701. *A Kinetic Investigation of the Decomposition of Phenyldichloroarsine in the Liquid State.*

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At temperatures above 500° K., liquid phenyldichloroarsine is converted at a measurable rate into diphenylmonochloroarsine and arsenious chloride and, in part, into triphenylarsine and arsenious chloride. These reactions have been investigated kinetically. The analysis of the former reaction shows it to be consistent with a reversible bimolecular mechanism, for which the apparent energy of activation of the forward step is 35 ± 2 kcals.

VERY few chemical reactions have been investigated in the liquid phase. The present paper gives an account of the conversion of phenyldichloroarsine in the liquid phase into diphenylmonochloroarsine and arsenious chloride, and in part, into triphenylarsine. The two decompositions are reversible and, although a rigorous kinetic treatment is not possible, the energies of activation and the absolute rates have been determined.

DISPROPORTIONATION EQUILIBRIA.

At temperatures above 200° c., the following equilibria become established for phenyldichloroarsine and diphenylchloroarsine :

$$2PhAsCl_2 \xrightleftharpoons[k_2]{k_1} Ph_2AsCl + AsCl_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

$$3PhAsCl_2 \xrightleftharpoons[k_4]{k_3} Ph_3As + 2AsCl_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

$$2Ph_2AsCl \rightleftharpoons Ph_3As + PhAsCl_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

As a preliminary to the study of the mechanism and kinetics of these and other reactions involving organic derivatives of arsine, it was necessary to know the equilibrium states attained as indicated by the expressions :

$$K_1 = k_1/k_2 = n_2^\epsilon n_0^\epsilon/(n_1^\epsilon)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$K_2 = k_3/k_4 = n_3^\epsilon(n_0^\epsilon)^2/(n_1^\epsilon)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_1, k_2, k_3, and k_4 are velocity constants of the reactions indicated, and n_0, n_1, n_2, and n_3 denote, respectively, the molar fractions of arsenic trichloride, phenyldichloroarsine, diphenylchloroarsine, and triphenylarsine in the liquid phase. The superscrpt $^\epsilon$ signifies equilibrium values.

The third constant

$$K_3 = n_1^\epsilon n_3^\epsilon/(n_2^\epsilon)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is given in terms of the other two by

$$K_3 = K_2/K_1^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence K_1 and K_2 give all the relevant information irrespective of the mechanisms implied.

Experimental.—Purification of phenyldichloroarsine. The crude product was distilled under 1-mm. pressure to give a colourless liquid, the middle fractions of which gave, on analysis, phenyldichloroarsine 97·3, diphenylchloroarsine 1·6, arsenic trichloride 0·7, and residue (including triphenylarsine) 0·4%. As these compounds are all present in the equilibrium system after disproportionation, no further purification was attempted for this part of the work.

Apparatus and procedure. Samples (10 c.c.) of phenyldichloroarsine were sealed at atmospheric pressure in Pyrex glass tubes of 40-ml. capacity, these volumes being adhered to as accurately as possible. Heating was carried out in an electrically heated oil-bath, thermostatically controlled to ±0·2°. Tubes were immersed in the bath for varying periods and on withdrawal chilled in water at 20° and analysed. No permanent pressure developed in the tubes.

Method of analysis. Hydrolysable chlorine (x) was determined by means of excess of standard alkali. Titration with iodine, first in acid, and then in alkaline, solution gave the organic arsenic (y) and the inorganic arsenic (taken to be arsenic trichloride) (z). Diphenylchloroarsine (d) was determined directly by oxidation to diphenylarsonic acid and extraction with chloroform. No satisfactory method of determining triphenylarsine was available but, at the temperatures employed, little of this substance was formed. Phenyldichloroarsine is given by ($x - d - z$). In a sample containing phenylarsenious oxide the same procedure gives the phenylarsenious oxide content ($y - x - z$). In the analysis of solid samples, inorganic arsenic was taken to be arsenious oxide.

Results.—The results quoted below, which are the averages of many concordant experiments, have been corrected for the 30-ml. vapour space in each sample tube, which, it has been assumed, contained only arsenic trichloride at the partial pressure indicated by its molar fraction in the liquid on application of Raoult's law. The volatilities of the phenylchloroarsines are so much lower that their presence in the vapour phase before chilling can be neglected. This correction did not alter any equilibrium constant by more than 5%. In Table I are shown the equilibrium concentrations as molar fractions, and the equilibrium constants at four different temperatures. The values at 273° c. refer to the disproportionation of originally pure diphenylchloroarsine. In the absence of an accurate method of determining triphenylarsine directly, the values of K_2 must be regarded as less reliable than those of K_1.

TABLE I.

Temp.	n_0^ϵ.	n_1^ϵ.	n_2^ϵ.	n_3^ϵ.	10^2K_1.	10^3K_2.	10^2K_3.
220°	0·1543	0·6676	0·1346	0·0139	4·52	1·07	—
240	0·1676	0·6397	0·1403	0·0192	5·74	2·06	—
260	0·1700	0·6285	0·1509	0·0162	6·50	1·88	—
273	—	0·1791	0·6421	0·1071	—	—	4·68

Results for the equilibrium constants are given again in Table II. The data marked * are those obtained concurrently by A. G. Evans, Todd, and Warhurst, which were communicated to us privately through the Ministry of Supply and have since been published (Evans and Warhurst, *Trans. Faraday Soc.*, 1948, **44**, 189). The most satisfactory correlation of all the results leads to the equations :

TABLE II.

Temp.	10^2K_1. Obs.	10^2K_1. Eqn. (5).	10^3K_2. Obs.	10^3K_2. Eqn. (7).	10^2K_3. Obs.	10^2K_3. Eqn. (6).
220°	4·52	4·43	1·07	3·3	—	—
240	5·74	5·37	2·06	7·4	—	—
252	—	—	—	—	5·9 *	3·20
256	5·7 *	6·21	—	—	—	—
260	6·5	6·41	1·88	1·55	—	—
273	—	—	—	—	4·7	4·80
304	7·0 *	9·08	—	—	8·0 *	8·07
338	—	—	—	—	13·0 *	13·4

$$\ln K_1 = 1{\cdot}784 - 4800/\boldsymbol{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\ln K_3 = 6{\cdot}639 - 10{,}500/\boldsymbol{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It follows that

$$\ln K_2 = 10{\cdot}207 - 20{,}100/\boldsymbol{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In Table II the experimental results are compared with those given by these equations. The changes in heat content and standard entropy are :

$$\Delta H_1 = 4{,}800 \text{ cals.} \qquad \Delta S_1{}^\circ = 3{\cdot}6 \text{ cals./degree.}$$

$$\Delta H_2 = 20{,}100 \text{ cals.} \qquad \Delta S_2{}^\circ = 20{\cdot}3 \text{ cals./degree.}$$

$$\Delta H_3 = 10{,}500 \text{ cals.} \qquad \Delta S_3{}^\circ = 13{\cdot}2 \text{ cals./degree.}$$

These heats of reaction are significantly different from those of Evans and Warhurst (*loc. cit.*). This is probably to be attributed to the facts that their calculations are based on two data only in each case, and that our results were obtained at lower temperatures where side-decomposition is inconsiderable.

Evans and Warhurst (*loc. cit.*) obtain the heat-capacity changes $\Delta H_1 = +2{\cdot}6$ and $\Delta H_3 = +3{\cdot}8$ kcals. and consider these small heat effects to be explicable if the strengths of all As–Cl bonds are equal, and the strengths of all As–C bonds are also equal for all the four molecular species concerned. On the other hand, the relatively large values found by us indicate considerable differences, especially between the strengths of the three types of Ph–As linkages.

DISPROPORTIONATION VELOCITIES.

There is no reason against application of the kinetic formulæ used for the rates of reaction in dilute solutions and in gases, with appropriate modifications, to the systems considered here.

The experimental method was that described above, the sample tubes now being chilled for analysis at precise intervals after their immersion in the oil bath.

The changes in fractional composition of purified phenyldichloroarsine with time, at 220°, 240°, and 260° c., are shown in Table III. During the later stages of a run the individual points tend to show some scatter.

Determination of the Course of the Reaction.—A stoicheiometrical check can first be made to determine whether the reversible reactions represented by equations (1) and (ii) are sufficient to explain these result. With the notation given above, these equations require the fulfilment at any instant of certain identities. From the constancy of hydrolysable chlorine and of phenyl radicals respectively,

$$n_1 + 0{\cdot}5n_2 + 1{\cdot}5n_0 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and

$$n_1 + 2n_2 + 3n_3 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Hence,

$$n_3 = 0{\cdot}5(n_0 - n_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equation 8, applied to results obtained at 220° and 260°, gives the figures shown in Table IV,

TABLE III.

The rate of disproportionation of phenyldichloroarsine.

Time (hours).	At 220°.			At 240°.			At 260°.		
	n_1.	n_2.	n_0.	n_1.	n_2.	n_0.	n_1.	n_2.	n_0.
0	0·980	0·009	0·007	0·974	0·013	0·009	0·974	0·013	0·008
0·5	—	—	—	0·947	0·020	0·015	0·914	0·013	0·049
1·0	—	—	—	0·936	0·022	0·026	—	—	—
1·5	—	—	—	0·921	—	—	0·793	0·067	0·100
1·9	—	—	—	0·898	—	0·038	—	—	—
3·0	—	—	—	0·876	0·028	0·054	0·700	0·110	0·148
4·0	—	—	—	—	—	—	0·655	0·128	0·180
5·0	0·932	0·028	0·033	0·811	0·072	0·094	—	—	—
5·25	—	—	—	—	—	—	0·606	0·147	0·178
6·0	—	—	—	0·760	0·101	0·106	0·642	0·138	0·182
8·0	—	—	—	0·626	0·152	0·154	—	—	—
10	0·889	0·044	0·056	0·700	0·120	0·154	—	—	—
15	0·843	0·062	0·080	—	—	—	—	—	—
20	0·800	0·080	0·102	—	—	—	—	—	—
25	0·767	0·097	0·119	—	—	—	—	—	—
30	0·740	0·114	0·135	—	—	—	—	—	—
35	0·718	0·126	0·147	—	—	—	—	—	—
40	0·700	0·133	0·155	—	—	—	—	—	—
45	0·687	0·135	0·159	—	—	—	—	—	—

TABLE IV.

The course of the disproportionation of phenyldichloroarsine.

Temp.	Time.	$0·5n_2$.	$1·5n_0$.	$(0·5n_2 + 1·5n_0)$.	$(1 - n_1.)$	n_2/n_3.
220°	5	0·014	0·049	0·062	0·068	11·6
	10	0·022	0·084	0·106	0·110	7·6
	15	0·031	0·120	0·152	0·157	4·6
	20	0·040	0·152	0·192	0·218	7·2
	25	0·049	0·179	0·227	0·251	9·2
	30	0·057	0·202	0·259	0·260	10·7
	35	0·063	0·220	0·283	0·282	11·8
	40	0·066	0·232	0·299	0·300	11·8
	45	0·068	0·239	0·307	0·313	18·7
260°	0·5	0·016	0·074	0·090	0·086	3·4
	1·5	0·034	0·150	0·184	0·207	6·2
	3·0	0·055	0·222	0·277	0·300	5·7
	4·0	0·064	0·270	0·334	0·345	5·0
	5·25	0·073	0·268	0·341	0·394	9·2
	6·0	0·069	0·273	0·342	0·358	6·3

where the agreement between columns 5 and 6 is seen to be satisfactory, having regard to the analytical difficulties. For 260° the figures in column 5 lag noticeably behind those in column 6, owing to decomposition, the formation of small quantities of benzene having been observed by some workers.

Column 7 gives the ratio n_2/n_3, the denominator being obtained by means of equation (10). The results are too scattered to indicate any definite trend, but the high value shows that reactions producing triphenylarsine are of a minor importance, especially at the lower temperatures.

Kinetics of the Reactions.—The simplest formulation of the net rate of decomposition of phenyldichloroarsine at any instant is :

$$-\mathrm{d}n/\mathrm{d}t = k_1n_1^2 - k_2n_2n_0 + k_3n_1^3 - k_4n_3n_0^2 \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

on the basis of opposing pairs of reactions (i) and (ii) where the velocity constants are in terms of molar fractions of the reactants.

It has not proved possible to integrate equation (11) directly, nor to apply to it the principle of initial rates owing to the difficulty of obtaining sufficiently accurate data during the earlier stages of the reaction. Since, however, the above calculations show that the formation of triphenylarsine is small, we may apply, in the earlier stages of the reaction at least, the kinetic formula for the opposing bimolecular reactions shown in (i), ignoring other simultaneous reactions. Then $n_2 = n_0 = \frac{1}{2}(1 - n_1)$, so that the kinetic equation is :

$$-\mathrm{d}n/\mathrm{d}t = k_1n_1^2 - k_2[(1 - n_1)/2]^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

which may be integrated to give both velocity constants, using the equilibrium constant K_1 :

$$k_1 = k_2K_1 = \frac{\sqrt{K_1}}{t} \ln \frac{1 - n_1 (1 - 2\sqrt{K_1})}{n_1(1 + 2\sqrt{K_1}) - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

For conversion into units involving concentration factors the corresponding form is :

$$k_1 = k_2K_1 = \frac{\sqrt{K_1}}{at} \ln \frac{1 - n_1(1 - 2\sqrt{K_1})}{n_1(1 + 2\sqrt{K_1}) - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

where a is the initial concentration of phenyldichloroarsine. The theoretical limit of n_1 (*i.e.*, n_1^{ϵ}) is then

$$n_1^{\epsilon} = 1/(1 + 2\sqrt{K_1}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This equation serves to indicate the extent of the discrepancy which results by ignoring triphenylarsine formation, as illustrated in Table V, from which it will be seen that it is algebraically feasible to apply equation (13) to 90% of the course of the reaction before alternative modes of disproportionation interfere seriously.

TABLE V.

Temp.	220°	240°	260°
Limiting value of $(1 - n)$, theor. (eqn. 14)	0·30	0·32	0·34
,, ,, exptal. (Table I)	0·32	0·36	0·37

TABLE VI.

Reversible bimolecular disproportionation of phenyldichloroarsine.

	220°.		240°.		260°.	
t (hours).	n_1.	10^5k_1 (sec.$^{-1}$).	n_1.	10^5k_1 (sec.$^{-1}$).	n_1.	10^5k_1 (sec.$^{-1}$).
0·5	—	—	0·947	(3·10)	0·914	5·29
1·0	—	—	0·936	1·91	—	—
1·5	—	—	0·921	1·62	0·793	5·33
1·9	—	—	0·898	1·69	—	—
3·0	—	—	0·876	1·35	—	—
5·0	0·932	0·411	0·811	1·42	0·700	5·29
6·0	—	—	0·760	1·78	—	—
10·0	0·889	0·354	—	—	—	—
15·0	0·843	0·372	—	—	—	—
20·0	0·800	0·399	—	—	—	—
25·0	0·767	0·427	—	—	—	—
30·0	0·740	0·470	—	—	—	—
Average 10^5k_1 :		0·406		1·63		5·30

TABLE VII.

Temp.	220°	240°	260°
10^5k_1 (sec.$^{-1}$), by eqn. (13), obs.	0·41	1·63	5·30
,, ,, (15), calc.	0·41	1·55	5·27
10^4k_2 (sec.$^{-1}$), ,, (13), obs.	0·92	3·04	8·27
,, ,, (15), calc.	0·92	2·86	8·20

Table VI shows the extent of agreement with equation (13) and Table VII lists the bimolecular reaction constants thus obtained by applying equation (13) until n_1 exceeds the theoretical limit. The constants may be reproduced by the linear equations

$$\log_{10} k_1 = 9{\cdot}4041 - 7293/T$$

$$\log_{10} k_2 = 8{\cdot}6285 - 6244/T$$

whence, by means of the Arrhenius equation $E_A = \boldsymbol{R}T^2(\mathrm{d} \ln k/\mathrm{d}T)$, we may obtain the apparent energies of activation $(E_A)_1 = 33{,}380$ and $(E_A)_2 = 28{,}590$ cals./g.-mol. If k_1 is proportional to the viscosity of the medium, the former of these quantities must be increased by 3750 calories, giving a corrected energy of activation of about 37,000 calories. Even without this correction, the observed energy of activation is considerably greater than any hitherto found for a bimolecular reaction in a condensed fluid state. It must not be overlooked, however, that the bimolecular character of the reaction is assumed, and, although leading to consistent results and to appropriate equilibrium relationships, cannot be directly established in a system of the kind investigated. To correct k_1 from mole-fractions per second to the more usual units of litres per g.-mol.-sec., the values given above must be multiplied by the factor $V_S/1000$, where V_S is the molar volume in ml. At the temperatures concerned, V_S lies within the range $160 \cdot 5 \pm 1 \cdot 4$ ml., and the pre-exponential term of the Arrhenius equation becomes $4 \cdot 1 \times 10^8$ l./g.-mol.-sec. There are no known reactions with which this figure can be compared.

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