AN INVESTIGATION OF THE CHEMICAL EQUILIBRIA INVOLVING THE MOLECULES ARSENIC TRICHLORIDE, MONOPHENYLCHLORARSINE, DIPHENYLCHLORARSINE AND TRIPHENYLARSINE.*

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One method of manufacture of ϕ_2AsCl consists in heating mixtures of $AsCl_3$ and ϕ_3As at about 250° C. This production of ϕ_2AsCl involves

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* Throughout this paper the following notation is used : $\phi AsCl_2$ = monophenylchlorarsine, ϕ_2AsCl = diphenylchlorarsine and ϕ_3As = triphenylarsine.

several reactions and equilibria between the four species $AsCl_3$, $\phi AsCl_2$, ϕ_2AsCl and ϕ_3As. This paper is an account of some work carried out to obtain quantitative data for these equilibria. The primary objective was to find the optimum conditions for the production of ϕ_2AsCl. Because of this the investigation was not as extensive as we should have wished, and the accuracy of the results not of an extremely high order. Nevertheless, we feel that the results as they stand are of some interest.

Of the possible equilibria involved in a mixture of the four species, only two are independent, so that the general state of equilibrium can be completely defined by two constants. We have therefore investigated the disproportionation of pure $\phi AsCl_2$ and pure ϕ_2AsCl in order to determine these equilibrium constants. We have also studied the reaction of $AsCl_3$ with ϕ_3As.

The equilibria are formulated below :—

$$2\phi AsCl_2 \underset{k_1^*}{\overset{k_1}{\rightleftharpoons}} AsCl_3 + \phi_2AsCl \quad . \quad . \quad . \quad (1)$$

$$K_1 = \frac{k_1}{k_1^*} = \frac{(AsCl_3)(\phi_2AsCl)}{(\phi AsCl_2)^2}$$

and

$$2\phi_2AsCl \underset{k_2^*}{\overset{k_2}{\rightleftharpoons}} \phi AsCl_2 + \phi_3As \quad . \quad . \quad . \quad (2)$$

$$K_2 = \frac{k_2}{k_2^*} = \frac{(\phi AsCl_2)(\phi_3As)}{(\phi_2AsCl)^2}$$

where K_1 and K_2 are equilibrium constants and k_1, k_1^*, k_2 and k_2^* are bimolecular velocity constants.

Experimental.

Method.—Samples of $\phi AsCl_2$, ϕ_2AsCl or known mixtures of $AsCl_3$ and ϕ_3As were placed in Pyrex tubes and sealed off *in vacuo*. The tubes were inserted in metal containers fitted with screw caps, and then placed in an air thermostat at the required temperature. After various time intervals, tubes were withdrawn, cooled rapidly to room temperature, and their contents analysed.

Materials.—The $AsCl_3$ was a commercial product, and was purified by two distillations. A colourless liquid was obtained, b. pt. 130·5° c. at 760 mm. The samples of purified $\phi AsCl_2$, ϕ_2AsCl and ϕ_3As were kindly provided by Prof. A. R. Todd. The degree of purity of these materials is shown by the following figures :

$\phi AsCl_2$—hydrolysable chlorine 89·2 cc. of N./10 NaOH per g. (theor. 89·7 cc.).
ϕ_2AsCl—iodine absorption 75·7 cc. N./10 iodine per g. (theor. 75·6 cc.).
ϕ_3As—m. pt. 60·5° c. ; iodine absorption 65·2 cc. N./10 iodine per g. (theor. 65·4 cc.).

Analysis.*—About 0·5 g. mixture was weighed out into a 100 ml. separating funnel containing 50 ml. dil. NaOH (approx. 2N.) and vigorously agitated for a few minutes. This brings about the replacement of the Cl atoms by OH groups giving a mixture of $As(OH)_3$, $\phi As(OH)_2$, $\phi_2As(OH)$ and ϕ_3As. This mixture was extracted three times by gentle agitation with about 15 ml. of chloroform. The chloroform extracts were washed successively with 10 ml. dil. NaOH in a second separating funnel and run off into a 500 ml. iodine flask. At this stage the aqueous layer contains the $As(OH)_3$ and $\phi As(OH)_2$, while the chloroform layer contains the $\phi_2As(OH)$ and ϕ_3As.

(*a*) **Determination of the $AsCl_3$ and $\phi AsCl_2$.**—To the aqueous portions a few drops of phenolphthalein were added and then dil. HCl (approx. 2 N.) until in excess. The solution was then titrated with standard iodine (approx. N./10) with starch indicator.

This gives the reaction :

$$\phi As(OH)_2 + I_2 + H_2O \rightarrow \phi AsO\,.\,(OH)_2 + 2HI.$$

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* Based on the methods described in the Sutton Oak Report to the Ministry of Supply, 3/12/1940, and the I.C.I. Ltd., General Chemicals Division Report to the Ministry of Supply (1/11/40).

After the addition of 2 to 3 g. $NaHCO_3$ the titration was continued to a further end point. The reaction determined in this stage is:

$$As(OH)_3 + I_2 + H_2O \rightarrow AsO(OH)_3 + 2HI.$$

(*b*) **Determination of ϕ_2AsCl and ϕ_3As.**—To the combined chloroform extracts about 50 ml. of distilled water were added, followed by a few drops of phenolphthalein and dilute HCl until just acid. About 1 g. of sodium bicarbonate was next added and the mixture was titrated with standard iodine until a faint permanent violet colour appeared in the chloroform layer. This reaction estimates the total arsenic in this layer:

$$\phi_2As(OH) + I_2 + H_2O \rightarrow \phi_2AsO\,.\,(OH) + 2HI$$
$$\phi_3As + I_2 + H_2O \rightarrow \phi_3AsO + 2HI.$$

The total hydrolysable chlorine was then determined by taking about 0·5 g of the mixture, adding 50 ml. absolute alcohol and shaking with 20 ml. N./5 NaOH in an atmosphere of nitrogen. The excess NaOH was then titrated with N./10 HCl using brom-phenol blue as indicator. The reactions involved in this stage of the estimation are:

$$AsCl_3 + 3NaOH \rightarrow As(OH)_3 + 3NaCl$$
$$\phi AsCl_2 + 2NaOH \rightarrow \phi As(OH)_2 + 2NaCl$$
$$\phi_2AsCl + NaOH \rightarrow \phi_2As(OH) + NaCl.$$

From the results the individual quantities of $AsCl_3$, $\phi AsCl_2$, ϕ_2AsCl and ϕ_3As in the mixture may be determined.

Results.

The results obtained are shown in Tables I-III, Fig. 1-4. The amounts of the four components found by analysis are shown as molar percentages of the total starting material. In the case of the more volatile components the analysis figures, which give the total amount of the component in the reaction tube, will not give the required value for the molar percentage in the liquid phase at the temperature of the experiment. They have accordingly been corrected by a simple equation based on Raoult's law and on the assumption that the vapours behave as perfect gases. It was found that the correction was very small for ϕ_2AsCl and ϕ_3As, small for $\phi AsCl_2$ and of considerable magnitude only in the case of $AsCl_3$. We have, therefore, introduced the correction only for the $\phi AsCl_2$ and $AsCl_3$ values.

TABLE I.

Equilibrium.	Temp. °c.	Equilibrium Constant (× 10²).	Velocity Constant (cc. mol.⁻¹ sec.⁻¹). (× 10³).	ΔH Heat of Reaction kcal.	*E* Activation Energy kcal.	*B* Temp. Independent Factor.
$2\phi AsCl_2 \rightleftharpoons \phi_2AsCl + AsCl_3$	256	$K_1 = 5·7$	$k_1 = 3·22$ $k_1^* = 56·5$	$\Delta H_1 = +2·6$		
	304	$K_1 = 7·0$	— —			
$2\phi_2AsCl \rightleftharpoons \phi AsCl_2 + \phi_3As$	252	$K_2 = 5·9$	$k_2 = 0·89$ $k_2^* = 15·1$	$\Delta H_2 = +3·8$	$E_2 = 37·6$	$B_2 = 10^{12·6}$
	304	$K_2 = \begin{cases} 8·0 \\ 8·4 \end{cases}$	$k_2 = 22·7$ $k_2^* = 284$		$E_2^* = 34·0$	$B_2^* = 10^{12·3}$

In some cases the reaction was accompanied by a certain amount of decomposition, shown by small quantities of a reddish-brown suspension, the amounts of which qualitatively increased with time. Furthermore, the hydrolysable chlorine and total arsenic were less than the corresponding theoretical values. The discrepancies increased with time and ran parallel to the amount of suspension formed. The solution was always centrifuged and the supernatant liquid used for analysis. We do not consider that this decomposition affects the accuracy of our results.

It was found that certain metals catalysed these reactions, and results of experiments in which iron was present in the reaction tube are shown in Fig. 1 and 2. The catalytic effect of various metals is shown in Table II. Their order in this table does not necessarily correspond to their catalytic efficiency, since the extent and nature of the surfaces were not known.

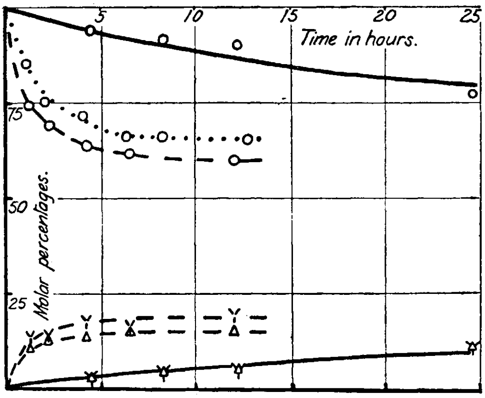

FIG. 1.—ϕ_2AsCl disproportionation at 309° C.

⊙ $\phi AsCl$. △ $\phi AsCl_2$. Y ϕ_3AsCl.

Discussion.

The equilibrium concentrations of the components, required for the calculation of K_1 and K_2, have been obtained by graphing the experimental data and interpolating the asymptotic values of the molar percentages. Examples of these curves are shown in Fig. 1, 2 and 3. In the case of the ϕ_2AsCl disproportionation at 252° C. equilibrium was not reached after 25 hr. (Fig. 1). We have, therefore, determined the equilibrium constant K_2, at this temperature, by catalysing the reaction with iron. In this way equilibrium was established after 6 hr., and the concentrations were unchanged, within experimental error, for a further 6 hr. The equilibrium concentrations were $\phi AsCl_2$ 14·1 %, ϕ_2AsCl 65·6 %, ϕ_3As 18·0 %, giving $K_2 = 5{\cdot}9 \times 10^{-2}$. For this experiment the fall in ϕ_2AsCl concentration is shown in Fig. 1 (dotted curve).

Iron was used as a catalyst also in one experiment on the reaction of $AsCl_3$ and ϕ_3As (Fig. 2). The value of K_2 ($8{\cdot}4 \times 10^{-2}$) obtained is in good agreement with that of $8{\cdot}0 \times 10^{-2}$ obtained from the disproportionation of ϕ_2AsCl at the same temperature (curves shown in Fig. 1). The uncatalysed reaction $AsCl_3 + \phi_3As$ was also studied. The slower rate of reaction can be seen from the plot of the ϕ_2AsCl concentration in Fig. 2 (broken curve).

TABLE II.—ϕ_2AsCl DISPROPORTIONATION IN PRESENCE OF METALS. TEMPERATURE 252° C.

Metal.	State.	% Disproportionation after 1 hr.
Fe	Pig iron turnings	11·4
Fe	Pure turnings	9·2
Sn	Molten	7·8
Co	Turnings	6·2
Ni	Turnings	4·6
72 % Cr/28 % Fe alloy	Small crystals	4·4
Cr	,,	3·4
As	,,	2·8
Cu	Turnings	2·2
Glass	—	1·5

Fig. 3 shows the curves for the $\phi AsCl_2$ disproportionation at 256° C., giving $K_1 = 5{\cdot}7 \times 10^{-2}$. This reaction was also studied at 304° C., and the equilibrium concentrations were $\phi AsCl_2$ 55·0 %, ϕ_2AsCl 14·6 %, $AsCl_3$ 14·6 %, giving $K_1 = 7{\cdot}0 \times 10^{-2}$. For this latter case the fall in $\phi AsCl_2$ concentration is shown in Fig. 3 (broken curve).

Heats of Reaction.—From the values of K_1 and K_2 at two different temperatures the heats of reaction, ΔH_1 and ΔH_2, have been determined as + 2·6 and + 3·8 kcal. respectively.

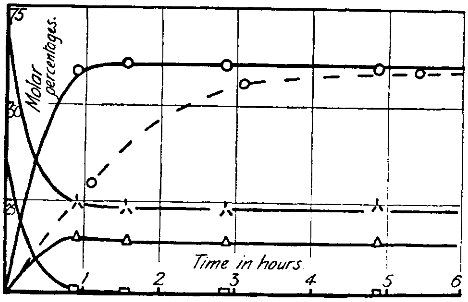

FIG. 2.—AsCl$_3$ + ϕ_3As reaction in presence of iron, at 304° c.

☐ AsCl$_3$. △ ϕAsCl$_2$. ○ ϕ_2AsCl. Y ϕ_2As.

These heat content changes are small. Such a state of affairs would obtain if the strengths of all the As—Cl bonds were the same and all the As—C bonds were the same for the four molecules. Small values for ΔH_1 and ΔH_2, could also obtain, even if these bond strengths were not constant; but this would require the gradations in the As—Cl and As—C bond strengths to be related in rather a special manner.

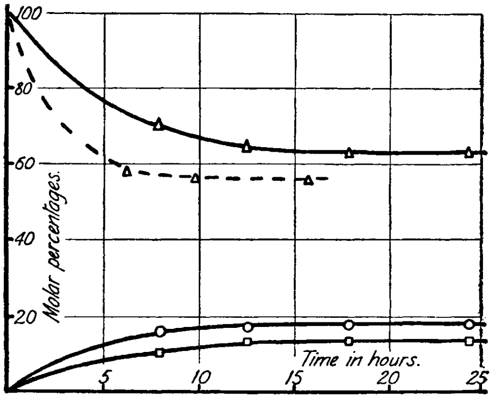

FIG. 3.

A rough calculation of the equilibrium constants for the reactions (1) and (2), based on heats of reaction of about 3 kcal. in the temperature range 250-300° c., and assuming the cancellation of the partition functions for translation, rotation and vibration (which is fairly plausible) leads to a value of about 2×10^{-2} for both K_1 and K_2. It is seen that our experimental values of K_1 and K_2 (Table I) are approximately equal and are of the same order as that given by the above calculation.

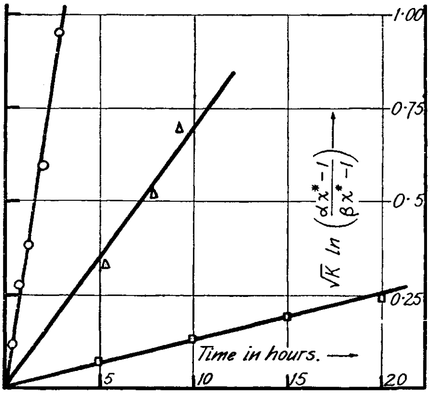

FIG. 4.

○ ϕ_2AsCl disproportionation at 304° C.
☐ ϕ_2AsCl disproportionation at 252° C.
△ ϕ_2AsCl$_2$ disproportionation at 256° C.

In the manufacture of ϕ_2AsCl from AsCl$_3$ and ϕ_3As the influence of variations in the molar ratio ϕ_3As/AsCl$_3$ of the starting material is of great practical interest. Since the constants K_1 and K_2 define completely the final state of equilibrium, the values of these constants enable the equilibrium concentrations of the four components to be calculated for starting materials of any ϕ_3As/AsCl$_3$ molar ratio. The method of calculation, for a starting material containing *a* moles of ϕ_3As and *b* moles of AsCl$_3$, is illustrated as follows :

$$\begin{array}{cccccc} \phi_3As & + & AsCl_3 \rightleftharpoons & \phi AsCl_2 & + & \phi_2AsCl \\ (a-x) & & (b-x) & x & & x \end{array}$$

$$\begin{array}{ccccc} \phi AsCl_2 & + & \phi_3As & \rightleftharpoons & 2\phi_2AsCl. \\ (x-y) & & (a-x-y) & & 2y \end{array}$$

The equilibrium amounts are thus : $AsCl_3 = b - x$; $\phi AsCl_2 = x - y$; $\phi_2AsCl = x + 2y$; $\phi_3As = a - x - y$; and substituting in the expressions for K_1 and K_2

$$x^2(1 + K_1) - bx - 2by + 2xy(1 - K_1) + K_1y^2 = 0$$
$$x^2(1 + K_2) - ax + ay + 4K_2xy + y^2(4K_2 - 1) = 0.$$

These can be solved to give x and y in terms of the ratio a/b. Hence the equilibrium concentrations can be evaluated in terms of the molar ratio $\phi_3As/AsCl_3$ of the starting material. Table III shows a few typical examples of results obtained by the above method.

TABLE III.

Molar Ratio $\phi_3As/AsCl_3$ of Starting Material.	Equilibrium Molar %.			
	$AsCl_3$.	$\phi AsCl_2$.	ϕ_2AsCl.	ϕ_3As.
0	100	0	0	0
0·5	17·5	65·0	17·5	0
1·0	3·5	46·5	46·5	3·5
1·5	1·0	28·5	60·0	10·5
2·0	0	18·0	63·5	18·5
4·0	0	5·0	50·0	45·0
∞	0	0	0	100

Kinetics of the Reactions.—It was found that in the disproportionation of $\phi AsCl_2$, the concentration of ϕ_3As formed during the reaction was negligible and that $AsCl_3$ and ϕ_2AsCl were produced in approximately equal concentration. Similarly, in the disproportionation of ϕ_2AsCl the concentration of $AsCl_3$ was found to be very small and the concentrations of $\phi AsCl_2$ and ϕ_3As were again approximately equal. We can, therefore, consider these disproportionation reactions to consist of two opposing bimolecular reactions, as formulated earlier.

In the general case :

$$2A \underset{k^*}{\overset{k}{\rightleftharpoons}} B + C, \text{ and } K = k/k^*,$$

let the concentration of A at zero time be a moles./cc. and the concentration at time t be $(a - x)$ moles./cc.

Then $$\frac{-\,\mathrm{d}(A)}{\mathrm{d}t} = +\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x)^2 - k^*.\frac{x^2}{4}.$$

Integrating: $$\frac{1}{a\sqrt{kk^*}} \ln \left\{ \frac{\left(\dfrac{4k - k^*}{2k + \sqrt{kk^*}}\right)\dfrac{x}{2} - a}{\left(\dfrac{4k - k^*}{2k - \sqrt{kk^*}}\right)\dfrac{x}{2} - a} \right\} = t.$$

This simplifies into :

$$\frac{\sqrt{K}}{a} \ln \left(\frac{\alpha x - a}{\beta x - a}\right) = kt$$

where
$$\alpha = \frac{1}{2}\left\{\frac{4k - k^*}{2k + \sqrt{kk^*}}\right\} = 1 - \frac{1}{2\sqrt{K}}$$

and
$$\beta = \frac{1}{2}\left\{\frac{4k - k^*}{2k - \sqrt{kk^*}}\right\} = 1 + \frac{1}{2\sqrt{K}}.$$

In our disproportionation experiments the starting material was pure $\phi AsCl_2$ or pure ϕ_2AsCl. In these cases, therefore, a is equal to $1/V_m$, where V_m is the molar volume at the particular temperature. We may thus write :

$$\sqrt{K} \ln \left(\frac{\alpha x^* - 1}{\beta x^* - 1}\right) = \frac{k}{V_m} \cdot t \quad . \quad . \quad . \quad (3)$$

where x^* is the amount per mole of A which has disappeared at time t

Although rough values of k can be obtained by estimating the slopes of the appropriate curves at zero time, the constants can be evaluated with much greater accuracy from eqn. (3). If the left-hand side of eqn. (3) is plotted against t, the result should be a straight line passing through the origin, the slope of which is k/V_m. The constant k^* can then be found from the relation $K = k/k^*$. This calculation has been carried out for the $\phi AsCl_2$ disproportionation reaction at 256° C. and for the ϕ_2AsCl disproportionation reaction at 252° C. and 304° C. These plots are given in Fig. 4 and the values of the velocity constants in Table I. The straight lines obtained from the experimental data support the view that the reactions involved in these equilibria are all bimolecular.

From the data for the ϕ_2AsCl disproportionation reaction at the two temperatures we have calculated the activation energies, E, and the temperature independent factors, B, for the forward and reverse reactions, using the expression $k = Be^{-E/RT}$. The results are given in Table I. The temperature independent factors for the forward and reverse reactions are seen to be very nearly equal, as would be expected from the similarity of the two reactions.

From these results we conclude that in these reactions states of true equilibrium are attained. The individual reactions are bimolecular, and involve small heat changes, as one would expect since they involve merely the exchange of chlorine and phenyl radicals from one arsenic centre to another.

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Summary.

We have examined the disproportionation reactions of $\phi AsCl_2$ and ϕ_2AsCl, and the reaction between $AsCl_3$ and ϕ_3As. We find that these reactions lead to states of true equilibrium by means of opposing bimolecular processes. We have determined the equilibrium constants, heats of reaction, velocity constants, activation energies and temperature independent factors involved in these reactions. From our data, the equilibrium concentrations of the four components can be calculated for starting material of any composition.

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