107. *The Reaction between Phosphorus and Iodine in Carbon Tetrachloride Solution.*

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The reaction between phosphorus and iodine in carbon tetrachloride has been investigated by means of iodine colour comparisons with standard solutions. In all cases the amounts of iodine present were less than that required to convert all the phosphorus into the tetraiodide. The rate of removal of iodine increased greatly at high phosphorus concentrations; in certain individual experiments the rate passed through a minimum as the concentration of reactants decreased.

The rate of reaction was accelerated by the addition of small amounts of other solvents which give brown solutions with iodine.

A mechanism is suggested which is in general agreement with these and other observations.

THE reactions of phosphorus with bromine and iodine in solution represent in general a very complicated system, in which not only the kinetics but also the actual compounds formed are uncertain. With iodine, only the di- and the tri-iodide have been isolated in a state of purity and stability, although claims have been made for the existence of P_3I_4 (Besson, *Compt. rend.*, 1897, **124**, 1349), P_4I (Bouloch, *ibid.*, 1905, **141**, 256) and P_2I_5 (Hampton, *Chem. News*, 1880, **42**, 180). The bromine compounds PBr_3 and PBr_5 are well known. A heptabromide has been also reported, but P_2Br_4, analogous to P_2I_4, has not been obtained (cf. Besson and Fournier, *Compt. rend.*, 1910, **150**, 102). The problem is rendered more complex by the transformation of white into red phosphorus by light, such a conversion being also catalysed by small amounts of iodine and bromine. No detailed information regarding the kinetics of such reactions was available, so attempts were made to determine such a mechanism from the rates of combination of the elements.

EXPERIMENTAL.

Preliminary measurements showed that equivalent amounts of phosphorus and halogen react rapidly. Visual comparison of halogen colours with standard solutions showed that for 0·005M-solutions in carbon tetrachloride, the rate with bromine (determined by a streaming method) was approximately 2000 times that of the corresponding rate with iodine, which, in carbon tetrachloride containing small amounts of water, itself reached the half-way stage in a few minutes. The rate of removal of halogen in dry solution was accelerated by exposure to light, and by the addition of small quantities of water, alcohol, ether, etc.; careful attention had to be paid to the drying of the carbon tetrachloride used as solvent before concordant results could be obtained. Precautions were also necessary to prevent access of oxygen to the solution.

Both P_2I_4 and PI_3 may be prepared by mixing solutions of white phosphorus and iodine in the correct proportions; solutions were accordingly made in which the amount of iodine was always less than that required to form P_2I_4. Orange crystals of P_2I_4, prepared by the method of Praxler and Germann (*J. Amer. Chem. Soc.*, 1927, **49**, 307), gave, immediately after preparation, no blue colour with aqueous starch; a faint blue colour was, however, obtained on the following day on treating a benzene extract with aqueous starch. Substitution of carbon tetrachloride or disulphide or *cyclo*hexane for benzene gave no blue colour. Direct experiments showed that a blue starch colour in such circumstances only became apparent at an iodine concentration of 0·002 g./l. In the actual measured rates of reaction between phosphorus and iodine, the concentration of the former was never less than that necessary to convert all the iodine into di-iodide, and when aqueous starch was added to the final products no blue colour was ever obtained. Under such conditions P_2I_4 may thus be regarded as undissociated. Only after the crystals of P_2I_4 had been kept for a week in a desiccator was some slight decomposition observed, with separation of red phosphorus.

Various methods of estimating the concentrations of reactants at different times during reaction were examined. Here even the preliminary determination of phosphorus alone in carbon tetrachloride proved unexpectedly difficult. Miller (J., 1928, 1859) determined oxides of phosphorus by oxidation with bromine in aqueous solution, and a similar method was here applied. For solutions of phosphorus content comparable to that of the actual rate experiments, 20 c.c. of liquid bromine were added to the carbon tetrachloride solution under water, the temperature raised to 30°, and 3—4 c.c. of 4N-sodium hydroxide added. After 10 minutes, 5 c.c. of concentrated nitric acid were added, and a stream of air was passed through the solution, the system being gently heated. Organic solvent and bromine were thus removed before the solution reached its b. p.; this precaution appeared to be essential, for results obtained otherwise were always low. Simply boiling to remove bromine introduced errors of 10—40%. A colorimetric method was employed to determine the resultant PO_4''' content, namely, the reduction of ammonium phosphomolybdate by quinol in sulphuric acid solution (" B.D.H. Reagents for Spot Tests," 5th Edn., p. 56). Phosphate is here indicated by a blue colour which attains maximum intensity in ½ hour and remains constant for a considerable time. Tests were carried out on phosphorus weighed out under water, and comparison was made with colours given by standard solutions of potassium dihydrogen phosphate. Results were as follows:

P_4 taken, g.	0·209	0·104	0·166	0·261	0·176
P_4 found, g.	0·208	0·105	0·167	0·260	0·175
Error, %	−0·5	+1·0	+0·6	−0·4	−0·6

In view of the fact that a colorimetric method was employed, such results were regarded as satisfactory. The method cannot, however, be employed to determine the concentration of phosphorus at any point during the reaction, and various attempts were made to find a reagent which would stop the reaction at a given point and could be used to estimate one reactant without being affected by the other or by any reaction product. In moist carbon tetrachloride, the rate was approximately 100 times that in the dry solvent, and the addition of aqueous reagents was thus in general unsuitable. Thiosulphate was unsatisfactory. The attempt to determine the change in phosphorus concentration during the reaction had to be abandoned, and only the change in iodine concentration determined under varied conditions, by employing the visual method based on comparison of iodine colours with standard iodine solutions. Experiments were carried out in a series of Pyrex stoppered test-tubes, blackened and kept at constant temperature by a thermostat. Samples of solution were removed at intervals by means of short lengths of the same glass tubing as that used to make the tubes containing the standard iodine colour solutions, and the colour of the sample was rapidly compared with the set of standards. Under standard conditions maximum errors in the final observed rates were of the order 10%. Although neither phosphorus nor its tetraiodide appreciably absorbs green light, a photoelectric cell system, measuring green light transmitted by the iodine solution, could not be used, such light being found to accelerate the reaction. Carbon tetrachloride was employed as solvent in view of its inertness and ideal solvent nature. White phosphorus was first heated with moderately concentrated nitric acid, and the element remained as a clear liquid which solidified on cooling. The solid was washed with water and then immersed in alcohol, ether, and in portions of carbon tetrachloride. The final solution was obtained by dissolving the residue in this solvent, previously saturated with carbon dioxide, keeping it overnight in a blackened stoppered container, and filtering the solution out of contact with air into a blackened flask filled with carbon dioxide and containing a little phosphoric oxide to remove water. Measured volumes of such solutions were removed by means of an attached burette system, also filled with carbon dioxide, and the concentration determined by the colorimetric method previously described. Solutions of iodine in dry air-free carbon tetrachloride were analysed by standard thiosulphate. Chosen volumes of the two reactant solutions, brought to 15° in a thermostat, were rapidly mixed in the blackened stoppered test-tubes, previously filled with carbon dioxide. In the absence of water, as ensured by the above methods, reaction was fairly slow, some hours being frequently required to complete a series of observations.

DISCUSSION OF RESULTS.

Even under conditions where P_2I_4 was the only probable product, the relation between rate and concentration of reactants was obviously very complex. Table I shows the rates observed for different phosphorus concentrations (in g.-mol./l.) at two fixed iodine concentrations. For the first, the rate of removal of iodine was observed over the range 0·00210—0·00190 g.-mol. of iodine, the mean value being taken to refer to $[I_2] = 0{\cdot}00200$; for the second, the rates refer to $[I_2] = 0{\cdot}00150$ (*i.e.*, from 0·00160 to 0·00140). The change in $[P_4]$ in any one experiment is small; the mean $[P_4]$ was calculated on the assumption that P_2I_4 was alone formed. Rates are expressed as the reciprocals of the times in minutes for a change in $[I_2]$ of 0·0001 mol./l.

TABLE I.

Initial $[I_2] = 0{\cdot}00250$.

$[P_4]$.	Rate at $I_2 = 0{\cdot}00200$.	$[P_4]$.	Rate at $I_2 = 0{\cdot}00150$.	$\frac{\text{Rate (0·00200)}}{\text{Rate (0·00150)}}$.
0·0049	0·036	0·0047	0·023	1·56
0·0099	0·098	0·0097	0·062	1·58
0·0149	0·36	0·0147	0·23	1·57
0·0199	0·94	0·0197	0·60	1·57
0·0249	2·0	0·0247	1·25	1·60
0·0299	3·5	0·0297	2·0	1·75
0·0349	6·0	0·0347	2·8	2·14

It will be observed that the rate increases very rapidly at the higher concentrations of phosphorus—a seven-fold increase in $[P_4]$ gives roughly a 160-fold increase in rate for $[I_2] = 0{\cdot}00200$. There is a fairly constant ratio of the rates at constant $[P_4]$, for the two iodine concentrations, although this ratio is greater (1·6) than the ratio of the iodine concentrations (1·33), and this suggests that in the earlier stages iodine is being used in a secondary process apart from the disappearance of phosphorus. The ratio 1·6 tends to increase with increasing phosphorus concentration, which would be in agreement with this suggestion, since the primary product will presumably be then at a higher concentration. The fact that the ratio of rates is not markedly different from the ratio of iodine concentrations may be due to a slow rate for the secondary reaction. Further experiment showed that the rate of iodine removal actually increased after reaction had been in progress for some time, as shown in Table II.

TABLE II.

Initial $[P_4] = 0{\cdot}0084$; initial $[I_2] = 0{\cdot}00400$.

$[P_4] \times 10^4$	399	398	397	396	396	395	394	394	393	392	392
$[I_2] \times 10^5$	350	300	275	250	225	200	175	150	125	100	75
$-d[I_2]/dt$	2·5	1·0	0·46	0·29	0·14	0·07	0·05	0·08	0·14	0·20	0·29

The rate of iodine removal at first decreases and then increases; in this experiment the rates at $[I_2] = 0{\cdot}00200$ and 0·00150 are approximately equal, instead of giving a 1·6 ratio as in Table I. The sharpness of such an increase depends on the phosphorus concentration, but for a constant $[P_4]$ it appeared to be more pronounced the lower the initial $[I_2]$ concentration, as indicated in the figure, in which initial $[P_4] = 0{\cdot}0163$ and $R = -\,d[I_2]/dt$.

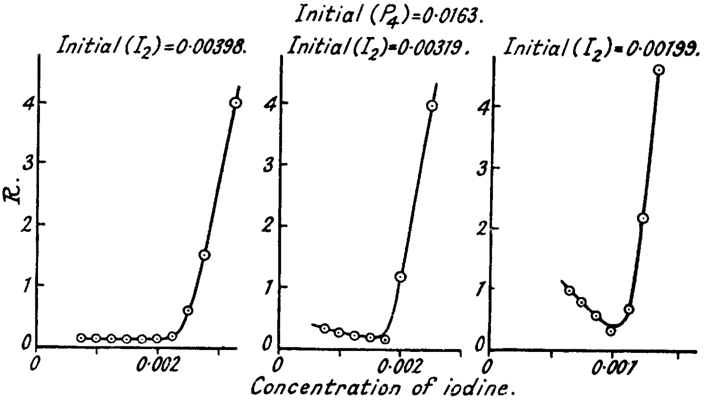
It does not seem possible to put forward any simple scheme in explanation of these results and at the same time include the rapid increase in rate as $[P_4]$ is increased. Such a mechanism must involve intermediate complexes which are not accessible to direct measurement. The following scheme, however, expresses in outline the general effects of altered concentrations of reactants referred to above, and is, moreover, not in disagreement with the catalytic conversion of white into red phosphorus by traces of iodine.

$$\begin{array}{llll} P_4 + I_2 \longrightarrow P_4I_2 & (1) & P_2 + I_2 \longrightarrow P_2I_2 & (4) \\ P_4I_2 \longrightarrow P_2I_2 + P_2 & (2) & P_2I_2 + I_2 \longrightarrow P_2I_4 & (5) \\ P_2I_2 + P_4 \longrightarrow P_4I_2 + P_2 & (3) & P_2I_2 + P_2I_2 \longrightarrow P_2I_4 + P_2 & (6) \end{array}$$

Assuming that the intermediates at once reach stationary concentrations, we derive the formula

$$\frac{-d[I_2]}{dt} = 4[I_2]\left(\frac{a[P_4][I_2]}{[I_2] - b[P_4]}\right) + c\left(\frac{a[P_4][I_2]}{[I_2] - b[P_4]}\right)^2 \quad . \quad . \quad . \quad . \quad (A)$$

where $a = k_1$, $b = 2k_3/k_5$, and $c = 4k_6/k_5^2$.



For suitable values of the constants a, b, and c and for relatively low concentrations of $[P_4]$, the rate of iodine removal is thus approximately proportional to the iodine concentration, as is found (see Table I). Also for $[I_2] = 0{\cdot}00200$ (Table I), values $a = 100$, $b = 0{\cdot}04$, $c = 0{\cdot}06$ give calculated values which agree reasonably well with experimental results in view of the wide range of variation in $[P_4]$, as shown in Table III. Further, where there is increase in rate with decreasing $[I_2]$, this is accounted for by the formula : the smaller $[I_2]$, the smaller the denominator ($[I_2] - b[P_4]$) of each factor. The whole expression does not become negative because of the squared term. The smaller the iodine concentration for a constant phosphorus concentration, the greater the relative acceleration due to the term ($[I_2] - b[P_4]$), as observed experimentally (see figure).

TABLE III.

$[P_4] \times 10^4$	50	100	150	200	250	300	350
$-d[I_2]/dt$, found	0·036	0·098	0·36	0·94	2·0	3·5	6·0
$-d[I_2]/dt$, calc.	0·050	0·104	0·29	0·94	1·9	2·4	9·0

The use of the numerical values for a, b, and c of Table III does not, however, give calculated values in good agreement with observed values throughout any one continuous experiment; the assumption that the various complexes reach stationary concentrations is not justified. As shown in Table IV, the results of Table I for $[I_2] = 0{\cdot}00150$ require slightly different values for a, b, and c from those used in Table III.

Reactions (2) and (3) of the scheme constitute a chain mechanism which, in the absence of an appreciable concentration of iodine, will result in an accumulation of P_2 molecules. The production of red phosphorus in the gas phase has been shown by Melville and Gray (*Trans. Faraday Soc.*, 1936, **32**, 271) to be due to the recombination of P_2 molecules, a process confirmed by King and Ludlam (J., 1938, 1500) by experiments in which P_2 molecules were produced by ultra-violet light illumination of P_4 vapour. The above scheme accordingly affords a mechanism whereby small amounts of iodine may catalyse the conversion of white into red phosphorus. The reactions claimed for the " compounds " P_4I and P_2I_4 can in general be obtained with P_2I_4–red phosphorus mixtures.

There remains for consideration the accelerating effect of small amounts of water, alcohol, and ether on such a system. Direct experiment showed a large increase in rate due to addition of ethyl and methyl alcohol, acetone, ether, water, small increases with benzene and toluene, and no increase with chloroform, carbon disulphide, hexane, and *cyclo*hexane. These groupings may be exactly paralleled by the different types of colour given by iodine in these solvents; *e.g.*, chloroform gives a violet, alcohol a reddish-brown, and benzene an intermediate colour. Although the addition of small amounts of water to a carbon tetrachloride solution of iodine produces no perceptible colour change, while greatly accelerating the rate of reaction with phosphorus, yet it seems very probable that the increased rate is due, largely at least, to solvation of iodine molecules. Other experimental evidence supports such a view (see, *e.g.*, Feigl and Chargaff, *Monatsh.*, 1929, **53**, 508). In the present case we might then expect the relative rates of reactions involving iodine to be increased; *i.e.*, a ($= k_1$) would be increased, b ($=2k_3/k_5$) would be less than before, and c ($= 4k_6/k_5^2$) less still. A series of experiments comparable to those of Table I were fully carried out with carbon tetrachloride solutions saturated with water. Calculated results were obtained by applying formula (A) with : $a = 10000$, $b = 0{\cdot}01$, $c = 0{\cdot}00001$, $[I_2] = 0{\cdot}00200$, as in Table V. There is good agreement between calculated and experimental figures : the constants a, b, and c have altered in the sense outlined above from 100, 0·04, and 0·06 respectively.

TABLE IV.

$[I_2] = 0{\cdot}00150$.

	$-d[I_2]/dt$.		
$[P_4] \times 10^4$.	Found.	Calc. from $a = 100$, $b = 0{\cdot}04$, $c = 0{\cdot}06$.	Calc. from $a = 80$, $b = 0{\cdot}03$, $c = 0{\cdot}06$.
50	0·023	0·023	0·015
100	0·062	0·120	0·066
150	0·23	0·39	0·19
200	0·60	1·13	0·45
250	1·25	3·4	0·98
300	2·0	4·9	2·2
350	2·8	15·5	5·2

TABLE V.

$[P_4] \times 10^4$	50	100	150	200	250	300	350
$-d[I_2]/dt$, found	0·45	0·96	1·5	2·2	3·0	4·2	6·4
$-d[I_2]/dt$, calc.	0·44	0·95	1·6	2·3	3·1	4·1	5·2

In general, it may be said that the suggested mechanism includes the main features of this complicated reaction. The visual method of analysis, however, lacks sufficient accuracy, and can only be applied to a limited range of halogen concentrations; accordingly, no attempt is here made to develop the theory further.

Bromine.—Phosphorus reacts with bromine to form the tri- and the penta-bromide. The compound P_2Br_4 has not been reported. The reaction is very rapid (see p. 583), and in order to apply the streaming method, solutions of phosphorus and bromine were caused to flow at measured rates into a vertical capillary in such a way that they mixed rapidly and the yellow colour disappeared as the mixture passed down the tube. The yellow colour was compared with that of solutions of bromine of known concentration, and the rate of the disappearance of bromine was thus calculable and found to be about 2000 times faster than in the case of iodine. The rate was much less affected than in the case of iodine by light or the nature of the solvent. There was no increase in rate comparable with that exhibited by dry solutions of iodine with increasing concentrations of phosphorus. We do not attempt to formulate any mechanism for the reaction.

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