crystalline material which separated was collected and dried to give 40 g. of crude material. This was recrystallized from ether to give 10 g. of white needles melting at 116–116.5° which gave no depression with an authentic sample of neopentylmercuric chloride.

The mother liquors were concentrated carefully and the semisolid residue distilled in vacuum twice through a side-arm flask. The dineopentylmercury boiled at 67–69° at 3 mm. and melted at 31–33°. The yield was 23.5 g., about 28.5% on the basis of the mercuric chloride used. An iodine titration indicated an impurity of approximately 7% of neopentylmercuric chloride.

Summary

1. Neopentyl bromide and neopentyl iodide react only slightly with ditolylmercury even under drastic conditions.

2. No evidence of a lengthening of the carbon chain was found.

3. Further evidence is given for the unusual inactivity of the neopentyl halides.

4. Dineopentylmercury has been prepared.

STATE COLLEGE, PENNA.   RECEIVED APRIL 3, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TECHNICAL COLLEGE]

The Electrolytic Condition of Aniline Hydrochloride, Aniline Hydriodide and α-Naphthylamine Hydriodide in Aniline Solution
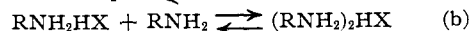
BY HERBERT H. HODGSON AND EWART MARSDEN

In connection with a study of the mechanism of the phenylation of α-naphthylamine,[1] it appeared reasonable to expect that the conductivities of the various aniline solutions employed

Fig. 1.—A, aniline hydriodide; B, α-naphthylamine hydriodide; C, aniline hydrochloride.

would throw light on the condition of the solute prior to phenylation. Accordingly, the conductivities of aniline hydrochloride, aniline hydriodide and α-naphthylamine hydriodide, dissolved in aniline, have been measured and plotted with

(1) Hodgson and Marsden, J. Chem. Soc., 1365 (1939); 1181 (1939).

respect to concentration. The curves thereby obtained all exhibit the same general form, and consequently the deductions made therefrom should be valid for each solution. Previous work by Pound[2] on the electrolytic behavior of solutions of aniline hydrochloride in aniline has been generally confirmed.

The chemical behavior of iodine during the catalytic phenylation process[1] would appear to indicate that a double compound is first formed between two molecules of aniline and one molecule of hydriodic acid in the case of diphenylamine formation, and a similar compound between one molecule each of α-naphthylamine and aniline for that of phenyl-α-naphthylamine, with subsequent expulsion of ammonium iodide and regeneration of hydriodic acid to continue the process. Such a type of double compound actually has been isolated by Mandel[3] from a solution of aniline hydrochloride in aniline.

If the assumption of double compound formation be valid, the various equilibria in solution would then be

$$RNH_2HX \rightleftharpoons RNH_3^+ + X^-   \text{(a)}$$
$$RNH_2HX + RNH_2 \rightleftharpoons (RNH_2)_2HX   \text{(b)}$$
$$(RNH_2)_2HX \rightleftharpoons (RNH_2)_2H^+ + X^-   \text{(c)}$$

From the graph of the conductivities plotted with respect to concentration (Fig. 1), it is found that over most of the concentration ranges measured, the conductivity decreases linearly with dilution. Since the conductivity of the active (ionizable) part of the total concentration of the
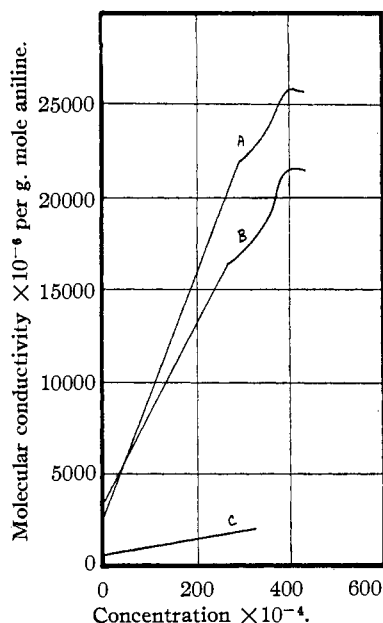
(2) Pound, J. Phys. Chem., **31**, 547 (1927).

(3) Mandel, Ber., **53**, 2216 (1920).

solute decreases, there is a concurrent increase in the formation of an almost un-ionizable solvated

TABLE I
CONDUCTIVITIES IN ANILINE SOLUTION AT 15°

The cell constant was 0.1101 reciprocal ohms (mean of 5 readings) and was redetermined for each substance measured. The concentrations are expressed per gram mole of aniline $\times 10^{-4}$, and the molecular conductivities per gram mole of aniline $\times 10^{-6}$.

Aniline hydrochloride Concn.	Cond.	Aniline hydriodide Concn.	Cond.	α-Naphthylamine hydriodide Concn.	Cond.
408.0	2565	625.0	24100	491.1	21980
380.0	2385	569.0	23520	470.2	22130
354.2	2300	524.0	23350	456.0	22270
331.8	2195	486.0	24160	441.1	22390
311.7	2070	453.0	24900	424.4	22560
294.0	2000	423.5	25900	397.0	22120
279.2	1922	397.8	25780	372.9	21090
263.5	1825	375.2	25280	351.5	20510
250.5	1770	355.0	25220	348.1	20450
238.7	1711	337.5	24550	315.2	19520
228.0	1664	328.0	23880	300.0	19450
219.0	1632	305.5	22380	286.1	19150
209.7	1562	292.0	22200	267.0	18840
201.7	1524	280.0	21840	260.2	18640
192.8	1462	268.7	21560	250.9	17700
180.2	1404	258.3	20680	241.1	17410
169.1	1344	248.5	20420	231.9	16750
159.3	1305	243.7	20270	216.3	16010
150.6	1242	231.2	19400	202.3	15320
142.8	1218	223.5	19040	190.8	14620
135.5	1193	216.0	17280	180.2	14200
129.0	1161	209.2	16900	170.7	13400
123.2	1138	202.8	16580	162.2	13220
118.0	1125	196.6	16170	154.5	12610
113.2	1100	191.2	15780	147.4	12300
108.6	1084	175.2	14480	141.0	11880
97.8	1032	168.4	14170	135.2	11640
90.2	1018	162.0	13810	129.7	11190
84.4	992	156.3	13280	117.6	10390
79.4	985	150.7	12970	109.6	10070
74.8	978	141.9	12000	102.7	9594
70.8	970	134.1	11460	96.54	9245
64.2	945	127.2	11160	91.09	8888
58.4	940	121.0	10910	86.26	8756
53.6	923	115.4	10420	81.89	8292
46.2	900	104.3	9622	77.96	8210
40.4	890	94.55	9000	74.39	7830
35.9	875	86.75	8690	71.12	7541
		80.30	8020	68.13	7297
		74.6	7915	60.39	6739
		69.7	7760	58.35	6343
		65.35	6890	56.15	6280
		61.50	6860	50.60	6141
		58.13	6460	47.42	5833
		56.18	5985	44.63	5766
		52.25	5915	42.16	5642
		49.80	5945	37.94	5110
		47.60	5700	36.13	5089
		45.18	5048	34.48	5139
		39.35	4465	33.83	4953
		36.22	4550	31.54	4677

compound similar to that depicted in (b) above.

The curves for solutions of aniline and α-naphthylamine hydriodides in aniline exhibit four distinct parts, viz.: (1) an initial very slight curvilinear portion where the conductivity increases with dilution; (2) a long straight line indicating a positive linear relationship between conductivity and concentration; (3) a curvilinear portion which attains a maximum and whose descending section for some distance exhibits a linear relationship between conductivity and square root of the concentration (Fig. 2); (4) an irregular portion in which behavior appears to be anomalous, and where the various effects described by Debye and Hückel come into prominence.
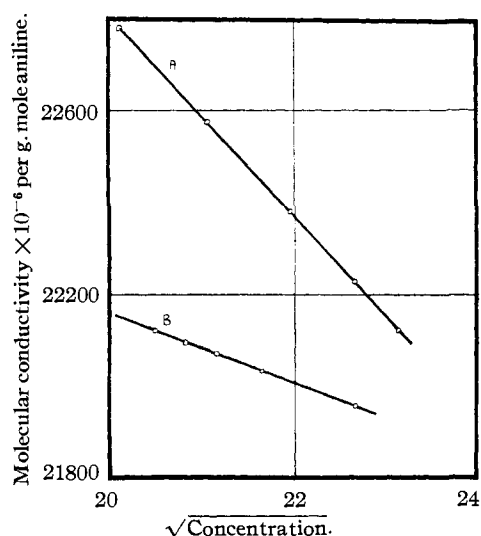

Fig. 2.—A, aniline hydriodide; B, α-naphthylamine hydriodide.

Solubility limitations have prevented the curve for aniline hydrochloride being prolonged beyond $C = 408 \times 10^{-4}$ (see table for mode of expression) where the linear relationship still holds, but much more complete data have been obtained for aniline and α-naphthylamine hydriodides.

Since the experimental data support the theoretical deduction above, it is reasonable to conclude that the state of the solute during the catalytic phenylation process by means of iodine is predominantly in a solvated form. The existence of this complex, which is clearly indicated by the actual chemistry of the process, thus receives support from the conductivity data now recorded.

Experimental

Materials.—Pure aniline was redistilled four times and kept *in vacuo* in the dark over caustic

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
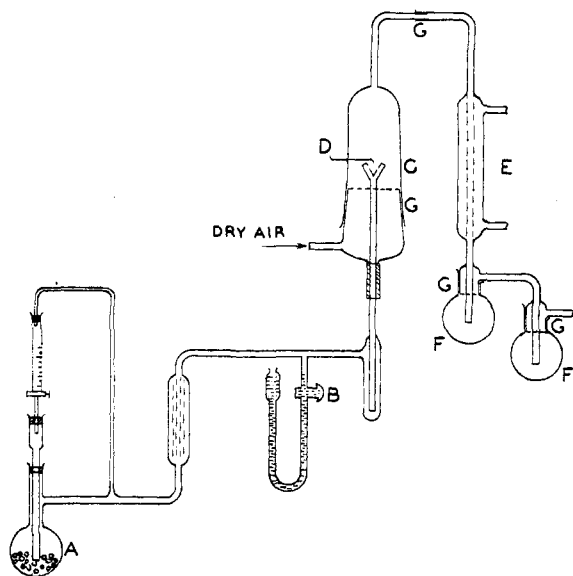

Fig. 1.—A, acetylene generator; B, pressure release valve; C, combustion chamber; D, sparkwire; E, water condenser; F, collecting bulbs; G, ground glass joints.

(1) Reyerson and Gillespie, THIS JOURNAL, **58**, 282 (1936).
(2) Hughes, Ingold and Wilson, J. Chem. Soc., 493 (1934).