The dipole moment, in debye units, derived from P_∞ and R_D, by the equation $\mu = 0.01281 \sqrt{P_\infty - R_D}$, is 3.40 ± 0.01 D. In view of the value, 3.40 ± 0.02 D, obtained by Oesper for 2-nitropropane, and the fact that in the gaseous state the moments of the nitroparaffins above nitromethane are equal within 0.02 to 0.03 D, we suggest that the solution value for the higher nitroparaffins, *i.e.*, the nitro-group moment, is more correctly 3.4 D than the usual figure, 3.3 D, found in the literature.

Summary

The dipole moment of 1-nitrobutane in benzene solution at 25° has been measured. The value obtained is 3.40 ± 0.01 D. Review of previously reported measurements of the higher nitroparaffins suggests that 3.4 D is a correct figure for the solution value of the nitro-group moment in these compounds.

PHILADELPHIA 4, PA. RECEIVED JULY 27, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Rate of Mutarotation of Glucose in Water–Methanol Mixtures Catalyzed by Acetic Acid. The Ionization of Acetic Acid in These Mixtures

BY JERRY J. GIULIANO[1] AND DOUGLAS G. HILL

In a previous publication[2] from this Laboratory, it was shown that the hydrochloric acid catalyzed mutarotation of glucose was greatly altered as the percentage of methanol was increased in a series of water–methanol mixtures used as solvent for the reaction. The catalytic constant for the solvent catalysis decreased on addition of methanol, while that for the solvated hydrogen ion increased. Both these changes are in qualitative accord with the predicted effect of a change in the dielectric constant of the medium on the rate of a reaction. It seemed of interest to measure the reaction rate with an acid catalyst of strength between water and hydrochloric acid. Measurements were therefore made in three mixtures of water and methanol at 35 and 45° using acetic acid as the catalyst. The ion concentrations were determined under each of the conditions used, so that the constant for each catalyst could be evaluated.

Experimental

Reagent grade absolute methanol was treated with magnesium and distilled. Stock mixtures of the purified methanol with distilled water from the laboratory supply were made up by weight to the desired percentage. Reagent grades of acetic acid, sodium hydroxide, hydrochloric acid and sodium chloride were used. Sodium acetate was prepared by mixing equivalent quantities of standard acetic acid and sodium hydroxide solutions. Pure alpha glucose was prepared by the method of Hudson and Dale.[3]

Temperature control was provided by a large water thermostat, constant to 0.05°. Its temperature was checked against a thermometer calibrated by the Bureau of Standards. Conductance measurements were made in a cell immersed in this thermostat, and rate measurements in a jacketed polarimeter tube through which water from the thermostat was pumped rapidly. In this case, the temperature was measured in the polarimeter tube and was constant to 0.1°.

For each rate measurement, a solution of water, methanol and acetic acid was prepared, and the acid concentration determined by titration. Approximately 0.5 g. of α-glucose was added to 25 ml. of this solution which had been allowed to take the temperature of the thermostat. The solution was poured into the polarimeter tube as soon as dissolved. As was shown by Lowry,[4] it is not necessary to know the exact concentration of the glucose, since the constant is found from a series of optical rotations.

The polarimeter was a Schmidt and Haensch instrument, which with a sodium vapor lamp and a 20-cm. cell was accurate to 0.01°. Readings of the rotation were made at short intervals, keeping the room dark during the experiment. Time intervals were measured by using two one-tenth second stop watches, starting one and stopping the other at the instant of reading the polarimeter. The equilibrium rotation was measured after allowing the solution to stand overnight.

Following Lowry's method, time in minutes was plotted against log $(a - a_\infty)$, and the first order rate constant k determined from the slope of the resulting straight line. As shown by check runs, the values of k were reproducible to 1.5%.

The concentrations of the ions in the various mixtures were determined by conductivity. Using a calibrated Freas conductivity cell and a conductivity bridge the equivalent conductances of a series of acetic acid solutions were determined in each solvent and at each temperature. Similarly a series of conductances were measured for solutions of sodium acetate, hydrochloric acid and sodium chloride at each temperature and methanol concentration. From these, the equivalent conductances of hydrogen ion and acetate ion were found.

Ion Concentration

By comparing the ion conductances and those of acetic acid by the method of MacInnes and Shedlovsky,[5] values were obtained for the degree of dissociation of acetic acid in our solvents at several concentrations. The concentrations of hydrogen ion and acetic acid could be calculated for the solutions used in the rate measurements The results which are believed accurate to 5% are given in Table I.

No activity coefficients are known for the solutions measured, so it is not possible to calculate the true ionization constant directly. Instead, the dissociation function $K' = C\alpha^2/(1 - \alpha)$ was

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[1] This paper is taken from a thesis submitted to the Graduate School of Duke University by Jerry J. Giuliano in partial fulfillment of the requirements for the degree of Master of Arts.

[2] Dyas and Hill, THIS JOURNAL, **64**, 236 (1942).

[3] Hudson and Dale, *ibid.*, **39**, 320 (1917).

[4] Lowry, *J. Chem. Soc.*, **75**, 211 (1899).

[5] MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932).

TABLE I

DEGREE OF DISSOCIATION OF ACETIC ACID IN METHANOL

Wt. % MeOH	Conc. AcOH (moles/l.)	$\alpha_{35°}(\times 10^4)$	$\alpha_{45°}(\times 10^4)$
39.4	0.917	17.8	17.8
	.698	20.9	20.0
	.494	26.1	25.1
	.343	32.5	31.5
	.183	45.6	44.5
	.0913	66.9	65.2
	.0457	95.1	93.7
	.0046	327	318
59.2	1.134	7.79	6.78
	0.843	9.68	8.80
	.533	13.4	12.5
	.195	24.4	22.9
	.0973	36.0	34.1
	.0487	51.8	49.3
	.0049	189	174
74.0	1.156	3.26	2.89
	0.869	4.45	4.03
	.550	6.66	5.09
	.197	12.8	11.5
	.0986	19.2	17.7
	.0493	29.3	26.7
	.0049	118	113

calculated, and is shown plotted logarithmically against the square root of the ionic strength in Fig. 1. If it be assumed that the activity coefficient of AcOH is unity, and that those of H^+ and Ac^- follow the limiting law, the above plot should be linear and the extrapolation of these curves to zero concentration should give a good value for the thermodynamic ionization constant. Table II gives the values so calculated.

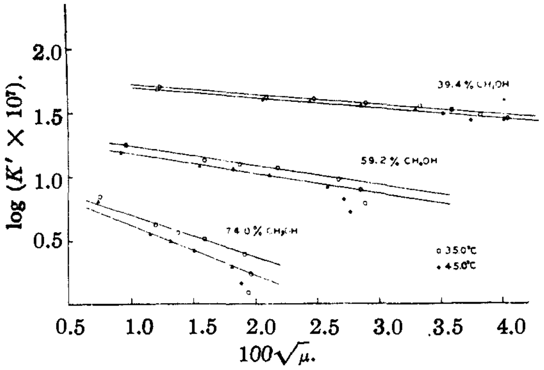

Fig. 1.—Dissociation function of acetic acid in methanol.

TABLE II

IONIZATION CONSTANT OF ACETIC ACID IN METHANOL

% MeOH	$K_{35}(\times 10^5)$	$K_{45}(\times 10^5)$
0	1.76[a]	1.66[a]
39.4	.63	.58
59.2	.25	.22
74.0	.103	.100

[a] Taken from the work of Harned and Ehlers.

If the logarithms of the ionization constants are plotted against the reciprocal of the dielectric constant, a satisfactory straight line is obtained. The lines, if extrapolated, pass through the values of Harned and Ehlers[6] in pure water which are included in Table II.

Kinetics

Values of the rate constant, k, in min.$^{-1}$ were obtained in each solvent at 35 and 45° at four different concentrations of acetic acid. Each of these is a sum of several terms—

$$k = k_0 + k_{H^+}C_{H^+} + k_{AcOH}C_{AcOH} + k_{AcO^-}C_{AcO^-}$$

It has been possible to evaluate all but the last term, which is so small as to be within our experimental error.

If the observed constant k is plotted against the *total* concentration of acetic acid in moles/liter (Fig. 2) a curve is obtained which is a straight line at low concentrations and may be extrapolated to zero. The intercept should be k_0, the constant or the solvent catalyzed reaction. These values are tabulated in Table III, along with k_0 in pure water, taken from the work of Kendrew and Moelwyn-Hughes[7] and recalculated to min.$^{-1}$. The measured rate is the sum of the rates of the forward and reverse reactions, so that our $k_0 = k_\alpha + k_\beta$ in their terminology.

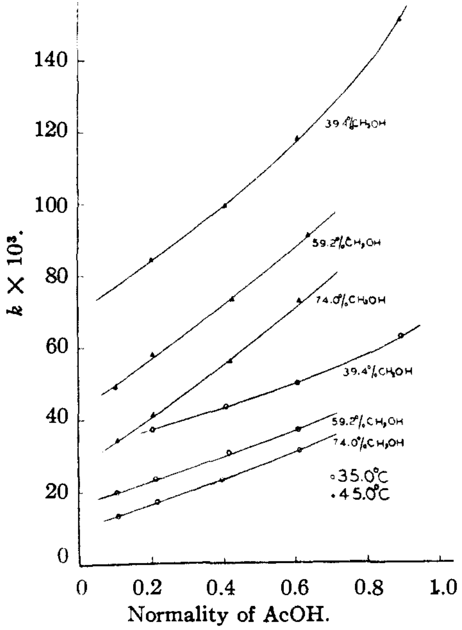

Fig. 2.—Total rate constants of mutarotation as a function of acidity.

Actually all the constants reported in this paper should be divided into those for the forward and reverse reactions as Kendrew and Moelwyn-Hughes did. This may be done if the equilibrium constants for the reaction are measured at each temperature and in each solvent, since $K = k_\alpha/k_\beta$.

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[6] Harned and Ehlers, THIS JOURNAL, **55**, 655 (1933).

[7] Kendrew and Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A176**, 352 (1940).

Although this was done in the work of Dyas and Hill,[2] it was not attempted in the present work since calculations made from the earlier paper showed that the effect of temperature and solvent changes on the individual constants were not significantly different from the same effects on their sums.

Dyas and Hill determined k_{H^+} at 20° and 30° in the same solvents used here. Using their values for k_{H^+} and the activation energy given in their paper, the value of k_{H^+} was found for the present experiments. Since the concentrations had been determined as above, k_{AcOH} was calculated, and averaged over the four concentrations of AcOH measured in each solvent. Table III gives the rate constants.

TABLE III

RATE CONSTANTS

% MeOH	k_0 35°	k_{H_2O} 35°	k_{AcOH} 35°	k_0 45°	k_{H_2O} 45°	k_{AcOH} 45°
0	0.0605[a]	0.00110		0.144[a]	0.00263	
39.4	.0302	.00096	0.0263	.0706	.00224	0.0566
59.2	.0162	.00079	.0278	.0412	.00202	.0625
74.0	.0096	.00077	.0302	.0270	.00216	.0578

k_{AcOH} 35° Av. = .028 k_{AcOH} 45° Av. = .059

[a] Kendrew and Moelwyn-Hughes.[7]

The values of k_{H_2O} given are approximate since

$$k_0 = k_{H_2O}C_{H_2O} + k_{MeOH}C_{MeOH}$$

and the data do not permit the evaluation of each constant. However, extrapolating the values in Table III shows that k_0 in water is at least ten times k_0 in absolute methanol. Therefore, it should be legitimate to neglect the methanol catalysis, and obtain k_{H_2O} by dividing k_0 by the molar concentration of water in each solution. The values in Table III were obtained by this method.

According to theory,[8] a plot of log k against $(D - 1)/(2D + 1)$ should give a straight line with a positive slope. In Fig. 3 these curves are shown for k_0 (circles) and for k_{H_2O} (squares). Both quantities are seen to agree with prediction. The values of k_{H_2O} have been multiplied by 10 for convenience.

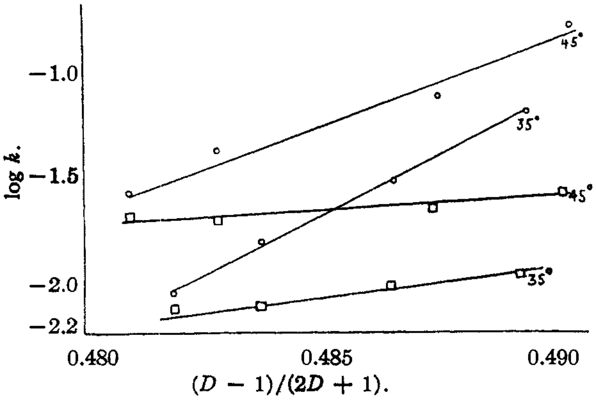

Fig. 3.—Solvent rate constants as function of dielectric constant: (k_0 = circles, k_{H_2O} (× 10) = squares.

However, the rate constant for acetic acid appears to be independent of the concentration of methanol, and thus of dielectric constant. Admittedly all errors in the work will accumulate in the value of this constant, but the fact that it scatters no more than 10% from the mean value shows that the dependence on dielectric constant for a reaction between two neutral molecules may be very small indeed. As a check on the very small magnitude of the effect, we have plotted in Fig. 4 the average log k_{AcOH} against the reciprocal of the absolute temperature. The line through our points passes equally well through the value (solid circle on plot) for the same constant as determined by Lowry and Smith[9] in pure water at 20°. This is a very stringent test, and establishes quite firmly that the catalytic effect of undissociated acetic acid on the mutarotation of glucose is essentially independent of added methanol.

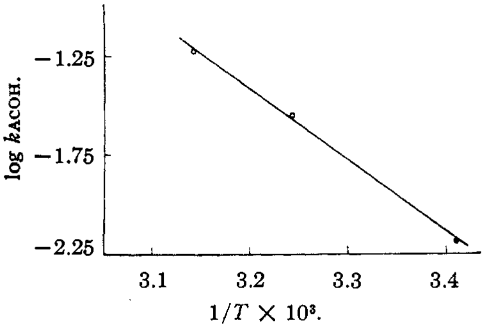

Fig. 4.—Temperature coefficient of catalyzed constant.

The Arrhenius activation energies were calculated for both catalysts in the usual manner, and are given in Table IV as E_0 and E_{AcOH}. The free energies of activation, $\Delta F_0^‡$ and $\Delta F_{AcOH}^‡$, were calculated from the Eyring equation and the entropies from the E and $\Delta F^‡$ values, assuming $E = \Delta H^‡$, and $\Delta S^‡ = (E - \Delta F^‡)/T$. The energies are in kilocalories, and the entropies in calories per degree.

TABLE IV

ACTIVATION ENERGIES AND ENTROPIES

% MeOH	E_0	E_{AcOH}	$\Delta F_0^‡$	$\Delta F_{AcOH}^‡$	$\Delta S_0^‡$	$\Delta S_{AcOH}^‡$
39.4	16.5	16.4	22.8	20.4	−22.0	−20.7
59.2	18.2	16.4	23.1	20.4	−17.9	−20.7
74.0	20.1	16.4	23.4	20.4	−12.6	−20.7

It would be possible to calculate the solvent activation energies from the values calculated for water instead of the total solvent rate constant, but the doubt in the values of the rates makes the energies still less trustworthy. We may note that E_0 and $\Delta S_0^‡$ agree only fairly well with the

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[8] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," Chapter VIII, McGraw-Hill Book Co., New York, N. Y., 1941, chap. VIII.

[9] Lowry and Smith, *J. Chem. Soc.*, 2548 (1927).

work of Dyas and Hill, and that $\Delta F_0^\ddagger$ agrees very well. The anomalous behavior of the former quantities previously found in 60% methanol was not found in the present experiments.

Discussion

Although the isomeric change accompanying the mutarotation of glucose is structurally a simple one, the mechanism by which it is brought about by various catalysts is not clear. While it is possible that the increased association of acetic acid which would be expected as methanol is added to the solution, might explain the unexpected constancy of the rate if the true catalyst were the dimer, there are no data on the extent of the dimerization in these solvents to support such a theory. Further work involving other catalysts, and an elucidation of the mechanism of the isomerization is needed.

Summary

The mutarotation of glucose has been studied using acetic acid as the catalyst in three mixtures of methanol and water at 35 and 45°. The catalytic coefficients for the solvent and for acetic acid have been evaluated. The ionization of acetic acid in the solvent mixtures used has been measured, and the ionization constants evaluated by extrapolation.

The catalytic constant for acetic acid has been found to be independent of the MeOH concentration, and thus of the dielectric constant of the medium.

DURHAM, NORTH CAROLINA RECEIVED JUNE 15, 1946

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE OHIO STATE UNIVERSITY]

An Apparatus for Measuring Joule–Thomson Effects in Gases by Direct Expansion Through a Valve[1]

BY HERRICK L. JOHNSTON

Introduction

A valve was used in the first experiment of Joule and Thomson[1a] but was abandoned by them in favor of a porous clay plug with "axial" flow because of the lesser difficulty with heat flow between the high and low pressure sides. A valve was used again by Olszewski[2] in determining inversion points for hydrogen, nitrogen and air. In 1909 both Bradley and Hale[3] and Dalton[4] the latter working in the Leiden Laboratory—published the results of throttle experiments with air. Since then the valve method has been abandoned in favor of apparatus built on the porous plug principle. The most extensive and most accurate determinations of Joule–Thomson coefficients have been made by Roebuck and co-workers,[5] at the University of Wisconsin, who used an unglazed porcelain cup with radial flow of gas through its walls as "porous plug." This type of plug was also used by Hoxton,[6] who gives in his paper an historical outline of Joule–Thomson work prior to 1919.

The use of a porcelain plug—and particularly of the cup shape with radial flow of gas—appears to possess a distinct advantage over other types of Joule–Thomson apparatus because of the low thermal conductivity of porcelain and the possibility of reducing errors resulting from heat leak between the low pressure and high pressure sides. However, an apparatus of the throttling type offers advantages in simplicity of design and operation. Its practicability depends upon ability to eliminate significant error from heat leak.

The measurements of Bradley and Hale,[3] and those of Dalton,[4] revealed clearly the principal sources of error in Joule–Thomson measurements. Bradley and Hale obtained direct evidence of the thermal effect of "jet kinetic energy" noticed originally in the early work of Joule and Thomson.[1a] By this is meant the conversion of disordered thermal energy into ordered kinetic energy in the high velocity jet. The effect is to lower the temperature of the gas in the jet and is greatest where the cross section of the gas stream is least—such as between stem and seat of the valve. It disappears a few centimeters beyond the nozzle, when the motion of the gas molecules has again become random. The effect may amount to several degrees adjacent to the nozzle and, presumably, may amount to several tens of degrees in the region of greatest constriction. This effect may introduce error into the measurement of Joule–Thomson effects in two ways: (1) the temperature measured in the low pressure gas stream may be too low if measured too near to the nozzle; (2) heat leak to the cold gas will be increased as

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(1) Presented before the Symposium on Low Temperature Research, at the Atlantic City meeting of the American Chemical Society, April 10, 1946.

This paper is based on work performed under Contract W-7405-eng-93 for the Manhattan Project by the Chemistry Department, The Ohio State University, and the information contained herein will appear in Division III of the Manhattan Project Technical Series.

(1a) Joule and Thomson, *Phil. Mag.*, **4**, 481 (1852).

(2) K. Olszewski, *Ann. phys.*, **7**, 818 (1902); *Phil. Mag.*, **13**, 722 (1907).

(3) W. P. Bradley and C. F. Hale, *Phys. Rev.*, **29**, 258 (1909).

(4) J. P. Dalton, Leiden Comm. No. 109c (1909).

(5) (a) Burnett and Roebuck, *Phys. Rev.*, **30**, 529 (1910); (b) Burnett, *ibid.*, **22**, 590 (1923); (c) Roebuck, *Proc. Am. Acad. Arts Sci.*, **60**, 537 (1925); *ibid.*, **64**, 287 (1930); (d) Roebuck and Osterburg, *Phys. Rev.*, **43**, 60 (1933); **45**, 332 (1934); **46**, 785 (1934); **48**, 450 (1935).

(6) L. G. Hoxton, *Phys. Rev.*, **13**, 438 (1919).