then the found ratio of the velocities expresses the relative ability for electron release (which may be a summation of the no-bond resonance effect and the inductive effect) of the two alkyl groups on the total benzene ring during a bromination reaction. The results are thus considered to lend support to the theory of alkyl conjugation with the benzene ring.

Summary

In 92% acetic acid toluene is brominated four times faster than *t*-butylbenzene. This is explained by no-bond resonance.

BRYN MAWR, PA. RECEIVED JUNE 27, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Dipole Moment of 1-Nitrobutane

BY JOHN G. MILLER AND HENRY S. ANGEL

The solution values of the dipole moments of the nitroparaffins are important reference standards for the estimation of the effect of resonance in nitro-compounds which cannot be studied in the gaseous state.[1] Inspection of the recorded solution measurements of the nitroparaffins reveals that only nitromethane has been studied in more than one laboratory, and its value is not a useful standard because of the low polarizability of the methyl group. The only values reported for higher nitroparaffins are those of Hunter and Partington[2] for nitroethane (3.19 *D*) and 1-nitrobutane (3.29 *D*), and that of Oesper reported by Smyth[3] for 2-nitropropane (3.40 *D*).

These higher nitroparaffins should have very nearly the same moments, to judge from the careful studies of the nitroparaffins in the gaseous state made by Smyth and his co-workers.[4] The wide variation in the values of these important reference compounds has led us to measure the moment of 1-nitrobutane, using benzene as solvent to conform with the previous work.

Experimental

Materials.—The 1-nitrobutane was prepared by the Commercial Solvents Corporation and was supplied us by courtesy of Dr. Glenn E. Ullyot of Smith, Kline and French Laboratories. It was repurified by distillation through an all-glass Widmer column. A 97-g. fraction boiling at 152.4 to 153.4° (cor.) was taken for the measurements. At 25° its density was 0.96825 g. per cc., and its refractive index, n_D 1.40840. The molar refractivity, R_D, calculated from these values is 26.29.

The benzene was C. P. material, dried over calcium chloride and freshly distilled over sodium before use. Its density and refractive index were 0.87391 and 1.49782 at 25°.

Apparatus.—The dielectric constant measurements were made with an apparatus and method described previously.[5] Seven frequencies were employed. The temperature used was 25 ± 0.01°.

Results and Discussion

Table I lists the solute mole fractions, N_2, dielectric constants, ϵ, and densities, d, of the solutions measured. Included in the table are two linear equations obtained from these data by the method of least squares, showing the dielectric constant and density as functions of the mole fraction of the solute. The errors listed in these equations are probable errors calculated by the method of Gauss.[6]

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA

N_2	ϵ	d
0.0015889	2.3021	0.87414
.0029209	2.3231	.87437
.0054479	2.3609	.....
.0100568	2.4353	.87507

$$\epsilon = 2.2768\ (\pm 0.0007) + 15.71\ (\pm 0.12)\ N_2$$

$$d = 0.87401\ (\pm 0.00004) + 0.1059\ (\pm 0.0067)\ N_2$$

The constants in these equations were used to calculate the polarization of the solute at infinite dilution, P_∞, by substitution in the Hedestrand formula.[7] The advantages of this method have been described by Halverstadt and Kumler.[8] The value of P_∞, obtained in this way, is 262.3 ± 1.8.

The Gauss calculation used here to show the precision of the measurements is a valuable adjunct to this method of estimating P_∞. In contrast to the analyses of precision usually accompanying such measurements, it provides a rigid, objective analysis and requires little additional work because it employs the normal equations already set up for the least squares calculations. By means of it, a proper weighting of the lower concentration values is obtained.

In the present case, the precision error in P_∞, ±1.8, is due entirely to the error, ±0.12, in the dielectric constant slope term. The density determinations, made at only three concentrations, contribute negligible error.

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[1] Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 137.

[2] Hunter and Partington, *J. Chem. Soc.*, 309 (1933).

[3] Smyth, in Weissberger, "Physical Methods of Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1946, Chap. XX, p. 996.

[4] Wiswall and Smyth, *J. Chem. Phys.*, **9**, 356 (1941); Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1942).

[5] Miller, *ibid.*, **64**, 117 (1942).

[6] Whittaker and Robinson, "Calculus of Observations," 2nd ed., Blackie and Son, London, 1937, pp. 243–247.

[7] Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[8] Halverstadt and Kumler, THIS JOURNAL, **64**, 2988 (1942).

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.

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[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).