645. *The Formation of Phenyl Radicals from Tetraphenyl-lead.*

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Tetraphenyl-lead reacts with silver nitrate in benzene–ethanol at about 60° to give metallic silver, triphenyl-lead nitrate, and phenyl radicals. Investigation of the products of the reaction shows that most of the phenyl radicals remove hydrogen from the ethanol, while a small proportion dimerise or react with benzene, to form diphenyl. The reaction is bimolecular, with a a temperature coefficient of $\sim$18,500 cal./mole and a temperature-independent factor of $\sim 10^{10}$ l. mole^{-1} sec.$^{-1}$.

THE object of the present work was to investigate the reaction between silver nitrate and tetraphenyl-lead, as a means of producing phenylsilver and hence free phenyl radicals in solution. The preparation of phenylsilver has several times been reported, but the products do not seem to have been well characterised. Thus, yellow solids of composition $AgPh_2,AgNO_3$ have been obtained by the action of excess of silver nitrate in ethanolic solution on triphenylbismuth [1] and on ethyltriphenyl-lead.[2] These solids were said to decompose, when warmed, into silver nitrate, silver, and diphenyl, and to be fairly soluble in benzene. Products claimed to be essentially phenylsilver were obtained by Reich [3] and by Krause and Wendt [4] by the action of phenylmagnesium bromide on silver chloride in ethereal suspension at a low temperature, but were unstable even at room temperature, and barely soluble in benzene. Gilman and Straley [5] used the same method and, without isolating the product, showed that the reaction mixture gave phenyl radicals, which reacted either with each other or with added reagents. Gilman and Woods [6] caused silver nitrate to react with tetraphenyl-lead in ethanolic suspension, and obtained metallic silver and a good yield of diphenyl.

The reaction between lead tetra-alkyls and silver nitrate in ethanolic solution has been investigated by Semerano and Riccoboni [7] and by Bawn and Whitby.[8] They have shown that the silver alkyl is first formed by a rapid electron-transfer, $PbR_4 + Ag^+ \longrightarrow AgR + PbR_3^+$, and later decomposes slowly by a unimolecular mechanism to give free alkyl radicals and metallic silver. These reactions occur below room temperature and provide a convenient source of free alkyl radicals in solution. Glockling [9] recently described similar experiments with *iso*but-1-enyltriethyl-lead. When lead tetra-alkyls react with cupric nitrate, however, cupric alkyls cannot be isolated [8] but free radicals are produced, presumably by the reaction : $Cu^{++} + PbR_4 \longrightarrow Cu^+ + PbR_3^+ + R\cdot$.

In the present work, the reaction between silver nitrate and tetraphenyl-lead in dilute solution was analogous to that between lead tetra-alkyls and cupric nitrate, in that metallic silver and phenyl radicals are produced, although phenylsilver cannot be separated from the reaction mixture.

EXPERIMENTAL

" AnalaR " silver nitrate was used without further purification. Tetraphenyl-lead was prepared by the action of lead chloride on phenylmagnesium bromide [10] and purified by re-crystallisation from benzene. Ethyl alcohol and benzene were dried in the usual way; in addition, the alcohol was refluxed with potassium hydroxide and silver nitrate and then distilled, in order to remove any acetaldehyde.

No single common solvent for silver nitrate and tetraphenyl-lead could be found, and it was therefore necessary to use a mixture of ethyl alcohol and benzene. Because of the low solubility

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[1] Challenger *et al.*, *J.*, 1921, **119**, 817; 1922, **121**, 104; 1934, 405.
[2] Krause and Schmidt, *Ber.*, 1919, **52**, 2150.
[3] Reich, *Compt. rend.*, 1923, **177**, 322.
[4] Krause and Wendt, *Ber.*, 1923, **56**, 2064.
[5] Gilman and Straley, *Rec. Trav. chim.*, 1936, **55**, 821.
[6] Gilman and Woods, *J. Amer. Chem. Soc.*, 1943, **65**, 435.
[7] Semerano and Riccoboni, *Ber.*, 1941, **74**, 1089, 1297; *Z. phys. Chem.*, 1941, **189**, *A*, 203.
[8] Bawn and Whitby, *Discuss. Faraday Soc.*, 1947, **2**, 228.
[9] Glockling, *J.*, 1955, 716.
[10] Gilman, *J. Amer. Chem. Soc.*, 1927, **49**, 2316.

of tetraphenyl-lead, the maximum concentration of this compound was about 0·015M. For the kinetic measurements, 25-ml. portions of an ethanolic solution of silver nitrate and of a benzene solution of tetraphenyl-lead were left to attain the temperature of a thermostat (60° unless otherwise stated). The solutions were then mixed rapidly in stoppered tubes, which were analysed after various times in the thermostat. Rapid filtration through a sintered-glass filter was followed by dissolution of the metallic silver in moderately concentrated nitric acid, and its determination by Volhard's procedure. The reaction was complete in about 24 hr. at 60°.

For the investigation of the products the mixed solutions were usually refluxed for at least 24 hr. A variation of Pozzi-Escot's steam-distillation technique[11] was developed into a moderately accurate procedure for the estimation of quantities of diphenyl of the order of 20 mg., present in about 400 ml. of solution. (The impossibility of using high concentrations, and the difficulty of handling large volumes, meant that larger quantities of diphenyl could not be expected.) The solution containing the diphenyl and other products was concentrated to 2—3 ml. by distillation, and the last traces of solvent were removed under reduced pressure. The residue was extracted three times with 3—4 ml. portions of ether, and the combined extracts were transferred to a small vessel for steam-distillation. The ether was first removed by evaporation in a stream of air, leaving diphenyl together with a small quantity of the lead-containing product. The diphenyl was now transferred by steam-distillation direct to a sintered-glass filter; after being washed with cold water, it was washed through, in ethereal solution, into another small vessel. The ether was allowed to evaporate in a stream of air, and the vessel dried to constant weight in a desiccator. In blank experiments with known weights of diphenyl, there was an average recovery of about 85%.

Products of the Reaction.—When solutions of silver nitrate and tetraphenyl-lead were mixed a yellow colour developed, which after a few minutes had deepened to black through orange and purple. This succession of colours was doubtless due to the increasing size of colloidal particles of silver. Within ½ hr., a silver mirror was usually visible on the walls of the tube, and thereafter the amount of silver continued to increase.

Phenylsilver. By analogy with the reaction between silver nitrate and tetramethyl-lead[8] the present reaction might have been expected to give phenylsilver by a rapid electron-transfer process, followed by a slow decomposition of the phenylsilver. According to previous workers, phenylsilver is quite stable at room temperature, and not very soluble in benzene. It should therefore have been possible to precipitate it by addition of excess of ethanol. However, a white precipitate which was slowly formed on addition of excess of ethanol to the reaction mixture proved to be unchanged tetraphenyl-lead. Nearly all this was, in fact, precipitated in this way, whether the ethanol was added as soon as the solutions of the reactants had been mixed, or after an interval. Moreover, when the freshly mixed solutions were evaporated under reduced pressure, the solid residue consisted almost entirely of unchanged silver nitrate and tetraphenyl-lead. Attempts were also made to prepare solid phenylsilver, according to directions given in the literature.[3,4] The products, however, were all insoluble in alcohol–benzene. These facts exclude the formation of phenylsilver by a rapid reaction, and indicate that the reaction may be either

$$\mathrm{Ag^+NO_3^- + PbPh_4 \xrightarrow{\text{Slow}} PbPh_3^+NO_3^- + Ag + C_6H_5\cdot} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\left.\begin{array}{r}\mathrm{Ag^+NO_3^- + PbPh_4 \xrightarrow{\text{Slow}} PbPh_3^+NO_3^- + AgPh}\\ \mathrm{AgPh \xrightarrow{\text{Fast}} Ag + C_6H_5\cdot}\end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The two-stage scheme (2) is mechanistically more probable than the reaction (1). However, the relative merits of these alternatives will not be discussed further, since kinetic measurements cannot distinguish between them.

The lead-containing product. This was isolated by evaporating the mixed solutions when the reaction was complete, and extracting unchanged tetraphenyl-lead with benzene. When the concentration of the mixed solution was 0·005M with respect to each reactant (as was always the case in the investigations of the products of the reaction, unless otherwise stated) the unchanged tetraphenyl-lead amounted, on the average, to about 30% of the total weight originally present. From the residue left after extraction of unchanged tetraphenyl-lead a crystalline compound was isolated, containing lead and the nitrate group in equimolecular proportions. Triphenyl-lead nitrate was made by several methods, such as the reaction between silver nitrate and

[11] Pozzi-Escot, *Bull. Soc. chim.*, 1904, **31**, 932.

triphenyl-lead bromide,[12] and it and the reaction product were shown by mixed m. p. determinations to be identical. In twelve experiments, the yield of triphenyl-lead nitrate varied between 65% and 75% of that to be expected on the basis of reaction (1) or (2) going to completion.

No evidence could be obtained for the presence of diphenyl-lead dinitrate, which might conceivably have been formed by the reaction :

$$PbPh_3{}^+NO_3{}^- + Ag^+NO_3{}^- \longrightarrow PbPh_2{}^{++}(NO_3{}^-)_2 + Ag + C_6H_5\cdot \quad . \quad . \quad . \quad . \quad (3)$$

Such a reaction, between two positive ions (or at any rate between two positively-polarised groups), is *a priori* unlikely. In fact, no separation of silver occurred when dilute solutions of silver nitrate and triphenyl-lead nitrate were mixed.

Diphenyl. The results of the diphenyl estimations, carried out as described above, were as tabulated. In the first six experiments, the total volume of the mixed solutions was 400 ml. The yields are calculated on the basis of 100% for reaction (1) proceeding to completion, and all the phenyl radicals giving diphenyl by dimerisation, and is corrected on the assumption of an 85% recovery of diphenyl in the actual estimations, as in the control experiments. Gilman and Woods[6] reported yields of diphenyl in the region of 70% from reactions in which the quantities and conditions were those of expt. 7. The discrepancy between their work and ours has not been explained, but the important point is certainly that the results of expts. 7 and 8 are not strictly comparable with those of the first six experiments. Thus, from the dilute solutions of expts. 1—6, the silver separated first as a mirror, while with the larger concentrations of expts. 7 and 8 it appeared in finely divided form throughout the reaction mixture, indicating that the reaction may then have been largely heterogeneous in character.

Expt.	Molar concn. of reactants		Wt. of diphenyl formed (g.)	Average yield (%)
1, 2	0·005		0·004, 0·005	2·3
3, 4	0·01		0·023, 0·027	9·4
5, 6	0·015		0·054, 0·051	13·0
7, 8	6·45, 2·55 g.	$PbPh_4 + AgNO_3$ refluxed in 40 ml. of EtOH or in 40 ml. of EtOH + 25 ml. of C_6H_6 for 12 hr.	0·023, 0·016	29·5, 20·0

Reactions of the phenyl radicals. Diphenyl might be formed by dimerisation of phenyl radicals or by nuclear substitution in the benzene present :

$$2C_6H_5\cdot \longrightarrow C_6H_5\cdot C_6H_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$C_6H_5\cdot + C_6H_6 \longrightarrow C_6H_5\cdot C_6H_5 + H\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Although reaction (5) seems *a priori* more likely in dilute solution, the small yields of diphenyl, increasing as the solutions become more concentrated, indicate that the dimerisation is in fact the more important reaction producing diphenyl. Most of the phenyl radicals must therefore react with the ethanol; the resulting $CH_3\cdot CH(OH)\cdot$ radicals may then dimerise to butane-2 : 3-diol or disproportionate to acetaldehyde and ethanol :

$$C_6H_5\cdot + CH_3\cdot CH_2\cdot OH \longrightarrow C_6H_6 + CH_3\cdot CH(OH)\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$2CH_3\cdot CH(OH)\cdot \longrightarrow CH_3\cdot CH(OH)\cdot CH(OH)\cdot CH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$2CH_3\cdot CH(OH)\cdot \longrightarrow CH_3\cdot CHO + CH_3\cdot CH_2\cdot OH \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Acetaldehyde. 400 ml. of the mixed solutions, 0·01M with respect to lead tetraphenyl and 0·005M with respect to silver nitrate, were refluxed. Excess of tetraphenyl-lead was used in order to minimise the possibility of reaction between acetaldehyde and unchanged silver nitrate. A stream of nitrogen was passed through the mixture, heated to 30°, thus blowing over any acetaldehyde into either an alcoholic solution of 2 : 4-dinitrophenylhydrazine or an aqueous solution of dimedone. The results were inconclusive; traces of the acetaldehyde derivatives of the test compounds were formed, but in quantities corresponding only to very small yields of acetaldehyde. It may be that some of the acetaldehyde was lost, because of its volatility, and that some reacted with silver nitrate. The latter possibility is discussed below.

Glycols. Estimations of glycol were carried out on the involatile residue from the preliminary distillations for diphenyl. This residue was extracted several times with cold water, in which any glycols should be soluble, and the other products insoluble. The aqueous extract was then treated with standard periodic acid solution (this reagent is specific for 1 : 2-glycols) and left for 15 min. (the recommended time for butane-2 : 3-diol). Excess of standard arsenite

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[12] Grüttner and Grüttner, *Ber.*, 1918, **51**, 1293.

solution was then added, and back-titrated with iodine. Blank estimations were carried out, concurrently with the actual estimations, on solutions containing no glycol. In this way it was shown that a 1 : 2-glycol was present in quantities varying between 7% and 16% of the amount to be expected if all the phenyl radicals had reacted to give this product. These figures are, of course, lower limits, since some glycol must have been lost during the preliminary distillation and, in view of the small concentrations of the solutions, this may have been a significant fraction of the total quantity present.

Metallic silver. The yield is given in the following Table, as the percentage reduction at the conclusion of the reaction, of the silver nitrate originally present. As shown, there was effectively 100% reduction of the silver nitrate when the initial concentrations were equal or when the tetraphenyl-lead was in excess. This would be expected from equation (1) if it were not for the fact that, as mentioned above, only about 70% of the tetraphenyl-lead usually reacted with silver nitrate when the initial concentrations were equal. When the initial concentration of silver nitrate was twice that of tetraphenyl-lead, and the limiting value for the percentage reduction should therefore have been 50%, the actual figures (runs 6 and 7) were 79·5% and 86·5%. Similarly, for run 8, with a four-fold excess of silver nitrate over tetraphenyl-lead, the actual percentage reduction was 47·5% compared with the limiting value of 25% expected from reaction (1). It is therefore plain that a second reaction producing silver, besides (1), must take place. This might be the reaction of silver nitrate with acetaldehyde produced as mentioned above, or with the $CH_3{\cdot}CH(OH){\cdot}$ radicals themselves:

Run	$AgNO_3$ (M)	$PbPh_4$ (M)	Reduction of $AgNO_3$ (%) at completion	k (l. mole^{-1} sec.$^{-1}$)
1	0·005	0·005	96	0·0083
2	0·01	0·01	98	0·0073
3	0·015	0·015	98	0·0083
4	0·005	0·01	100	0·0073
5	0·005	0·015	99·5	0·0069
6	0·005	0·0025	79·5	0·0087
7	0·01	0·005	86·5	0·0083
8	0·02	0·005	47·5	0·0074

$$2AgNO_3 + CH_3{\cdot}CHO + C_2H_5{\cdot}OH \longrightarrow 2Ag + CH_3{\cdot}CO_2Et + 2HNO_3 \quad . \quad . \quad (9)$$

$$2AgNO_3 + 2CH_3{\cdot}CH(OH){\cdot} \longrightarrow 2Ag + CH_3{\cdot}CO_2Et + 2HNO_3 \quad . \quad . \quad (10)$$

On this basis, each phenyl radical could give rise to a further atom of silver, and this would account for the observed yields of metallic silver and also for the non-occurrence of acetaldehyde among the products. Silver nitrate was shown to react with acetaldehyde in ethanol at concentrations of the order used in the main experiments, but it was not possible to obtain self-consistent results for the kinetics of this reaction. A further possibility is that hydrogen atoms formed by reaction (5) might react at once with silver nitrate:

$$AgNO_3 + H{\cdot} \longrightarrow Ag + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

In view of the small importance of reaction (5), however, most of the silver must have been formed through reactions (1), (9), and (10).

Summary.—It thus appears that tetraphenyl-lead and silver nitrate do not give phenyl-silver (except perhaps as a transient intermediate) in benzene–ethanol solutions of the concentrations used in the present work (~0·01M). Metallic silver and triphenyl-lead nitrate are formed and, presumably, phenyl radicals. Of the latter, not more than about 10% dimerise or react with the benzene, to give diphenyl. Most of the phenyl radicals remove hydrogen from the ethanol molecules present, and the $CH_3{\cdot}CH(OH){\cdot}$ radicals produced then either dimerise or disproportionate. Metallic silver is produced not only by reaction (1), but also by reaction of the acetaldehyde or $CH_3{\cdot}CH(OH){\cdot}$ radicals with the silver nitrate.

KINETICS OF THE REACTION

For a given temperature and given concentrations of the reactants, about twenty determinations were made of the weight of silver produced after various times; the rate curve obtained by plotting the thiocyanate titre against time was reproducible. Interpretation of these results is confused by the simultaneous occurrence of at least two silver-producing reactions. Nevertheless, the main reaction (of silver nitrate with tetraphenyl-lead) is likely to be much more important than any other in the early stages. In agreement, reasonable second-order plots were obtained from experimental results corresponding to the consumption of up to about one-third of the silver nitrate originally present; inclusion of later points produced a pronounced curvature and a markedly greater "scatter" in these plots, clearly because of the greater importance of secondary reactions in the later stages. Concentrations were varied as widely as possible, within the somewhat narrow limits set by solubility considerations and the method of silver estimation used. The figures in the foregoing Table all refer to a temperature of 60°. As shown, the second-order rate constants for different initial concentrations agree reasonably well with one another. With both reactants at initial concentrations of 0·005M, the following values of the second-order constant were obtained, at various temperatures:

T (°K)	323	328	333	338
k (l. mole^{-1} sec.$^{-1}$)	0·0035	0·0070	0·0083	0·0146

The usual plot gives a temperature coefficient of ~18,500 cal./mole for the reaction, and a temperature-independent factor of $\sim 10^{10}$ l. mole^{-1} sec.$^{-1}$.

Thus the initial process taking place between tetraphenyl-lead and silver nitrate in benzene–ethanol is the bimolecular reaction (1) or (2), giving metallic silver, triphenyl-lead nitrate, and phenyl radicals which either dimerise or react with the benzene and ethanol. Reactions (1) and (2) have been written in terms of ion-pairs, but might conceivably involve free ions: $Ag^+ + PbPh_4 \longrightarrow PbPh_3^+ + Ag + C_6H_5\cdot$, etc., even though the dissociation of silver nitrate in 0·01M-solution is estimated as not more than about 1% from the very small conductivity of the solution. The corresponding reaction between silver nitrate and lead tetra-alkyls, indeed, was stated by Semerano and Riccoboni [7] to be virtually instantaneous in ionising solvents even at −80°, but extremely slow in non-ionising solvents. The present reaction in ethanol–benzene may represent an intermediate case. In any event, it is likely that the silver ions or silver–nitrate ion-pairs will be surrounded mainly by ethanol molecules, and the tetraphenyl-lead molecules mainly by benzene molecules. The fairly high temperature coefficient and low A factor of the reaction may thus be due to some extent to the differing characters of the solvation shells of the reactants.

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