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Quaternary Ammonium Amalgams

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DESPITE a report of the existence of tetramethylammonium amalgam[1] and the postulated intermediacy in certain reactions of tetra-alkylammonium amalgams,[2] it has been generally held that the tetra-alkylammonium salts do not form compounds analogous to the Group I metal amalgams.[3]

We report the preparation and isolation of such quaternary ammonium amalgams by electrolysis of quaternary ammonium salts at a mercury cathode in dry polar aprotic media, such as acetonitrile and *NN*-dimethylformamide, under pure nitrogen at low temperatures. In our initial experiments we observed a residual potential between the mercury cathode and a saturated calomel reference electrode when the voltage was no longer applied; it was this effect which led to the conclusion that an amalgam had been formed. In a conventional divided cell we have prepared the quaternary ammonium amalgam R_4N/Hg, where R is a straight-chain alkyl group of the series methyl to n-butyl, by electrolyzing 0·1M—1M-solutions of the corresponding quaternary ammonium salt using an applied voltage of 10—20 v. This range may be extended: thus, we have also prepared quaternary ammonium amalgams from cetyltrimethyl- and dodecyltrimethyl-ammonium salts and from quaternary ammonium salts in which there are different C_1—C_4 alkyl groups.

The composition of these products were determined by colorimetric measurement of the quaternary ammonium ion formed, relative to the weight of mercury, on decomposition of the amalgam with water. The results showed one tetra-alkylammonium species to be accompanied by 12—13 mercury atoms, and from constant-potential electrolyses we concluded that one electron was transferred to each tetra-alkylammonium cation involved in amalgam formation.

Furthermore, preliminary stoicheiometric measurements indicate that solvent may be incorporated in the amalgam. The tetramethylammonium amalgam has been shown by *X*-ray powder photographs to be crystalline in nature and to the naked eye appears in the form of many-faceted dendrites.

These compounds are unstable to heat, to oxygen, and to water, and we have shown that they transfer electrons readily to suitable organic substrates such as activated olefins, polycyclic aromatics, and alkyl halides. We have measured a range of reduction potentials from $-2·2$ to $-2·7$ v in the series tetramethyl to tetra-n-butyl by observing the e.s.r. spectrum which arises on the transfer of electrons to appropriate model compounds.

In addition to the direct electrolytic preparation we have made the amalgams by metathesis with sodium amalgam as shown:

$$Na/Hg + R_4N^+X^- \rightarrow R_4N/Hg + Na^+X^-$$

In media in which the sodium halide produced is insoluble, conversions of up to 50% have been obtained.

We are continuing our work on these compounds and are extending our studies to analogous systems such as those given by phosphonium, sulphonium, and oxonium compounds.

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