soda. Aniline hydrochloride and aniline hydriodide were recrystallized four times from water and dried in the dark over concentrated sulfuric acid.

The Cell.—The electrodes consisted of two platinized platinum plates sealed into glass with mercury contacts. The plates were each 2 cm. by 1 cm. fixed 0.5 cm. apart and installed in a wide-necked flask of 200 cc. capacity. The cell was placed in a jar surrounded by solid caustic soda and the jar immersed in an oil-bath thermostatically controlled at 15°.

The Circuit.—The usual Wheatstone bridge circuit was used, balance being obtained along a bridge wire 1 meter long and graduated in millimeters. The current was obtained from a small induction coil and the resistance box used was non-inductively wound and correct to 0.02%.

The best minimum obtained in telephone earphones was given by using a one-valve amplifier fitted with rheostat to control filament current, and a variable condenser to control the inflow current. Compensating condensers were found to be unnecessary for balancing the capacity of the cell.

Summary

The conductivity data for dilute solutions of aniline hydrochloride, aniline hydriodide and α-naphthylamine hydriodide in aniline afford graphs which support the assumption of solvate formation. This view-point is in accord with the actual chemistry of phenylation by means of acids or by iodine.

A Chemical Separation of the Isotopes of Hydrogen

BY L. H. REYERSON, O. JOHNSON AND C. BEMMELS

Earlier work[1,2] has indicated the possibility of effecting a partial separation of the hydrogen isotopes in heavy water solutions by reaction with calcium carbide. The results of a more detailed study of this reaction are presented at this time. Initial results showed that great care must be exercised in keeping out all traces of ordinary water.

An all glass system was constructed as shown diagrammatically in Fig. 1. A metal forked jet type of burner gave the best results. A flat intense flame was obtained giving clean combustion without any traces of carbon. A 25-ml. Pyrex distilling flask (A) with its side-tube bent at an angle of 90° served as the generator. The heavy water was allowed to drip from the short buret into a long tube leading into the carbide. The end of this tube was flared with a wad of glass wool wired over the opening. This permitted the water to seep into the carbide giving an even flow of acetylene. The side-arm of the generator was connected to the top of the buret to equalize the pressure on both ends of the buret and permit an easier control over the amount of water flowing into the carbide.

Approximately 12 g. of carbide and 5 ml. of water were used for each run. A slight excess of water was used to ensure complete decomposition of the carbide and reduce the amount of impurities in the water recovered by heating the calcium hydroxide residue in the generator. The carbide used was dried in a muffle furnace at 850° for two hours and stored in a vacuum desiccator over phosphorus pentoxide. After generation the acetylene was passed through a calcium carbide drier and then through a tube immersed in an alcohol–carbon dioxide mixture. From this tube the gas flowed through a tube to the burner in the combustion chamber (C). Thoroughly dried air was admitted to the combustion chamber. The acetylene was ignited by a spark, from a high tension coil, produced between the wire (D) and the burner jet. The air used was purified and dried as follows. It was first passed
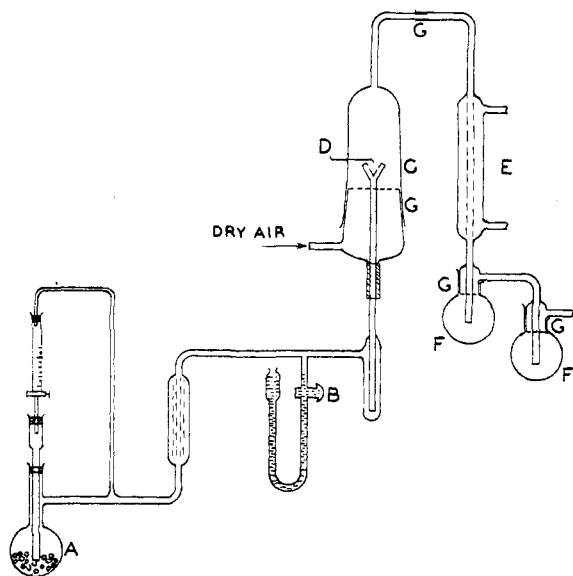

Fig. 1.—A, acetylene generator; B, pressure release valve; C, combustion chamber; D, sparkwire; E, water condenser; F, collecting bulbs; G, ground glass joints.

(1) Reyerson and Gillespie, THIS JOURNAL, **58**, 282 (1936).

(2) Hughes, Ingold and Wilson, *J. Chem. Soc.*, 493 (1934).

TABLE I

These calculations were made assuming the mole fraction of heavy water to be a linear function of the specific gravity.[3] The formula used was: $\Delta s = 0.1074 N_{D_2O}$ where $\Delta s = d^{25}_{25} - 1$. The value $d^{25}_{25} = 1.1074^4$ for pure D_2O was used.

		Original water	Water from combustion	Water from Ca(OH)₂
Run A	d^{25}_{25}	1.0515	1.0438	1.0478
	n_{D_2O}	0.4795	0.4078	0.4451
	% D₂O	50.58	43.35	47.13
Run B	d^{25}_{25}	1.0507	1.0464	1.0486
	n_{D_2O}	0.4721	0.4320	0.4525
	% D₂O	49.84	45.80	47.87
Run C	d^{25}_{25}	1.0222	1.0202	1.0202
	n_{D_2O}	0.2067	0.1881	0.1881
	% D₂O	22.45	20.47	20.47
Run D	d^{25}_{25}	1.0000	0.9998	
Run E	d^{25}_{25}	1.0511	1.0407	1.0545
	n_{D_2O}	0.4758	0.3790	0.5075
	% D₂O	50.21	40.41	53.38
Run F	d^{25}_{25}	1.0000	1.0001	0.9999
Run G	d^{25}_{25}	1.0469	1.0409	1.0495
	n_{D_2O}	0.4367	0.3808	0.4609
	% D₂O	46.28	40.59	48.72
Run H	d^{25}_{25}	1.0462	1.0407	1.0468
	n_{D_2O}	0.4302	0.4790	0.4358
	% D₂O	45.62	40.41	46.19
Run I	d^{25}_{25}	1.0242	1.0220	1.0254
	n_{D_2O}	0.2253	0.2048	0.2365
	% D₂O	24.24	22.25	25.60
Run J	d^{25}_{25}	1.0844	1.0827	1.0855
	n_{D_2O}	0.7858	0.7700	0.7961
	% D₂O	80.30	78.81	81.27

(3) Lewis and Luten, THIS JOURNAL, **55**, 5061 (1933).
(4) Tronstad, *et al.*, *Nature*, **136**, 515 (1935).

over wire form copper oxide heated to a dull red heat in two tubes 15 × 1 cm. Organic material was thereby oxidized. The air was then cooled and the bulk of the water vapor removed by passing through two bulbs immersed in cold brine. The last traces of water vapor were removed by passing successively through five bulbs immersed in an alcohol–solid carbon dioxide mixture, then through three bulbs immersed in liquid air, and finally through a tube filled to a height of 7 cm. with phosphorus pentoxide. A continuous all-glass system was used beginning with the five tubes immersed in the alcohol–carbon dioxide mixture. All ground glass joints shown were used without lubrication. Hence pressures slightly above atmospheric were maintained in the system.

The products of combustion were passed through the condenser (E) and the water was trapped in the bulbs (F) immersed in an alcohol–carbon dioxide mixture. The water so obtained was triply distilled in an enclosed all-glass system and its density determined by means of a pycnometer of one-half ml. capacity.

The results are given in Table I. Runs A, B and C, were made before the system was assembled in its final form. They indicate the care that is needed to remove the last traces of moisture. Runs D and F were made with redistilled conductivity water to check the possible effect of other impurities. If such impurities exist they do not affect the density beyond the fourth decimal place. The results of runs E, G, H, I, and J show definitely that a separation of the isotopes has been effected.

Summary

A partial separation of the isotopes of hydrogen has been achieved by the action of water, containing various percentages of deuterium, on calcium carbide.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

cis–trans-Isomerization with Boron Fluoride

BY CHARLES C. PRICE AND MORRIS MEISTER

In a previous communication[1] it was suggested that the catalytic effect of boron fluoride or aluminum chloride in causing olefins to condense with aromatic compounds or to polymerize involved activation of the carbon–carbon double bond by association with the catalyst.
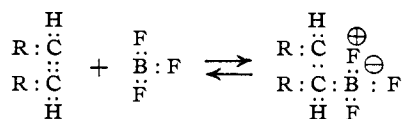
A consequence of such association should be establishment of equilibrium between *cis–trans* isomers. This has now been confirmed experimentally for the case of the isomeric stilbenes.
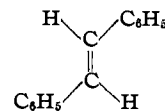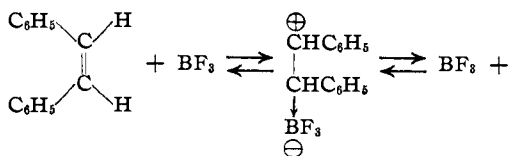
The conversion may be accomplished in the course of a day or so at room temperature using the boron fluoride–ether complex or in fifteen

(1) Price and Ciskowski, THIS JOURNAL, **60**, 2499 (1938).