[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

Absolute Verdet Constants for Benzene over a Range of Temperatures and Visible Wave Lengths

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The purpose of this paper is to present absolute Verdet constants for benzene over a range of temperatures and visible wave lengths. These constants were obtained from experimentally determined values of the magnetic rotation of benzene and from precise measurements of the field strength of the solenoid employed. The uncertainty in the values so obtained was found to be ±0.05%. These results constitute the first determination of absolute Verdet constants for this substance.

I. Introduction

Since its discovery in 1845, the Faraday effect has been widely studied because of its inherent connection with both the universal magnetizability of matter and the electromagnetic theory of light. At present, however, there is still no general theory for liquids and solids. The Larmor-Becquerel theory,[2] while derived on a basis independent of the actual origin of magnetic rotatory polarization, has served to give a general picture of the effect. In its present state, however, it does not account for the temperature dependence, apart from volume effects, of the normal Faraday effect except insofar as it is conditioned by the optical characteristics of the molecule. In connection with this, Schultz[3] has pointed out a need for exact and controlled observations of the dependence on temperature of magnetic rotatory dispersion of various pure materials on which to base extensions of present theory. To the same end, Ingersoll[4] has indicated the necessity for determinations of the dependence upon wave length of the temperature coefficient of the Faraday effect.

In experiments carried out for the purpose of using the results on which to base extensions of current theory, benzene has been widely studied. However, no systematic studies of the type indicated by Schutz and by Ingersoll have been done. In addition, no actual absolute Verdet constants are given in the literature for this compound. In view of its importance as a standard substance, it was felt that such studies should be carried out. It is the purpose of this paper, therefore, to present absolute Verdet constants for benzene, over a range of temperatures and wave lengths, obtained using a precision Faraday effect apparatus[5] and experimentally determined magnetic field strengths.

II. Experimental

The benzene employed in the measurements was reagent grade, thiophene free. It was dried over P_2O_5 and distilled in a 30-plate Oldershaw column from P_2O_5. The middle fraction of this distillation, from which sample 1 was obtained, was redistilled in the same column. Sample 2 was obtained from the middle fraction of this distillation. The criterion of purity used was the refractive index measured on a Bausch and Lomb precision Abbe refractometer. At 25°, the two samples of benzene differed by only 0.018% with the literature values[6] at 589 mμ.

Measurements of k, the rotation per ampere, were made in the usual way[7] over a range of temperatures from 5 to 60° for each of the wave lengths 589, 578, 546 and 436 mμ. Each value for the rotation is an average of thirty-six polarimeter readings, eighteen in the positive and eighteen in the negative direction of the current flow through the magnet. Appropriate corrections were made in all the k values for the rotation due to the air in the light path and to the rotation due to the end plates in the quartz cell. The variations of the rotation constant, k, for benzene, with temperature at the various wave lengths are presented in Fig. 1. The complete data may be found elsewhere.[8]

Values of the magnetic field strength of the Faraday effect solenoid, at points over a range 14 cm. along the axis on either side of the center, were obtained from measurements made by a method based upon proton nuclear magnetic resonance.[9] Four least square equations of field strength as a function of axial position were derived from the data.[10] The most suitable, according to the Gauss criterion, was extrapolated over the 56 cm. length of the Faraday effect cell to obtain a value of magnetic potential per ampere over this length. The value so obtained was 2152.6 gauss cm. per ampere with an uncertainty of ±0.03%.

Densities of the benzene samples were determined over a range of temperatures from 8 to 60° in a precision pycnometer whose volume had been carefully determined with pure water. All values were corrected for vapor density and for buoyancy. In Table I are given the density values calculated for arbitrary temperatures from a least squares equation, (1), derived from the data.

$$d = 0.90012 - 1.0766_1 \times 10^{-3}t;\ 8 < t < 60 \quad (1)$$

Literature values of densities of benzene[11] at the corre-

TABLE I

LEAST SQUARES VALUES OF THE DENSITY OF BENZENE AS A FUNCTION OF TEMPERATURE

Temperature, °C.	Least squares densities 5×10^{-5}	Literature values[11] of density 2×10^{-4}
5.00	0.89474	0.8947
10.00	.88935	.8894
15.00	.88397	.8841
20.00	.87859	.8787
25.00	.87321	.8734
30.00	.86782	.8680
40.00	.85706	.8573
50.00	.84629	.8465
60.00	.83552	.8356

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(1) The data presented were submitted in partial fulfillment of the requirements of the Ph.D. degree at the University of Connecticut.

(2) H. Becquerel, *Compt. rend.*, **125**, 679 (1897); J. Larmor, "Ether and Matter," Cambridge, 1900, p. 352.

(3) W. Schutz, in Wien and Harms, "Handbuch der Experimentalphysik," Akad. Verlags, Leipzig, Vol. 36, Part 1, 1936, p. 38.

(4) L. R. Ingersoll, *Phys. Rev.*, **9**, 257 (1917).

(5) Samuel Steingiser, George J. Rosenblit, Robert L. Custer and Chas. E. Waring, *Rev. Sci. Instruments*, **21**, 119 (1950).

(6) N. B. S. Circular C461, 1947, p. 67.

(7) Samuel Steingiser, Ph.D. Thesis, University of Connecticut, 1949.

(8) ONR contract N6ori 216 T.O. No. 1, Technical Report No. 6 (May, 1950).

(9) Richard H. Spencer, M.S. Thesis, University of Connecticut, 1950.

(10) Chas. E. Waring, Richard H. Spencer and Robert L. Custer, Contract N6 ori 216 T.O., No. 1, Technical Report No. 4, October (1950).

(11) "International Critical Tables," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., Table 1, 1929, p. 29.

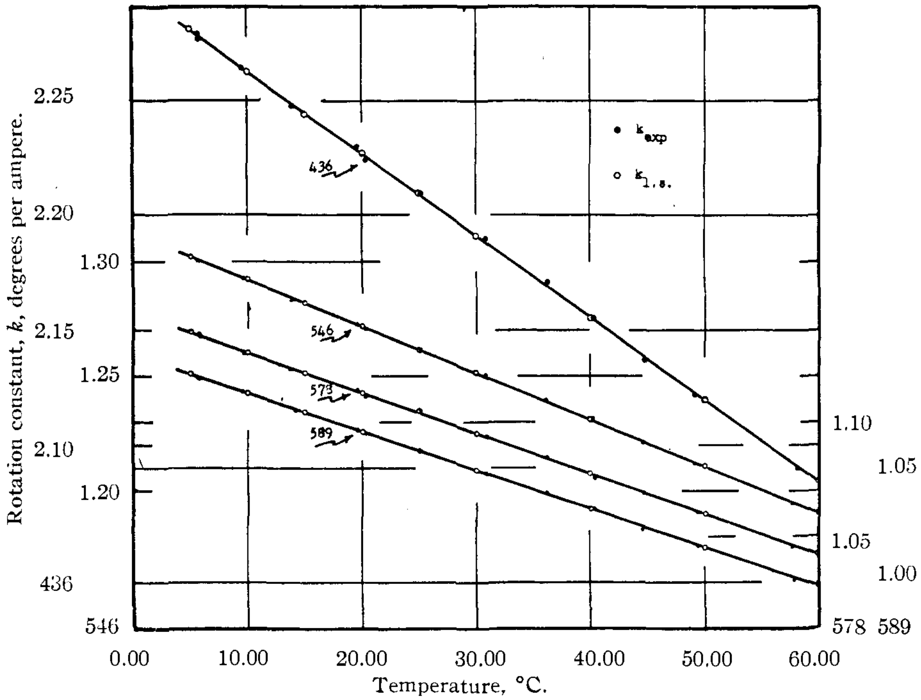

Fig. 1.—Variation of k, the rotation constant for benzene, with temperature.

sponding temperatures are listed for comparison in column 3 of Table I. It is seen that the agreement is excellent.

III. Results

Least squares equations for the variation of k, the rotation constant for benzene, as a function of temperature for each of the four wave lengths were derived from the data represented in Fig. 1. These equations are shown in Table II.

TABLE II

LEAST SQUARES EQUATIONS OF k FOR BENZENE AS A FUNCTION OF TEMPERATURE

λ	Equation	
589	$k = 1.09942 - 1.68538 \times 10^{-3}t$	(1)
578	$k = 1.14823 - 1.76710 \times 10^{-3}t$	(2)
546	$k = 1.31227 - 2.02342 \times 10^{-3}t$	(3)
436	$k = 2.29848 - 3.57593 \times 10^{-3}t$	(4)

Values of k for arbitrary temperatures were calculated from the equations in Table II. These values are shown in Table III.

TABLE III

LEAST SQUARES VALUES OF k FOR BENZENE AS A FUNCTION OF TEMPERATURE

λt→	5	10	15	20	25	30	40	50	60
589	1.0910	1.0826	1.0741	1.0657	1.0573	1.0489	1.0320	1.0152	0.9983
578	1.1394	1.1306	1.1217	1.1129	1.1040	1.0952	1.0775	1.0599	1.0422
546	1.3022	1.2920	1.2819	1.2718	1.2617	1.2516	1.2313	1.2111	1.1909
436	2.2806	2.2627	2.2449	2.2270	2.2091	2.1912	2.1554	2.1197	2.0839

TABLE IV

DISPERSIONS, k_λ/k_{589}, FOR BENZENE AS A FUNCTION OF TEMPERATURE

λ	5	10	15	20	25	30	40	50	60
578	1.0444	1.0443	1.0443	1.0443	1.0442	1.0441	1.0441	1.0440	1.0440
546	1.1936	1.1934	1.1935	1.1934	1.1933	1.1932	1.1931	1.1930	1.1929
436	2.0904	2.0901	2.0900	2.0897	2.0894	2.0890	2.0886	2.0880	2.0874

Values of the dispersions k_λ/k_{589}, calculated from the data in Table III are shown in Table IV.

Absolute values of the Verdet constants for benzene were calculated from the data in Table III from the relation, $V = 60\ k/2152.6$. These, together with specific Verdet constants, V/d, calculated on the basis of the data in Table III using the density values of benzene in Table I, and molecular Verdet constants, MV/d, are shown in Table V.

The absolute Verdet constants for benzene were calculated with uncertainties of ±0.04–0.05%. A value of 3.02×10^2 was derived by Richardson[12] for this constant at 589 mμ and 20° from his data on the basis of the Verdet constant given by Rodger and Watson for water at the same wave length and temperature. Since this value would suffer the same precision limitations as that on which it was based, no reliable comparison can be made.

These results of determinations of absolute Verdet constants for benzene are the first to have been derived for this substance on the basis of precise values of the magnetic field strength of the solenoid employed in the determinations of its magnetic rotation. Thus, the uncertainties in the constants are

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(12) S. S. Richardson, *Proc. Roy. Soc.* (*London*), **31**, 454 (1916).

TABLE V

ABSOLUTE VERDET CONSTANTS OF BENZENE

Temp., t, °C.	Density	λ = 589 mμ $V \times 10^2$	$V/d \times 10^2$	$V/d \cdot M$	λ = 578 mμ $V \times 10^2$	$V/d \times 10^2$	$V/d \cdot M$	λ = 546 mμ $V \times 10^2$	$V/d \times 10^2$	$V/d \cdot M$	λ = 436 mμ $V \times 10^2$	$V/d \times 10^2$	$V/d \cdot M$
5	0.89474	3.0412	3.3990	2.6550	3.1759	3.5495	2.7725	3.6295	4.0565	3.1685	6.3568	7.1046	5.5494
10	.88935	3.0175	3.3929	2.6502	3.1512	3.5433	2.7677	3.6013	4.0494	3.1630	6.3069	7.0916	5.5392
15	.88397	2.9940	3.3870	2.6456	3.1266	3.5370	2.7627	3.5731	4.0421	3.1573	6.2571	7.0784	5.5289
20	.87859	2.9705	3.3810	2.6409	3.1020	3.5306	2.7577	3.5449	4.0348	3.1516	6.2073	7.0651	5.5185
25	.87321	2.9470	3.3749	2.6361	3.0773	3.5241	2.7527	3.5167	4.0273	3.1457	6.1574	7.0514	5.5078
30	.86782	2.9235	3.3688	2.6314	3.0527	3.5177	2.7477	3.4886	4.0199	3.1399	6.1076	7.0379	5.4973
40	.85706	2.8765	3.3562	2.6215	3.0035	3.5044	2.7373	3.4321	4.0045	3.1279	6.0079	7.0099	5.4754
50	.84629	2.8296	3.3435	2.6116	2.9542	3.4908	2.7267	3.3757	3.9888	3.1156	5.9083	6.9814	5.4532
60	.83552	2.7826	3.3304	2.6014	2.9049	3.4767	2.7156	3.3193	3.9727	3.1031	5.8086	6.9521	5.4303

less than those for any previous Verdet constants.

It is seen from the data in Table IV that the dispersion for benzene is not constant but decreases slightly with temperature. This behavior is similar to that found previously for the magnetic rotatory dispersion of water above 25°.(13)

The results in Table V show that the molecular Verdet constants, MV/d, decrease with temperature over the entire range. Richardson(14) has suggested that the origin of the temperature dependence of the normal Faraday effect might be in the thermal opposition to the precessional motion of finite magnetic moments, thus, to a mean paramagnetic polarization. These results, therefore, might be interpreted in terms of a slight paramagnetic polarization in the case of benzene. It is of interest to note that the temperature coefficient at 436 mμ is approximately twice that at 589 mμ. Further extensions of theory would have to account for this behavior.

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(13) Chas. E. Waring and Robert L. Custer, THIS JOURNAL, **74**, 2506 (1952).

(14) S. S. Richardson, *Proc. Roy. Soc.* (*London*), **31**, 232 (1918).

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Kinetics of the Condensation of Melamine with Formaldehyde

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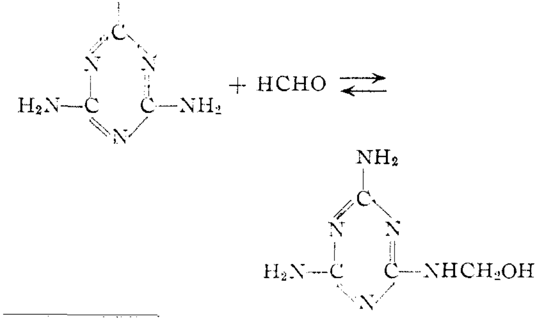
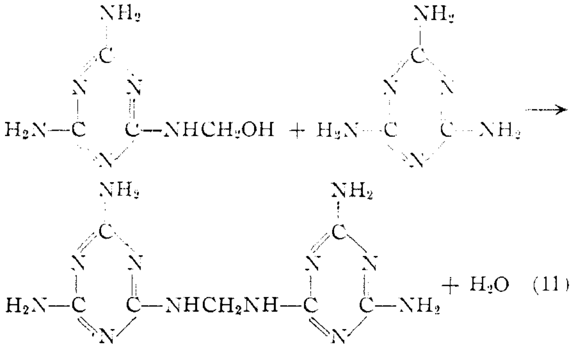
The rates of the condensation of melamine with formaldehyde in aqueous media in the pH's varying from 3 to 10.6 have been estimated at 35, 40 and 70° by employing both iodometric and sulfite methods. The primary product of the condensation, methylolmelamine, was found to consume iodine like formaldehyde itself, and therefore the result of the iodometric method indicates the amount of formaldehyde together with that of methylol group present, while the sulfite method estimates solely formaldehyde unreacted. From the data obtained by these two methods, the rates of the formation of methylolmelamine, *e.g.*, (I), and methylene-bonded melamines, *e.g.*, (II), were determined. There were found evidences that only the formation of methylol compounds occurs at 35–40° except in acidic solution and that the reaction is reversible all through the pH range, its forward rate being proportional to either [melamine] [formaldehyde], [melamine] [conjugate acid of formaldehyde], or [conjugate base of melamine] [formaldehyde] according to the pH's of the media. The rate of the irreversible condensation of methylolmelamine with melamine in neutral and acidic media at 70°, where the hydroxymethylation (I) is very rapid, is determined by the condensation step of conjugate acids of methylolmelamines with melamine, the rate being expressed as [melamine]^2 [formaldehyde]. The rate equations based on the reaction mechanisms which are suggested from these results satisfied the relationship between pH and the rate constant experimentally found.

It has been pointed out that the nature and structure of the melamine–formaldehyde condensate are considerably varied with reaction conditions, especially molar ratio of reactants, pH and temperature of the solution.(1) There seems to be no decisive kinetic evidence for this condensation mechanism, although the primary process may be presumed from the similar reactions such as those of urea–formaldehyde and aniline–formaldehyde.(2)



(I)



(II)

(1) T. S. Hodgins, *et al.*, *Ind. Eng. Chem.*, **33**, 769 (1941).

(2) T. S. Hodgins and A. F. Hovey, *ibid.*, **30**, 1021 (1938); K. Frey, *Helv. Chim. Acta*, **18**, 491 (1935).