residue. A 44% yield of the 2,3-di-*n*-butyl-1,4-dioxane has been obtained.

Difficulty was encountered in working up the reaction products in the 2,3-dimethyldioxane synthesis. The crude product yielded two fractions of practically equal quantity when fractionated by a small Vigreux column.

With a limited amount of material, the following experiment was attempted: 29 g. of the crude product, b. p. 127–133° (752 mm.), was heated with 100 cc. of 15% potassium hydroxide solution for seven hours. A quantity of anhydrous potassium carbonate was added, the dimethyldioxane layer separated, dried over solid sodium hydroxide for several hours, and metallic sodium added. After the liquid had stood over the metallic sodium one week, it was fractionally distilled, using a small (7-mm., 60-cm.) Podbielniak type column with a vacuum jacket. The bulb containing the material was heated by an oil-bath at 190–201°. These fractions were obtained at 752 mm. (g., °C., $n^{20}{}_D$): 1.3, 126.4–127.2, 1.4239; 9.9, 127–129, 1.4249; 11.3, 130.2–132.7, 1.4259; 3.2 g. left in bulb.

Redistillation resulted in two chief fractions: (a) b. p. 127.7–129° (750.8 mm.), $n^{20}{}_D$ 1.4237, $d^{20}{}_{20}$ 0.960; (b) b. p. 132.2–132.7° (750.8 mm.), $n^{20}{}_D$ 1.4259, $d^{20}{}_{20}$ 0.967. Each of these fractions give satisfactory analyses for $C_6H_{12}O_2$. Two 2,3-dimethyl-1,4-dioxanes are indicated by this work. This is interesting as it differs from the results on diaryldioxanes obtained from Grignard reagents, where only one form has been isolated.

Slightly lower yields of the dimethyl and di-*n*-propyl derivatives were obtained when cadmium chloride was used. Also, more difficulty was encountered in obtaining them pure.

Practically all the 2,3-dialkyl-1,4-dioxanes herein described tend to possess a boiling-point range.

Summary

1. A number of 2,3-dialkyl-1,4-dioxanes have been prepared for the first time.

2. The unisolated reaction product of cadmium chloride and a Grignard reagent has been used with excellent results as a reagent in synthesis.

EVANSTON, ILLINOIS

RECEIVED FEBRUARY 21, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Methanol–Water Mixtures from Electromotive Force Measurements[1]

BY HERBERT S. HARNED AND HENRY C. THOMAS

Recently,[2] the electromotive force of the cell

$$H_2 \mid HCl\ (m)\ \text{in}\ X\ \%\ CH_3OH,\ Y\ \%\ H_2O \mid AgCl\text{-}Ag \quad (1)$$

has been measured. Two solvents were employed which contained 10 and 20% methyl alcohol by weight. Results were obtained from 0 to 40° at 5° intervals and the acid concentration was varied between 0.004 and 0.1 *M*. From these the standard potential of the cell was determined from 0 to 40°. These measurements have now been extended to include results from 0.005 to 2 *M*. From these data, a study of the thermodynamics of hydrochloric acid in these solutions has been made, which when combined with the similar study of the properties of this acid in water made by Harned and Ehlers,[3] leads to a comprehensive knowledge of the behavior of an electrolyte in media of high dielectric constant.

Experimental Results

The electromotive forces of cell (1) as a function of the temperature may be computed with an accuracy of the order of ±0.05 mv. by the equation

$$E = a + b(t - 20) + c(t - 20)^2 \quad (2)$$

Since the original observations were not made at round concentrations, each isothermal series of results was smoothed against a suitable function of *m*, and values of *E* at round concentrations were obtained. The constants of equation (2) were then evaluated by the method of least squares. These constants are given in Table I. Values of *E* computed by this equation are valid from 0 to 40°.

TABLE I

CONSTANTS OF EQUATION (2)

X = % Methanol by Weight

	$X = 10$			$X = 20$		
m	$a = E_{20}$	$(b \times 10^6)$	$(-c \times 10^6)$	$a = E_{20}$	$(b \times 10^6)$	$(-c \times 10^6)$
0.005	0.48989	382.53	4.034	0.48361	409.13	4.609
.01	.45629	271.17	4.016	.45012	297.73	4.571
.02	.42303	161.63	3.996	.41697	187.93	4.521
.05	.37960	15.03	3.865	.37374	47.13	4.494
.1	.34698	− 84.33	3.903	.34150	− 51.83	4.144
.2	.31400	−183.70	3.652	.30875	−153.07	4.229
.5	.26845	−323.17	3.158	.26370	−292.13	4.030
1	.23027	−427.83	2.896	.22594	−396.70	3.587
1.5	.20477	−493.63	2.596	.20084	−449.83	3.112
2	.18431	−537.47	2.240	.18049	−502.37	3.074

For purposes of theoretical calculations, it is necessary to know the concentrations of the acid

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[1] This communication contains material from a dissertation presented by Henry C. Thomas to the Graduate School of Yale University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1935.

[2] Harned and Thomas, THIS JOURNAL, **57**, 1666 (1935).

[3] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

in moles per liter of solution, c. Density determinations were made, and it was found that the ratio of normality to molality is accurately given at all temperatures by the equation employed by Harned and Ehlers,[3] namely

$$c/m = d_0 - b_1 m \qquad (3)$$

where d_0 is the density of the pure solvent, and b_1 is an empirical constant. Table II contains values of d_0 and b_1.

TABLE II

CONSTANTS OF EQUATION (3)

X = % Methyl Alcohol by Weight

	X = 10		X = 20	
	d_0	b_1	d_0	b_1
0	0.9842	0.0165	0.9721	0.0173
5	.9839	.0172	.9709	.0177
10	.9834	.0176	.9696	.0178
15	.9825	.0177	.9681	.0178
20	.9813	.0178	.9663	.0181
25	.9799	.0179	.9644	.0181
30	.9782	.0181	.9622	.0179
35	.9763	.0180	.9598	.0179
40	.9742	.0178	.9572	.0175

The data in Tables I and II, combined with the values of the standard potentials, E_0', given in Table IV of our earlier communication[2] are sufficient for the subsequent computations.

Activity Coefficients

Theoretical considerations indicate that hydrochloric acid is a completely dissociated electrolyte in water, and in 10 and 20% by weight methanol–water mixtures. At 25° the dielectric constant of water is 78.54 according to Wyman.[4] From the results of Åkerlöf,[5] 10 and 20% methanol–water mixtures possess dielectric constants of 74.05 and 69.20, respectively. Harned and Ehlers[3] found that the mean distance of approach of the ions of this acid in water is 4.3 Ångstrom units and is constant from 0 to 60°. We may use this value of "a," and Bjerrum's theory[6] of ionic association, to estimate the extent of ionic association in the media of dielectric constant less than that of water. According to this theory, if $a > q$, the electrolyte is completely dissociated. In water, the distance of minimum probability of ionic association, q, is 3.5 Å., and becomes equal to 4.3 Å. in a medium of dielectric constant of 64. Consequently, hydrochloric acid should behave as a typical completely dissociated electrolyte in the two methanol–water solvents under consideration, since the lowest dielectric constant of any of these mixtures, that of the 20% methanol–water mixtures at 40°, is 64.2.

As pointed out in our earlier communication, the evaluation of the standard potential, E_0', could be carried out with an accuracy comparable to that obtained in aqueous solutions. Since the error involved is estimated to be of the order of ±0.05 mv., values of γ computed by the equation

$$E = E_0' - (2RT/F)\log \gamma m \qquad (4)$$

should be valid to ±1 in the third decimal place of γ. Values of γ in water at 25° computed from the data of Harned and Ehlers are given in the second column of this Table III. Our values in the methanol–water mixtures at 0, 25 and 40° are given in the other columns of this table.

Interesting and valuable conclusions may be drawn by the calculation of these results by means of the equation

$$\log \gamma = -\frac{u\sqrt{c}}{1 + A\sqrt{2c}} + bc - \log\left(1 + \frac{2G_0 m}{1000}\right) \qquad (5)$$

u is the universal constant of the Debye and Hückel theory, A is the constant which involves the mean distance of approach of the ions, b is an empirical constant, and G_0 is the mean molecular weight of the solvent. This equation accounts accurately for the activity coefficients of hydrochloric acid in water at concentrations up to 1 M at a given temperature. The parameter A is related to the mean distance of approach of the ions, a, by

$$A = K'a \qquad (6)$$

where K' varies as the reciprocal of $(DT)^{1/2}$. Harned and Ehlers[3] found that equation (5) represented the data for hydrochloric in water from 0 to 60° with an accuracy of ±0.001 in γ. Their computations showed that "a" was a constant, not a function of the temperature, but that b decreased with increasing temperature. We had exactly the same experience with the results in the methanol solutions in which independent determinations of "a" varied by not more than ±0.1 Å. from their mean value through the temperature range from 0 to 40°. Further, within the error of determination of this quantity, "a" had the same value in these solutions as in water, namely, 4.2 Å. Further, it was observed that an accurate calculation could be made if the value of b at a given temperature was the same for the methanol–water mixtures as for water. These results are illustrated by the data in Table III, where the numbers in brackets represents the de-

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(4) Wyman, *Phys. Rev.*, **35**, 623 (1930).

(5) Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

(6) Bjerrum, *Kg. Danske. Videnskab. Selskab.*, **VII**, 9 (1926).

TABLE III

ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN SOME METHANOL–WATER MIXTURES

The numbers in parentheses represent the deviation in the third decimal place of γ of observed values and those calculated by equations (5) and (6). Positive when calculated values are greater than observed.

	$X = 0$		$X = 10\%$	$G_0 = 18.84$		$X = 20\%$	$G_0 = 19.74$
m	γ_{25}	γ_0	γ_{25}	γ_{40}	γ_0	γ_{25}	γ_{40}
0.001	0.966 (0)	0.964 (0)	0.962 (1)	0.961 (1)	0.961 (0)	0.959 (0)	0.957 (1)
.002	.952 (1)	.951 (0)	.948 (1)	.946 (1)	.946 (1)	.943 (−1)	.941 (1)
.005	.928 (0)	.926 (1)	.922 (1)	.919 (2)	.919 (1)	.915 (1)	.912 (1)
.01	.904 (1)	.901 (1)	.897 (1)	.893 (2)	.893 (1)	.888 (1)	.884 (1)
.02	.875 (0)	.872 (0)	.866 (1)	.861 (2)	.862 (0)	.856 (1)	.850 (0)
.05	.830 (1)	.825 (5)	.819 (−1)	.812 (0)	.814 (−2)	.806 (−3)	.798 (−1)
.1	.796 (0)	.790 (0)	.780 (1)	.772 (1)	.771 (−2)	.762 (0)	.751 (2)
.2	.767 (0)	.762 (−2)	.747 (1)	.736 (2)	.741 (1)	.727 (−1)	.715 (0)
.5	.758 (1)	.754 (−1)	.737 (−1)	.718 (2)	.726 (2)	.708 (0)	.693 (−2)
1	.809 (−1)	.809 (0)	.783 (1)	.756 (2)	.772 (5)	.747 (3)	.722 (1)
1.5	.896	.898	.861	.827	.855	.814	.781
2	1.009	1.020	.966	.917	.965	.911	.860
u	0.5063	0.5264	0.5524	0.5717	0.5786	0.6114	0.6354
K'	.2324	.2356	.2393	.2421	.2432	.2477	.2508
b	.1368	.142	.1366	.128	.142	.1366	.128

viations in the third decimal place between the observed activity coefficients, and those computed by equation (5). The required parameters are given at the bottom of the table. The values of the dielectric constant employed in these computations were obtained by Åkerlöf.[5] It is apparent that the difference between the calculated and observed results is of the order of ±0.001 to ±0.002 in γ.

The value of this computation resides in the fact that we have been able to compute the activity coefficient of the acid in non-aqueous solvent–water mixtures of high dielectric constant from parameters determined in the pure aqueous solutions. The only restriction upon this result is that the dielectric constant must be sufficiently high so that the ionic association is not appreciable. The various parameters have the following characteristics: u varies as the reciprocal of $(DT)^{3/2}$; A as well as K' vary as the reciprocal of $(DT)^{1/2}$; a is a constant, and is not a function of D or T, b is a function of T but not of D. Unless this is pure coincidence for the case of the methanol–water mixtures, these same parameters should yield accurate results in other water–non-aqueous solvent media of dielectric constant of the order of 60 or greater. The measurements of Lucasse[7] of the activity coefficient of hydrochloric acid in glycerol–water mixtures may be computed in the same manner.

The Standard Potential of the Cell in Pure Methyl Alcohol Solutions.—The electromotive force of cell (1) in an alcohol–water mixture of any composition is given by

$$E = E_0 + \frac{RT}{F}\ln y - \frac{2\,RT}{F}\ln \gamma\, m = E_0' - 2k\log \gamma\, m \quad (7)$$

E_0 is the standard potential in water, E_0' the standard potential in the solvent in question, and k equals RT/F. γ and m are the activity coefficient and molality of the acid, respectively. In water, $y = 1$, $E_0 = E_0'$. In the other solvents, y is given by

$$\log y = 2\log(\gamma_1/\gamma_2);\ m \longrightarrow 0 \quad (8)$$

where $\gamma_1 = 1$ is the activity coefficient of the acid at zero concentration in water, and γ_2 is an activity coefficient of the acid at zero concentration in the other solvent measured relative to the value in water.

In the solvents of high dielectric constant, E_0' has been evaluated by the equation

$$E' = E + 2\,k\log(c/d_0) - 2\,ku\sqrt{c} = E' - Bc \quad (9)$$

obtained from equation (7) by the introduction of $(-u\sqrt{c} + Bc)$ for $\log \gamma$, and c/d_0 for m. u is the Debye–Hückel constant. Since pure methyl alcohol has a dielectric constant of magnitude 31.5, considerable association of ions is to be expected in this solvent. It is possible, therefore, that the use of the above function for extrapolation may lead to the wrong value of E_0'. It is impossible to evaluate accurately the degree of dissociation, α, but this quantity may be estimated approximately by Bjerrum's theory if we assume that "a" is 4.2 Å. units. Such a calculation gives 0.044 for the ionization constant K at

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[7] Lucasse, *Z. physik. Chem.*, **121**, 254 (1926).

25° and values of α equal to 0.95, 0.91, 0.87 and 0.84, at normal concentrations 0.005, 0.01, 0.02 and 0.03, respectively. The thermodynamic equation for the ionization constant of the acid, K, including values of γ was employed in this computation. Although this is a very rough estimate of α, it will be shown to be sufficient to settle an important point in obtaining satisfactory values of E_0'.

We have carried out the extrapolation of the results at 25° of Nonhebel and Hartley[8] in three ways. Curve (1) in Fig. 1 is the plot of the left side of equation (9) *versus c*. If we introduce the Debye and Hückel equation containing the apparent ionic diameter, we obtain

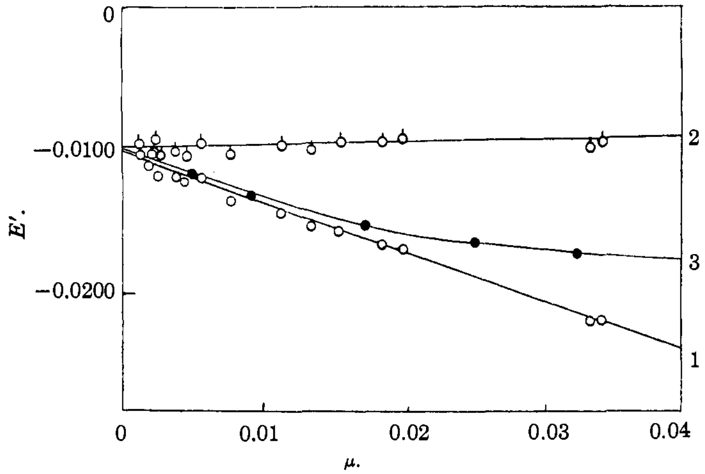

Fig. 1.—Extrapolation for evaluation of E_0' in pure methyl alcohol according to (9), (10) and (11).

$$E' = E + 2\,k \log \frac{c}{d_0} - \frac{2ku\ \sqrt{c}}{1 + A\ \sqrt{2c}} = E_0' - Bc \quad (10)$$

Further, if we consider the acid as partially dissociated the equation of the cell may be written

$$E' = E = 2\,k \log \frac{\alpha c}{d_0} - \frac{2ku\ \sqrt{\alpha c}}{1 + A\ \sqrt{2\alpha c}} = E_0' - Bc \quad (11)$$

Since both α and $(1 + A\ \sqrt{2\alpha c})$ approach unity as c approaches zero, equations (9), (10) and (11) should yield upon extrapolation the same values of E_0'. Curve (2) shows the plot of the left side of equation (10) *versus c*, and curve (3) a similar plot of the left side equation (11). It is clear that the results are of such a character that all three methods give the same value of E_0' within the limit of experimental error. The value of -0.0101 ± 0.0003 volt is in close agreement with that determined by Lucasse, but differs by approximately 0.1183 log $(1/d_0)$ from that of Nonhebel and Hartley.[7,8]

These considerations show that E_0' in a medium of dielectric constant of 30 may be accurately determined. This is important because the derived thermodynamic quantities may be accurately evaluated even though the exact extent of ionic association is not known.

Transfer at Unit Activity.—From equations (7) and (8), we have at 25°

$$\frac{E_0 - E_0'}{0.05915} = -\log y = \log \frac{\gamma_2{}^2}{\gamma_1{}^2} \quad (12)$$

$(E_0 - E_0')$ is the electromotive force of transfer of the acid at unit activity from the alcoholic to the pure aqueous solution. According to the Born equation,[9] these quantities are given by

$$\log \frac{\gamma_2{}^2}{\gamma_1{}^2} = \frac{E_0 - E_0'}{0.05915} = \frac{z^2e^2}{4.606kT}\left(\frac{1}{a_+} + \frac{1}{a_-}\right)\left(\frac{D_1 - D_2}{D_1D_2}\right) = 1.210 \times 10^2 \left(\frac{D_1 - D_2}{D_1D_2}\right) \Sigma \frac{1}{a_i} \quad (13)$$

where D_1 is the dielectric constant of water, D_2 that of the alcoholic solvent, and $\Sigma\ 1/a_i$ is the sum of the reciprocals of the ionic radii in Ångström units. We have computed this latter quantity from the values of the standard potentials, and the known values of the dielectric constants of these media. The result is clearly indicated in Table IV.

TABLE IV

COMPUTATION ACCORDING TO EQUATION (13)

X = weight % alcohol; E_0 = 0.22239; values of the dielectric constants were taken from the data of Åkerlöf.[5]

X	D_{25}	E_0'	$(D_1 - D_2)/D_1D_2$	$\Sigma\ 1/a_i$
0	78.54	.....	......	...
10	74.05	0.21535	0.000772	1.275
20	69.20	.20881	.001718	1.104
100	31.5	− .0101	.01901	1.71

Although the values of $\Sigma\ 1/a_i$ are not constant, they are of the order of magnitude of 1.18, computed from the values of the radii of the hydrogen and chloride ions. The dimensions of these radii were evaluated from crystallographic data by Bragg and Pauling.[10]

The Relative Partial Molal Heat Content and Specific Heat of Hydrochloric Acid in 10 and 20% Methyl Alcohol-Water Mixtures.—The equation

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[8] Nonhebel and Hartley, *Phil. Mag.*, **50**, 729 (1925).

[9] Born, *Z. Physik*, **1**, 45 (1920).

[10] Bragg, *Phil. Mag.*, [6] **40**, 169 (1920); Pauling, THIS JOURNAL, **49**, 765 (1927).

$$\frac{\partial \ln \gamma^2}{\partial T} = -\frac{\overline{L}_2}{RT^2} \tag{14}$$

relates the activity coefficient, and the relative partial molal heat content, $\overline{L}_2$. By rearranging equation (7) and differentiating with respect to T (m constant), we obtain

$$\frac{\partial \ln \gamma^2}{\partial T} = -\frac{F}{R}\frac{\partial}{\partial T}\left(\frac{E - E_0'}{T}\right) = -\frac{\overline{L}_2}{RT^2}$$

or

$$\overline{L}_2 = FT^2\frac{\partial}{\partial T}\left(\frac{E - E_0'}{T}\right) \qquad 15)$$

Equation (2) expresses E as a function of t, and, similarly, the numerical equations at the end of our earlier contribution[2] gives E_0' as a quadratic function of $(t - 20)$. By the substitution of $t = T - 273.1$, these equations may be converted to

$$\begin{aligned} E &= A + BT + CT^2 \\ E' &= A_0 + B_0T + C_0T^2 \end{aligned} \tag{16}$$

Upon subtraction, division by T, substitution in equation (15), and subsequent differentiation, we obtain

$$\overline{L}_2 = -F(A - A_0) + F(C - C_0)T^2 = \alpha + \beta T^2 \tag{17}$$

and

$$\overline{C}_p - \overline{C}_{p0} = \frac{d\overline{L}_2}{dT} = 2\beta T \tag{18}$$

The quadratic equations for expressing the electromotive forces are sufficient for treating these results since a short temperature range (0 to 40°) is under consideration.

Since the constants α and β were obtained by the subtraction of the least squared constants in equations (16), they are subject to an accumulation of errors. For this reason, they were smoothed against concentration. α was plotted against the square root of the acid concentration, and log β was plotted against m. From these curves the smoothed values given in Table V were read. $\overline{L}_2$ and $(\overline{C}_p - \overline{C}_{p_0})$ may be computed from these values of α and β by equations (17) and (18).

TABLE V

CONSTANTS OF EQUATIONS (17) AND (18)

	10% CH_3OH		20% CH_3OH	
m	$-\alpha$	$\beta \times 10^6$	$-\alpha$	$\beta \times 10^6$
0.001	46	828	3	438
.002	65	1161	36	977
.005	104	1816	126	2239
.01	144	2582	182	3119
.02	198	3556	258	4266
.05	304	5520	388	6383
.1	436	7762	500	8400
.2	658	10960	646	11000
.5	1184	18620	941	15600
1.0	1854	28180	1656	25820
1.5	2388	36300	2377	36810
2.0	2858	44160	2992	47860

The values of $\overline{L}_2$ determined as described have properties very similar to those of hydrochloric acid in aqueous solutions. In fact, at 25°, $\overline{L}_2$ for hydrochloric acid at concentrations from 0 to 2 M is approximately the same as in water. $\overline{L}_2$ is found to increase rapidly with concentration at lower concentrations. From 0.2 to 0.5 M, it increases less rapidly, and at concentrations above the inflection point at about 0.5 M, it again increases more rapidly.

The values of $(\overline{C}_p - \overline{C}_{p_0})$ may only be considered as a rough estimate since they are obtained from second derivatives of the original electromotive forces. The values obtained from these data are of the order of magnitude of those of the acid in pure water. The forms of the $(\overline{C}_p - \overline{C}_{p_0})$ vs. $m^{1/2}$ plots are the same as in water. In general, it appears that this quantity is greater in the alcohol solutions than in water.

Summary

1. Electromotive force measurements of the cells

H_2 | HCl (m) in X% CH_3OH, Y% H_2O | AgCl–Ag

from 0 to 40° at 5° intervals have been made in methanol–water mixtures containing 10 and 20% by weight of methanol. The acid was varied from 0.003 to 2 M. The accuracy was of the order of ±0.05 mv.

2. The densities of the solutions were determined.

3. The activity coefficient of the acid in these solutions was computed. It was found that at a given temperature, the activity coefficient of the acid in the methanol–water mixtures of high dielectric constant could be computed from the parameters of the equation of the extended Debye and Hückel theory which were obtained in aqueous solution. This leads us to suspect that with a knowledge of the "apparent ionic diameter" and the constant of the linear term in equation (5), obtained from data in aqueous solution, the activity coefficient of a strong electrolyte ($a \sim 4$ or >4) may be computed at a given temperature in media of dielectric constant of the order of 60 or greater. A knowledge of the dielectric constants of the media is required.

4. A study of methods of extrapolation of electromotive force data of the above cell in pure methanol solutions has been made, and the standard potential of the cell in this solvent has been recalculated.

5. The electromotive force of transfer of the acid at unit activity from one solvent to another has been discussed in relation to the Born theory, and values of the sum of the reciprocals of the ionic radii have been evaluated from the electromotive force data.

6. Equations and their parameters are given by means of which the relative partial molal heat content and specific heat of the acid in the 10% and 20% methanol-water mixtures may be computed.

NEW HAVEN, CONN. RECEIVED MARCH 3, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Kinetics of Thermal Cis–Trans Isomerizations. V

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

In a continuation of previously reported studies on the rate of *cis–trans* isomerizations,[1,2,3,4] isomers of butene-2, which have recently become available in this Laboratory,[5] were selected for investigation. The equilibrium between the isomers has also been studied. Todd and Parks[6] have determined their entropies at room temperature, while the data of Kistiakowsky *et al.*,[5] give the heat of isomerization. As all these measurements have been made on identical samples, the results should form a consistent picture.

Experimental Details

The butene-2 isomers were prepared by dehydration of secondary butyl alcohol with concentrated sulfuric acid at a temperature not far from 100°. They were purified by distillation as described elsewhere.[5]

The apparatus consisted of the usual static arrangement, a Pyrex flask in an aluminum block furnace, manually controlled. The gas pressure was read with the aid of a quartz spiral manometer and the flask was connected to the rest of the apparatus through a metal valve. The reaction was followed by determining the melting temperature of the reaction mixture. Pure butene-2 *cis* melts at −139.3°[5] and pure *trans* at −105.8°.[5] The melting points of several known mixtures were determined and a curve constructed. A eutectic is formed which melts at −143.0° and contains 15.8% of the *trans* isomer. The melting points were determined in a cell which was sealed directly into the line. It consisted of a jacketed 10-mm. tubing, the interspace of which could be either evacuated or filled with air for a more rapid heat exchange. Around the outside of the inner tubing a few turns of fine platinum wire were wrapped. A long capillary mounted centrally within the inner tube through a ring seal at the top served as a thermocouple well for a very fine Cu–Constantan couple. A small soft iron band wrapped around the upper portion of the capillary in conjunction with an outside electromagnet actuated by interrupted current served to set the capillary in oscillatory motion providing efficient stirring of the sample. The lower portion of the cell was immersed in an unsilvered Dewar cylinder filled with filtered liquid air. A fine pencil of light was focused on the sample. After the hydrocarbon was condensed and frozen in the cell, the interspace was evacuated and a current passed through the heater sufficient to produce a slow melting rate. The temperature at which the last crystals of the solid disappeared was observed. It could be reproduced to somewhat better than 0.1°, which corresponds to about 0.5% accuracy in determining the composition of the mixture. This procedure was found to be considerably more accurate than a determination of the freezing temperature.

Experimental Results

The pressure in all runs at both temperatures studied remained constant to ±1 mm. In all cases the condensed reaction mixture was colorless. The possibility of a balanced polymerization and decomposition appeared very slight since it is very unlikely that both reactions possess the same activation energy.

Sickman and Rice[7] have found that the polymerization of ethylene is greatly accelerated by free methyl radicals. Similar experiments per-

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[1] Kistiakowsky and Nelles, *Z. physik. Chem.*, **152**, 369 (1931).

[2] Nelles and Kistiakowsky, THIS JOURNAL, **54**, 2208 (1932).

[3] Kistiakowsky and Smith, *ibid.*, **56**, 638 (1934).

[4] Kistiakowsky and Smith, *ibid.*, **57**, 269 (1935).

[5] Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 876 (1935).

[6] Todd and Parks, *ibid.*, **58**, 134 (1936).

[7] Sickman and Rice, *ibid.*, **57**, 1384 (1935).