that the monosulfide was not formed in the original reaction between silicon and sulfur at atmospheric pressure and that the monosulfide which later appeared was entirely due to the high temperature reaction under vacuum. Reactions were run between silicon and sulfur with the atomic ratio S/Si varying from 1.0 to 2.0, and in all cases the only initial product was SiS_2. This was demonstrated by the fact that the crude reaction mixture did not evolve hydrogen upon treatment with dilute NaOH. The monosulfide reacts quantitatively with aqueous NaOH according to the equation

$$SiS + 2OH^- + H_2O \longrightarrow SiO_3^{=} + H_2 + H_2S$$

The number of moles of H_2 evolved per formula weight of SiS in two determinations was 1.01 and 0.98.

The structure of SiS in the solid state is not known and the product may possibly be a disproportionated intimate mixture of SiS_2 and finely divided silicon. X-Ray spectrograms of both the yellow and red forms failed to resolve this question, as amorphous patterns were obtained in both cases.

Sublimation of the sulfides was carried out by placing the crude products of direct synthesis in a large porcelain boat and heating under vacuum in a sublimation tube constructed of 38 mm. o.d. clear quartz and Vycor. The quartz section was one foot long and one foot of Vycor was fused to the quartz at either end. The heating unit was a Hoskins electric furnace.

The test for the presence of SiS in the solid products was carried out by the addition of 0.05 *N* NaOH to the solid under vacuum. H_2S and water vapor were condensed at −196° and any increase in pressure in the system was attributed to the presence of H_2. Under these conditions SiS gave a strong positive test, whereas the initial product of reaction between Si and S gave negative tests.

The preparation of pure SiS_2 was most conveniently accomplished by the reaction between Al_2S_3 and SiO_2.[6] The reaction of the product with finely divided Si resulted in the formation of SiS. *Anal.* Calcd. for SiS: Si, 46.7; S, 53.3. Found: Si, 45.3, 45.0; S, 54.5, 54.5.

Analysis of the sulfides was carried out by decomposing the sample in concentrated HNO_3, filtering off silica and then precipitating barium sulfate. Quantitative determination of the number of Si–Si bonds in SiS was carried out by the measurement of the volume of H_2 evolved upon decomposition of samples in 1 *N* NaOH. Samples were prepared by adding the finely ground powder to weighed, thin-walled

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(1) From part of a thesis presented by W. J. Bernard to the Department of Chemistry, M. I. T., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) National Science Fellow, 1953–1954.

(3) H. Gabriel and C. Alvarez-Tostado, THIS JOURNAL, **74**, 262 (1952).

(4) L. Malatesta, *Gazz. chim. ital.*, **78**, 702 (1948).

(5) E. J. Kohlmeyer and H. W. Retzlaff, *Z. anorg. Chem.*, **261**, 248 (1950).

(6) E. Tiede and M. Thimann, *Ber.* **59**, 1703 (1926).