Quaternary Phosphonium and Tertiary Sulphonium Amalgams

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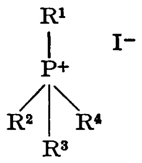
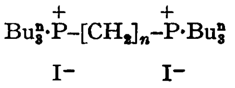
THE formation of quaternary ammonium amalgams has recently been reported by Littlehailes and Woodhall.[1] We now report that quaternary phosphonium[2] and tertiary sulphonium amalgams may be prepared,[1] by electrolysis at a mercury cathode of 1—2% solutions of the respective salts in dry, polar, aprotic, media under dry nitrogen at low temperatures.

The facts which led us to conclude that an amalgam had been formed were (i) that a residual potential existed between the mercury cathode and a standard calomel electrode when the electrolysing voltage was switched off, (ii) that hydrogen was evolved when water was added to the amalgam, and (iii) that the amalgam would transfer electrons to other molecules, *e.g.* nitrobenzene and aromatic hydrocarbons. The following compounds showed these characteristics:

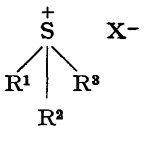


(Ia) $R^1 = R^2 = R^3 = R^4 = Me$
(Ib) $R^1 = R^2 = R^3 = R^4 = Bu^n$
(Ic) $R^1 = R^2 = R^3 = R^4 = Ph$
(Id) $R^1 = R^2 = R^3 = Ph, R^4 = Me$
(Ie) $R^1 = R^2 = Ph, R^3 = R^4 = Me$
(If) $R^1 = Ph, R^2 = R^3 = R^4 = Me$

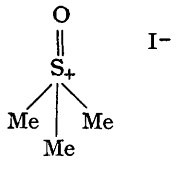


$$\underset{I^-}{Bu^n_3\cdot\overset{+}{P}}\text{–}[CH_2]_n\text{–}\underset{I^-}{\overset{+}{P}\cdot Bu^n_3}$$

(IIa) $n = 1$
(IIb) $n = 2$
(IIc) $n = 3$
(IId) $n = 4$



(IIIa) $R^1 = R^2 = R^3 = Me, X = I$
(IIIb) $R^1 = R^2 = R^3 = Bu^n, X = I$
(IIIc) $R^1 = R^2 = R^3 = Ph, X = Br$
(IIId) $R^1 = R^2 = Ph, R^3 = Me, X = PF_6$



(IV)

Moreover, with compounds (Ia), (Ib), and (IId), a black dust formed on the surface of the mercury cathode which showed the characteristics of Littlehailes and Woodhall's tetramethylammoniun amalgam, *i.e.* instability to heat, oxygen, and water.

We could not isolate these amalgams before the onset of decomposition; but we made use of their ability to transfer electrons readily to polycyclic aromatic hydrocarbons to measure the reduction potentials of the amalgams by observing the e.s.r. spectra which arose on the transfer of electrons to appropriate model compounds.[3] Values of greater than or equal to −2·7 v were obtained for all the compounds listed above which formed visible amalgams (*cf.* sodium amalgam, −2·1 v). From polarographic measurements it was concluded that one electron was transferred to each phosphonium or sulphonium cation involved in amalgam formation.

Thermal decomposition of the phosphonium amalgams gave tertiary phosphines and hydrocarbons. Decomposition of the sulphonium amalgams afforded sulphides and saturated and unsaturated hydrocarbons. No dimeric products were isolated, in either case.

Further experiments are in hand using other amalgam-forming metals.

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[1] J. D. Littlehailes and B. J. Woodhall, *Chem. Comm.*, 1967, 665.
[2] L. Horner, F. Röttger, and H. Fuchs, *Chem. Ber.*, 1963, **96**, 3141.
[3] J. Myatt and P. F. Todd, *Chem. Comm.*, 1967, 1033.