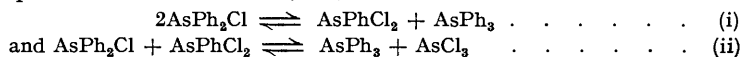


### 85. *The Action of Heat on Diphenylchloroarsine.*

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The disproportionation of diphenylchloroarsine on heating has been investigated and the existence of an equilibrium at various temperatures above 200° has been established. No disproportionation takes place below 200° and diphenylchloroarsine can be distilled unchanged below that temperature. Evidence is brought forward to show that two equilibria are operating simultaneously at temperatures from 215° to 325°, *viz.*,



DIPHENYLCHLOROARSINE is known to undergo disproportionation on heating, and, since distillation is a stage in some methods which would otherwise be more convenient on a manufacturing scale, the conditions under which disproportionation takes place have been investigated.

The main reaction which occurs when diphenylchloroarsine is heated is (i); but since Pope and Turner (*J.*, 1920, **117**, 1447) obtained 80% yields of diphenylchloroarsine by heating phenyldichloroarsine with triphenylarsine at 300° it appears probable that the reaction is reversible and that an equilibrium could be set up. Hence the composition of the equilibrium mixture and the length of time required for the establishment of equilibrium at various temperatures has been investigated by heating quantities of about 1 g. of diphenylchloroarsine and of an equimolecular mixture of phenyldichloroarsine and triphenylarsine in a pair of similar sealed tubes in an electrically heated air-bath for varying times at known temperatures. The composition of the product was then determined by estimating the quantity of triphenylarsine present by precipitation with mercuric chloride, which La Coste and Michaelis (*Annalen*, 1880, **201**, 242) used as a qualitative reagent for the separation of triphenylarsine from diphenylchloroarsine. It has now been shown that this reagent can be used quantitatively and the necessary technique devised. The possibility of using mercuric iodide similarly was investigated, but this reagent was found to be unsuitable. The process was repeated using successively longer times of heating until both tubes were found to contain the same amount of triphenylarsine per g. of diphenylchloroarsine (or of the equimolecular mixture of phenyldichloroarsine and triphenylarsine) taken. It could then be taken for certain that equilibrium had been established. This was done at 200°, 230°, 250°, 275°, 290°, 300°, and 315°. At the lower temperatures equilibrium was only slowly established; in fact, below 220° the reaction was so slow that it was impracticable to heat long enough for an equilibrium to be reached: several days' heating would probably have been needed. At 300°, however, equilibrium was much more rapidly established, no further change being observed after one hour in the case of

diphenylchloroarsine. But the triphenylarsine-phenyldichloroarsine mixture still required about three hours for the attainment of equilibrium, even at 300°.

## EXPERIMENTAL.

*Mercuric Chloride Solution as a Quantitative Reagent for Triphenylarsine* (cf. La Coste and Michaëlis, *loc. cit.*).—After many experiments the following procedure was found satisfactory for the estimation of triphenylarsine. The mixture of phenyldichloroarsine, diphenylchloroarsine, and triphenylarsine, obtained by heating diphenylchloroarsine, the triphenylarsine content of which it is desired to determine, is dissolved in 25 c.c. of pure alcohol and treated with 20 c.c. of an alcoholic mercuric chloride solution (10 g. in 200 c.c. of alcohol). The solution is stirred and left for about 15 minutes (if left for longer than this, a precipitate is formed, possibly of  $\text{AsPh}_3\text{O}\cdot\text{OHg}$ , which might be confused with  $\text{AsPh}_3\text{HgCl}_2$ ). It is then filtered through a weighed Gooch crucible, washed with 50 c.c. of alcohol, dried at 100° in a steam-oven, and weighed. The following results of test estimations indicate the degree of accuracy attainable.

Mixture.			Triphenylarsine found by above process (g.).
Phenyldichloro- arsine (g.).	Diphenylchloro- arsine (g.).	Triphenyl- arsine (g.).	
—	0.5632	0.3014	0.2968
—	0.7113	0.1418	0.1397
0.2493	0.5141	0.3101	0.2991
0.3027	0.6002	0.3279	0.3198

*Action of Heat on Diphenylchloroarsine.*—Vertical, cylindrical, electrically-heated air-baths (about 30 cm. high and 8 cm. in diameter) were used, the temperature of which could be varied between 200° and 320°. Each air-bath was fitted with a lid carrying a thermometer and four vertical test-tubes, in which sealed up tubes containing diphenylchloroarsine (or a mixture of phenyldichloroarsine and triphenylarsine) could be placed. Any one or all of the four sealed tubes could be removed after heating, and cooled rapidly to room temperature, thus freezing the equilibrium. About 1 g. of diphenylchloroarsine was weighed into a glass tube sealed at one end, which was then sealed. The equimolecular mixture of phenyldichloroarsine and triphenylarsine was weighed out into another similar tube, which was also sealed. A solution of exactly equimolecular amounts of phenyldichloroarsine and triphenylarsine in ether was prepared, containing 12.2360 g. of triphenylarsine and 8.9120 g. of phenyldichloroarsine, in 100 c.c. Portions of 5 c.c. were transferred to a tube sealed at one end. This was then gently heated electrically to remove ether, leaving a mixture of exactly equimolecular amounts of phenyldichloroarsine and triphenylarsine. The temperature of the vessel was never allowed to rise above 100°, at which temperature no reaction between the phenyldichloroarsine and triphenylarsine takes place. The tube was then sealed and heated in the air-bath. Four tubes prepared in this way were simultaneously heated to 300° for 1 hour; the contents on analysis gave respectively the following amounts of triphenylarsine per g. of mixture: 0.2091, 0.2090, 0.2093, 0.2095. Since these values are sensibly the same as those of 0.2089 and 0.2090 obtained in another experiment, in which the phenyldichloroarsine and triphenylarsine were weighed out into tubes, it is seen that the possible presence of traces of ether in triphenylarsine-phenyldichloroarsine mixtures obtained by the above process has no effect on the reaction taking place.

The following table gives the results obtained for temperatures between 200° and 320°.

<i>t.</i>	<i>a.</i>	<i>b.</i>	<i>t.</i>	<i>a.</i>	<i>b.</i>	<i>t.</i>	<i>a.</i>	<i>b.</i>
Temperature, 200°.			Temperature, 230° ( <i>contd.</i> ).			Temperature, 290°.		
1	0.5786	0.0007	4	0.2783	0.0953	1	0.3026	0.1509
2	0.5785	0.0008	5	0.2249	0.1092	2	0.2437	0.1637
3	0.5780	0.0010	6	0.1853	0.1237	3	0.2095	0.1731
			7	0.1589	0.1347	4	0.1833	0.1802
			8	0.1390	0.1392	5	0.1809	0.1806
Temperature, 215°.			Temperature, 250°.			Temperature, 300°.		
1	0.5786	0.0030	1	0.4860	0.1179	1	—	0.1356
3	0.5701	0.0095	2	0.3791	0.1280	2	0.2091	0.1519
5	0.5602	0.0319	3	0.2690	0.1362	3	0.1735	0.1513
6	0.5509	0.0457	4	0.1437	0.1422	4	0.1513	0.1510
7	0.5405	0.0683	5	0.1420	0.1420			
8	0.5297	0.0816				Temperature, 320°.		
9	0.5183	0.1073				1	—	0.1253
Temperature, 230°.			Temperature, 275°.			1	—	0.1709
1	0.4890	0.0510	1	0.4910	0.1372	2	0.2001	0.1637
2	0.4087	0.0673	2	0.3400	0.1498	3	0.1647	0.1375
3	0.3326	0.0801	3	0.2398	0.1537	4	0.1339	0.1158
			4	0.1679	0.1670	5	0.1166	0.1009
			5	0.1670	0.1671		0.1010	0.0998

*t* = Time of heating (hours).

*a* = Weight (g.) of triphenylarsine left from 1 g. of phenyldichloroarsine-triphenylarsine.

*b* = Weight (g.) of triphenylarsine formed from 1 g. of diphenylchloroarsine.

Since practically no triphenylarsine was produced on heating diphenylchloroarsine at 200°, it seemed likely that distillation under reduced pressure, at or below this temperature, might be possible without any decomposition taking place. This was found to be so. Diphenylchloroarsine was distilled (b. p. 193°/20 mm.) and a portion of the distillate was dissolved in alcohol and treated with mercuric chloride solution. No precipitate was observed, indicating that no decomposition with formation of triphenylarsine had occurred under these conditions. As a result of this work it may be concluded that :

(1) No marked disproportionation of diphenylchloroarsine takes place at, or below, 200°. Hence diphenylchloroarsine can be distilled without decomposition below this temperature.

(2) Disproportionation is only very slow below 215°.

(3) A definite equilibrium exists which, if represented by equation (i), moves to the right as the temperature is raised to about 285° (after which it moves to the left again). This might be due to a change in the sign of the heat of reaction, but this is improbable. It is more probably due to the reaction being more complex than was at first thought, the relative speeds of the different reactions involved changing with temperature. This conclusion is also supported by the fact that at temperatures up to 300° the amount of triphenylarsine formed on heating diphenylchloroarsine increases with time until equilibrium is reached. But at 320° the amount of triphenylarsine formed by heating diphenylchloroarsine increases rapidly during the first  $\frac{3}{4}$  hour and then *falls* to the equilibrium value during the next 3 hours.

Since diphenylchloroarsine was obtained by Michaelis (*Annalen*, 1902, **320**, 271 ; **321**, 141) by heating triphenylarsine with arsenic trichloride, a probable further reaction is  $\text{AsPh}_3\text{Cl} + \text{AsPhCl}_2 = \text{AsPh}_3 + \text{AsCl}_3$ . If this be so, it is likely that arsenic trichloride would be present in the equilibrium mixture, and a qualitative test for it was therefore made. Diphenylchloroarsine was heated for two hours at 315°, allowed to cool, and treated with water to convert any arsenic trichloride present to arsenious acid, the other arsenicals forming an insoluble residue. The liquid was acidified with hydrochloric acid and treated with hydrogen sulphide. A slight yellow precipitate was observed. The neutral solution similarly gave a brown precipitate with silver nitrate. Hence a small amount of arsenic trichloride is present in the reaction mixture. It would seem likely therefore that when diphenylchloroarsine is heated reactions (i) and (ii) take place simultaneously.

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