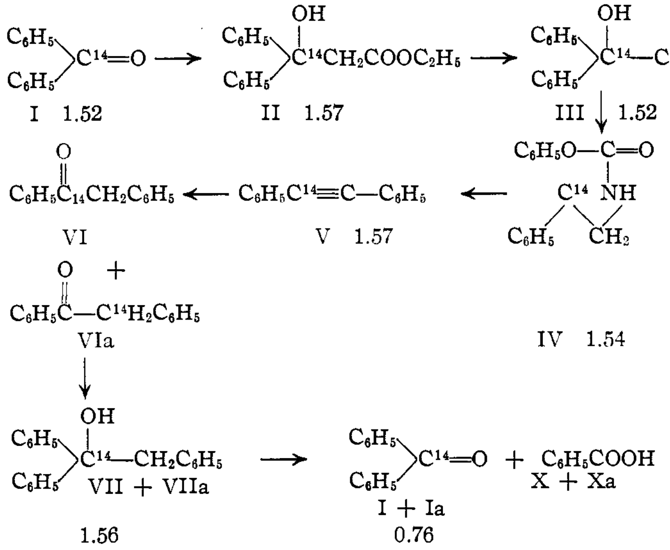

elements of water across the C^{12}–C^{14} triple bond (*i.e.*, the isotope effect),[3] of this substance.

This has now been done. The series of reactions employed is shown in the scheme above. The arabic numerals represent the radioactivities in microcuries per millimole. The average of ten determinations upon the compounds I through VII was 1.55 ± 0.02 μc. of C^{14}/mmole (average derivation). When this is compared with the value of 1.52 ± 0.01 μc. of C^{14}/mmole which is twice the observed activity of the degradation product, I + Ia, it is apparent that any isotope effect in the hydration of diphenylacetylene must be less than 1–2%. The results of the assays upon the other degradation product, benzoic acid (X), could not be applied to this study, since the low value obtained, 0.66 μc. of C^{14}/mmole, indicates that the benzoic acid obtained must have been diluted during the oxidation of VII + VIIa with benzoic acid from some inactive source.

Experimental[4]

Diphenyl Ketone-C^{14}.—Thirty-five grams of aluminum chloride was added portionwise to a mixture of 56 g. of benzene, 60 ml. of carbon disulfide, 28.1 g. of benzoyl chloride and 50.1 mg. of benzoic acid containing about 1 mc. of carbon-14. After stirring overnight, the mixture was hydrolyzed, the product processed and then distilled. The distillate was 26.34 g. (72%); the still was chased with 21.33 g. of inactive benzophenone, of which 19.70 g. was recovered in the distillate, making a total of 46.04 g. (253 mmoles) of crystalline benzophenone. A portion of this was converted to the oxime, m.p. 141°, which was recrystallized for assay. The assay showed 1.50, 1.53 μc. of C^{14}/mmole.

Ethyl 3-Hydroxy-3,3-diphenylpropionate-3-C^{14}.—This was prepared by the procedure of Rupe and Busolt,[5] in essentially quantitative yield as a solid, which, after crystallization, melted at 85–86°. It contained 1.56, 1.58 μc. of C^{14}/mmole.

3-Hydroxy-3,3-diphenylpropionic Acid-3-C^{14} Hydrazide.—This was prepared by refluxing the above ester, 13.5 g., with a mixture of 10 ml. of 95% hydrazine hydrate and 25 ml. of ethanol for three hours. The yield was 16 g. of colorless solid which after crystallization from benzene melted at 130° and contained 1.52 μc. of C^{14}/mmole.

5,5-Diphenyl-2-oxazolidone-4-C^{14}.—A solution of the hydrazide (7.2 g.) in 60 ml. of acetic acid and 6 ml. of 6 *N* hydrochloric acid was treated, with stirring, with a solution of 2.1 g. of sodium nitrite in 15 ml. of water. The suspension of white solid which formed was heated on the steam-bath until cessation of gas evolution and the resulting clear yellow solution cooled and diluted with water. The pale yellow crystalline solid which formed was filtered (4.1 g.), m.p. 196–198°, and crystallized from ethanol to give colorless crystals melting at 200°, and containing 1.56, 1.52 μc. of C^{14}/mmole.

Diphenyl-(acetylene-1-C_1^{14}).—The above oxazolidone was converted through the nitroso compound to the acetylene by the procedure described by Newman and Kutner.[3] The acetylene was obtained in 60% yield as a pale cream solid, m.p. 52–55°. Recrystallization from alcohol–water gave colorless needles melting at 56–57° and containing 1.59, 1.56 μc. of C^{14}/mmole.

Benzyl Phenyl Ketone-C^{14}.—A portion of the above acetylene (0.50 g.) was warmed with a mixture of 5 ml. of concentrated sulfuric acid and 15 ml. of acetic acid until a clear solution resulted (about one hour), then a few crystals of mercuric chloride was added and warming continued for a few minutes. The solution was poured into water, and the pale yellow precipitate filtered and air-dried. It weighed 500 mg. and melted at 51–52°. The mixture melting point of this with authentic desoxybenzoin (m.p. 51–52°) showed no depression but the mixture melting point with diphenylacetylene (m.p. 56–57°) was 35–45°.

Benzyldiphenyl-(carbinol-C^{14}).—The above product was added to the Grignard solution prepared from 3 g. of bromobenzene and 0.5 g. of magnesium, and the resulting turbid suspension stirred overnight. Hydrolysis and crystallization of the product from hexane gave 480 mg. of nearly colorless needles which melted at 88° and contained 1.56 μc. of C^{14}/mmole.

Oxidation of Benzyldiphenylcarbinol-C^{14}.—After about 100 mg. of the above material had been reserved for analysis, the residual product was heated for one hour on the steam-bath with a solution of 0.5 g. of chromic oxide in 10 ml. of acetic acid. The dark green solution was poured into water, and the water solution was ether extracted. This ether extract was shaken with 1 *N* sodium hydroxide and water, then dried and evaporated. The residual darkish oil was heated with hydroxylamine hydrochloride, pyridine and ethanol to give after crystallization from dilute ethanol, 150 mg. of benzophenone oxime, whose melting point and mixture melting point with authentic oxime (m.p. 141°) was 141°. It contained 0.756, 0.758 and 0.763 μc. of C^{14}/mmole. The alkaline extract obtained above was acidified and ether extracted. The darkish oil obtained from the ether was treated with a large excess of thionyl chloride and the solution heated under vacuum to remove excess thionyl chloride and any acetyl chloride. The residue from this was dissolved in benzene and treated with excess aniline. The benzene solution after washing with water and drying was evaporated, and the residual solid crystallized from benzene. The benzanilide was so obtained as colorless plates which melted at 161° and contained 0.690, 0.656, 0.660 and 0.676 μc of C^{14}/mmole.

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[3] *Cf.* G. A. Ropp and O. K. Neville, *Nucleonics*, **9**, 22 (1951), for a general review of the isotope effect.

[4] C-14 assays were accomplished by wet combustion of the compounds and ionization chamber counting of the evolved carbon dioxide on a vibrating reed electrometer. Melting points were taken upon a Kofler hot-stage.

[5] H. Rupe and E. Busolt, *Ber.*, **40**, 4537.

Dielectric Constant for the Dioxane–Water System from 20 to 35°

BY FRANK E. CRITCHFIELD, JOHN A. GIBSON, JR., AND JAMES L. HALL[1]

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This paper is a report of the dielectric constants of dioxane–water mixtures over the range of tem-

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[1] Address communications to James L. Hall.

perature 20 to 35°. In performing some studies of conductance at high frequencies it was necessary to have solutions of accurately known dielectric constant. Dioxane–water mixtures have been used for this purpose, but our attempts to verify previously published data[2] for certain mixtures were not successful and so the entire system was redetermined. The data reported here enable use of dielectric constant to determine accurately the composition of dioxane–water mixtures.

Experimental

Materials.—The water used in these measurements was prepared by three distillations. Tap water was ordinarily distilled using a Barnstead still. The distillate was distilled in Pyrex equipment from an alkaline solution of permanganate. The middle third fraction from the second distillation was again distilled in Pyrex equipment retaining the middle third fraction which had a specific conductance of 1×10^{-6} ohms^{-1} cm.$^{-1}$.

Dioxane from the Carbide and Carbon Chemical Corporation was purified according to the method of Hess and Frahm[3] except the recrystallization was omitted. Time–temperature cooling curves were then run on the purified dioxane, employing an N.B.S. calibrated resistance thermometer and a Leeds and Northrup Co. Mueller Bridge. The freezing point was found to be 11.73° and the purity, as determined from the shape of the curves by the method of Rossini,[4] was not less than 99.95%.

Method.—For measurements of the dielectric constant of the various mixtures a General Radio Co. Twin-T Impedance Measuring Circuit was used.[5] A General Radio Co. Type 805-C Standard Signal Generator served as the frequency source. The detector unit consisted of a Hallicrafters SX-42 Receiver with a Du Mont Type 208-B Oscillograph for visual indication of the null point. All measurements were made at a frequency of one megacycle.

A new non-inductive type cell was constructed which is somewhat similar in design to one described by Ferry and Oncley,[6] and modified by Conner, Clarke and Smyth.[7] This cell is improved, as compared with previous ones of similar design, by the use of Teflon as the insulation material. Further, the lower Teflon plug and the inner electrode were threaded so as to permit complete dismantling of the cell. Several sizes of the central electrode were made to provide a range of capacitance. The metal parts of the cell were heavily nickel plated brass. At temperatures varying greatly from that of the room, temperature control within this water-jacketed cell may be not quite as precise as if the cell were in a thermostat, but this slight disadvantage is more than compensated for by the elimination of large lead corrections. Throughout all the measurements the temperature remained constant well within ±0.05°. The thermometer used was compared with an N.B.S. calibrated thermometer.

In the calibration of the cell, the dielectric constant of water was assumed to be 78.48 at 25° as reported by Albright.[8] All readings of capacitance from the Twin-T Circuit were corrected for drum variance using the manufacturer's calibration. The cell capacitance, $d\epsilon/dC$ was 1.83 μμf. and the lead capacitance was 1.4 μμf. To verify the method and to check the properties of the cell over a range of dielectric constant, the methanol–water system was studied at 25°. For this temperature the results of Albright and Gosting[9] were duplicated within one part in 1000.

Results

The values shown in Table I were obtained for the system dioxane–water at the temperatures shown.

TABLE I

DIELECTRIC CONSTANT FOR THE DIOXANE–WATER SYSTEM

Weight % dioxane	Temperature, °C. 20	25	30	35
0.00	80.38	78.48	76.72	74.97
10.00	72.02	70.33	68.74	67.10
20.00	63.50	61.86	60.38	58.96
30.00	54.81	53.28	51.91	50.60
40.00	45.96	44.54	43.33	42.24
50.00	36.89	35.85	34.81	33.88
60.00	28.09	27.21	26.45	25.74
70.00	19.73	19.07	18.58	18.07
80.00	12.19	11.86	11.58	11.26
90.00	6.23	6.07	5.96	5.85
95.00	3.99	3.89	3.83	3.76
100.00	2.24	2.21	2.20	2.19

Due to the low capacitance of the measuring cell the results in the low range of dielectric constant are limited to an accuracy of about one part in 200. The accuracy of the data at the higher dielectric constants listed is believed to be about one part in 2000. The value of the dielectric constant of pure dioxane at 25° is in excellent agreement with the value, 2.213, reported by Conner, Clarke and Smyth.[7] The value for pure dioxane differs from that given by Åkerlöf and Short[2] by one part in 20. In the low range our values for the mixtures differ from those of Åkerlöf and Short[2] by as much as 12%. The percentage difference decreases with increasing dielectric constant.

Acknowledgment.—This work was in part a joint undertaking of the Department of Chemistry of West Virginia University and the Office of Ordnance Research. Appreciation is expressed to James B. Hickman for assistance in determination and analysis of the time–temperature cooling curves and to H. N. Critchfield for assistance in construction of the cell.

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[2] G. Åkerlöf and O. A. Short, THIS JOURNAL, **58**, 1241 (1936).

[3] K. Hess and H. Frahm, *Ber.*, **71B**, 2627 (1938).

[4] B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

[5] D. B. Sinclair, *Proc. Inst. Radio Engrs.*, **28**, 310 (1940).

[6] J. D. Ferry and J. L. Oncley, THIS JOURNAL, **63**, 272 (1941).

[7] W. P. Conner, R. P. Clarke and C. P. Smyth, *ibid.*, **64**, 1379 (1942).

[8] P. S. Albright, *ibid.*, **59**, 2098 (1937).

[9] P. S. Albright and L. J. Gosting, *ibid.*, **68**, 1061 (1946).

The Introduction of Isotopic Hydrogen into Purine Ring Systems by Catalytic Exchange[1]

BY MAXWELL LEIGH EIDINOFF AND JOSEPH E. KNOLL

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Tritium or deuterium can be introduced by isotopic exchange in the presence of reduced platinum catalyst into atomic positions in adenine and guanine that do not exchange isotopic hydrogen under the usual conditions of aqueous acid or alkali. The presence of such non-labile atomic positions has been demonstrated in this Laboratory for adenine, guanine, cytosine and uracil using a biosynthetic procedure.[2] The catalytic exchange procedure described below makes it possible to prepare labeled products of tritium or deuterium content equal in order of magnitude to that of the aqueous medium used. The isotopic content of the products, relative to that of the reaction media,

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[1] This work was supported in part by grants-in-aid from the Atomic Energy Commission #AT(30-1)-910.

[2] M. L. Eidinoff, H. C. Reilly, J. E. Knoll and D. H. Marrian, *J. Biol. Chem.*, **199**, 511 (1952).