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DI(*n*-OCTYL)ARSENIC ACID (DOAA) AS A REAGENT FOR LIQUID-LIQUID EXTRACTION – I

EXTRACTION OF MINERAL ACIDS

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Abstract – Solutions of dioctylarsinic acid (DOAA), $(n\text{-}C_8H_{17})_2AsOOH$, in chloroform have been equilibrated with aqueous solutions of perchloric, hydrochloric, hydrobromic, nitric, sulfuric and hydriodic acids. The loading experiments with perchloric acid indicate that $0{\cdot}1\,M$ DOAA, after equilibration with $HClO_4$ of initial concentration $5M$–$9M$, forms a dimeric specie $(DOAA{\cdot}HClO_4)_2$. Except for sulfuric and hydriodic acids, the loading curves for the other mineral acids are similar to the curve for $HClO_4$ with well defined plateaus at equimolar ratios of $[H^+]_0/[DOAA]_0$ in the range of initial aqueous acid concentration from about $3M$–$7M$. Reagent dependence studies showed that the mineral acids formed 2:1 adducts with DOAA at $0{\cdot}1\,M$ aqueous acid concentrations. Sulfuric acid was not extracted at this concentration, but formed a mixture of 2:1 and 2:2 adducts between $0{\cdot}5\,M$ and $1{\cdot}0\,M$ aqueous acid. Hydriodic acid reacted with DOAA. Water was coextracted with all mineral acids and the concentration of water in the organic phase decreased at aqueous acid concentrations greater than $6\,M$.

INTRODUCTION

VARIOUS organic arsenic compounds have been investigated as reagents for the liquid-liquid extraction of metal ions during the past decade[1–6]. Pietsch *et al.* [3, 7] have studied the extraction of many metal ions by water-soluble dialkylarsinic and alkylarsonic acids and found that the extraction efficiency increased with increasing chain length[8]. Long chain dialkylarsinic acids have become available only recently[9]. The amphoteric character of these arsinic acids has long been known[10]. In most cases mineral acids are therefore coextracted with the metal ions. This behavior of arsinic acids towards mineral acids has been mentioned in the literature[11], but has not been thoroughly investigated. We have, therefore, undertaken a detailed study of the extraction of perchloric, hydrochloric, hydrobromic, nitric and sulfuric acids by dioctylarsinic acid in chloroform solution. These data will be used to find the best conditions for the extraction of metal ions and should lead to a better understanding of the extraction process involving DOAA, mineral acids and transition metal ions in two phase systems.

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EXPERIMENTAL

Materials

Dioctylarsinic acid (DOAA) was prepared in 81 per cent yield by the method described by Irgolic *et al.*[9] and purified by recrystallization from ethanol/water. Solutions of DOAA in ethanol-free chloroform pre-equilibrated with water were prepared shortly before they were used to avoid complications from the decomposition of the ethanol-free diluent. The concentrations of the DOAA solutions were checked by base titration.

Reagent grade chloroform (1 l.) was shaken ten minutes with 250 ml of concentrated sulfuric acid. The separated organic phase was washed several times with distilled water until both phases became clear and neutral to litmus paper. After standing for 1 hr, the two phases were carefully separated.

The reagent grade mineral acids were purchsed from J. T. Baker Chemical Company (HCl, 37·2%; HBr, 48·2%; HNO_3, 70·2%; H_2SO_4, 96·8%) and Mallinckrodt Chemical Company ($HClO_4$, 60%). Karl Fischer Reagent, SO-K-3, standardized with reagent grade disodium tartrate dihydrate, was used for all water determinations.

Procedure

Equal volumes (usually 5 ml) of aqueous mineral acid solutions were shaken with solutions of DOAA in ethanol-free chloroform for 30 minutes at room temperature in 35 ml centrifuge tubes. After centrifugation, a 2 ml aliquot of the organic phase was diluted with 95 per cent ethanol and titrated with sodium hydroxide using phenolphthalein as indicator. A second 2 ml aliquot was used for the water determination. All computations were done on a Model 2115-A Hewlett-Packard computer.

Reaction between DOAA and dry HCl

Dry HCl gas was passed over solid DOAA until constant weight was attained. The liquid product was dried over anhydrous Na_2SO_4 and then vacuum distilled. Two fractions boiling at 36°/3 mm ($C_8H_{17}Cl$) and 100°/3 mm ($C_8H_{17}AsCl_2$) were collected:

$C_8H_{17}Cl$, calcd. (found): C, 64·60 (63·15); H, 11·54 (11·09); Cl, 23·86 (23·42).

$C_8H_{17}AsCl_2$, calcd. (found): C, 37·07 (37·77); H, 6·62 (6·59); Cl, 27·38 (27·25).

Synthesis and isolation of $(CH_3)_2AsOOH{\cdot}HCl$

Equal volumes of 0·2 *M* cacodylic acid in 95 per cent ethanol and 0·5 *M* HCl in 95 per cent ethanol were equilibrated by shaking for 15 min. The solution was evaporated in an oil bath at 90°C. The solid residue was washed with dry ether and absolute alcohol and dried in a vacuum desiccator over anhydrous $CaSO_4$ for 48 hr. The crystalline product had a melting point of 75°C.

$(CH_3)_2AsOOH{\cdot}HCl$, calcd. (found): Cl, 20·34% (20·12%, 19·98%);
neutralization equivalent, 87·25 (91·88, 89·94); water by Karl Fischer according to equation (3), 2 mole (1·78, 1·80 mole).

Molecular formula determination at loading

Equal volumes of 5·5 *M* $HClO_4$ and 0·10 *M* DOAA in chloroform were equilibrated. After centrifugation an aliquot of the organic phase was titrated with base. Perchloric acid and DOAA were present in equimolar amounts. Analysis of the organic phase using a Model 302-B Hewlett-Packard vapor pressure osmometer gave an average concentration of 0·0460 *M*; [0·0500 *M*, calcd. for $(DOAA{\cdot}HClO_4)_2$].

DISCUSSION

Calculations and general considerations

The extraction of a mineral acid by DOAA is described by equation (1):

$$m(\mathrm{DOAA})_{2(o)} + n\mathrm{HX}_{(a)} = [(\mathrm{DOAA})_2]_m \,.\, \mathrm{HX}_{n(o)} \tag{1}$$

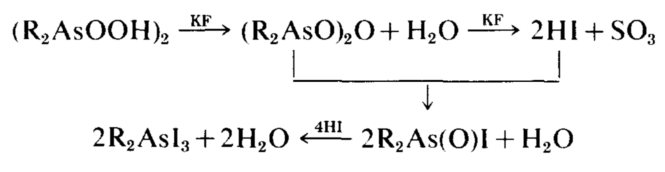
where (*o*) and (*a*) refer to the organic and aqueous phase, respectively. The $(DOAA)_2$ dimer is used in equation (1) since it was found that the dimer is the predominant species at the concentrations studied. The association constant

$K_A = 10^{+3}$ was included in all calculations to account for the monomer-dimer equilibrium.* We have calculated the concentration equilibrium quotients K for DOAA adducts of the stoichiometry $(DOAA)_2 \cdot HX$ ($m = n = 1$), $DOAA \cdot HX$ ($m = 1/2$, $n = 1$) and $(DOAA)_2 \cdot HX$ ($m = 1$, $n = 2$), and have used the constancy of K to determine the composition of the adduct. A plot of $\log E_a{}^o = \log [HX]_o/[HX]_a$ (for $m = n = 1$ and $m = 1/2, n = 1$) and $\log P_a{}^o = \log E_a{}^o/2[HX]_a$ (for $m = 1$, $n = 2$) versus the logarithm of the uncomplexed $(DOAA)_{2(o)}$ or $DOAA_{(o)}$ gave straight lines whose slopes gave additional evidence for the stoichiometry of the extracted species. It is not possible to decide on the basis of the extraction data whether the DOAA monomer or dimer is the actual extracting agent. However, it was established by means of molecular formula determinations with chloroform solutions containing equimolar amounts of DOAA and $HClO_4$ that the adduct in the organic phase is the dimeric species $(DOAA \cdot HClO_4)_2$. The strongly hydrogen bonded arsinic acids[9, 12] do not dissociate upon formation of adducts with mineral acids, as expected. The adducts are therefore formulated with dimeric $(DOAA)_2$ in the following discussion.

Attempts were made to determine independently the concentration of uncomplexed DOAA after equilibration with mineral acids. Both n.m.r. and i.r. techniques failed to give the desired information because of the limited solubility of DOAA in chloroform and the problems encountered in assigning the frequencies to the various types of hydroxyl groups present in the system.

Coextraction of water

The determination of coextracted water was complicated by the solubility of water in chloroform and by the reaction of DOAA with Karl Fischer reagent. The solubility of water in chloroform was found to be 0·088 mole/l., which compares well to the literature value of 0·083 mole/l.[13], and was assumed to remain constant. Chloroform solutions of DOAA titrated with Karl Fischer reagent (KF) showed that a volume of reagent equivalent to 2 mole of water per mole of DOAA was consumed. We propose the following stoichiometry for this reaction:



$$\begin{array}{c}(R_2AsOOH)_2 \xrightarrow{KF} (R_2AsO)_2O + H_2O \xrightarrow{KF} 2HI + SO_3 \\ \downarrow \\ 2R_2AsI_3 + 2H_2O \xleftarrow{4HI} 2R_2As(O)I + H_2O\end{array} \qquad (2)$$

Triiododialkyl derivatives of arsenic are unknown[14], and when formed as intermediates probably dissociate under these conditions into I_2 and R_2AsI[15], so that the overall reaction (3) produces 2 mole of water per mole of arsinic acid.

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* A detailed description of the association of dialkylarsinic acids will be published later.

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$$(R_2AsOOH)_2 \xrightarrow{KF} I_2+2R_2AsI+4H_2O \qquad (3)$$

It was necessary to isolate an adduct having equimolar amounts of reagent and mineral acid to see whether the complexed reagent is also reactive towards Karl Fischer solution. The $(DOAA\cdot HCl)_2$ adduct formed a gummy residue which could not be crystallized. We were, however, able to isolate and purify the crystalline $(CH_3)_2AsOOH\cdot HCl$ adduct. This compound consumed Karl Fischer reagent approximately equivalent to two moles of water. Water in the DOAA case was therefore calculated by subtracting the amount of water found in a DOAA/$CHCl_3$ solution blank from the total amount of water detected in the organic phase after equilibration with the appropriate mineral acid. The results of the coextraction of water are summarized in Fig. 1, where the ratio of coextracted water to mineral acid in the organic phase is plotted as a function of the initial aqueous mineral acid concentration. The molar ratios $[H_2O]_o/[H^+]_o$ remain fairly constant from 2·0 *M* to 5·5 *M* initial aqueous acid concentrations. This shows that over this concentration range one to two moles of water enter the organic phase with each mole of mineral acid. The low values obtained with hydrochloric acid are perhaps indicative of the more covalent character of the HCl adduct as compared to the proposed ion-pair structure of the other species. The smaller ratios at acid concentrations greater than 6 *M* are caused by the lower activity of water in the concentrated aqueous mineral acid solutions. At low mineral acid concentrations, the high ratios obtained have a large uncertainty since the volume of base consumed by the extracted mineral acid was obtained as the small difference between the relatively large base volumes corresponding to the base consumption caused by DOAA and DOAA and mineral acid together.

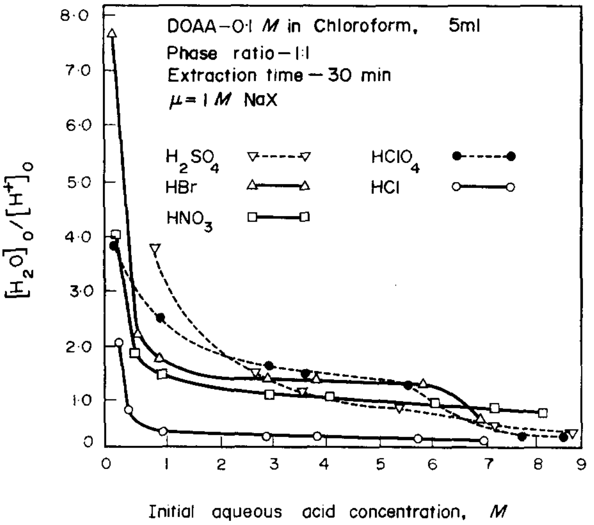

Fig. 1. Extraction of water by dioctylarsinic acid as a function of acid concentration.

Extraction of mineral acids

The concentration equilibrium quotients, K and the least squares slopes of the reagent dependence plots are listed in Table 1. Each concentration equilibrium quotient reported is an average of 5–10 K values, and an absolute deviation is shown for each concentration equilibrium quotient. The loading experiments are summarized in Figs. 2 and 3. The only reagent dependence plot included (Fig. 4) is the one for $HClO_4$. All the others are similar.

Perchloric, hydrochloric and hydrobromic acid are extracted about equally well at initial acid concentrations $\geqq 1\,M$. Sulfuric acid shows a lesser tendency to enter the organic phase, while nitric acid is extracted to a greater extent. At 0·1 *M* acid concentration perchloric and nitric acid extract much better than hydrochloric and hydrobromic acid, while sulfuric acid does not react at all with DOAA.

The K values for the 2:1 complexes at 0·1 *M* acid concentration have a large uncertainty since the volumes of base consumed by the extracted mineral acid were obtained as the small difference between relatively large base volumes corresponding to the base consumption caused by DOAA and DOAA and mineral acid together. A mixture of 2:1 and 2:2 complexes was found for 0·5–1·0 *M* H_2SO_4 in which about 90 per cent of the reagent is complexed as the 2:1 complex. The K values for the 2:1 complex at 0·5 and 1·0 *M* H_2SO_4 were calculated by assuming a K value of 0·135 (the average of K's found for 3·0 *M*

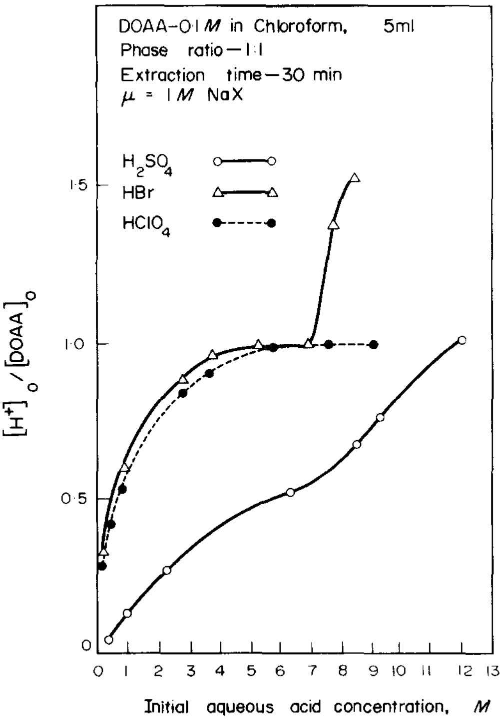

Fig. 2. Extraction of mineral acids by dioctylarsinic acid as a function of acid concentration.

Table 1. Concentration equilibrium quotients, K, for the extraction of mineral acids as a function of the $(DOAA)_2$ concentration in the range 0·01–0·1 *M* K (absolute deviation)

Mineral Acid Molarity	0·1 *M*	0·5 *M*		1 *M*		2 *M*	3 *M*	5 *M*
Type of Complex	(2:1)	(2:1)	(2:2)	(2:1)	(2:2)	(2:2)	(2:2)	(2:2)
$HClO_4$	23·98 ± 4·76 1·06*	—	—	—	1·25 ± 0·14 0·94*	0·54 ± 0·08 1·05*	0·67 ± 0·04 1·02*	—
HCl	3·91 ± 0·66 1·18*	—	—	—	1·64 ± 0·18 1·02*	0·75 ± 0·07 1·10*	0·92 ± 0·16 1·01*	—
HBr	7·44 ± 0·50 1·10*	—	—	—	1·79 ± 0·11 0·92*	0·90 ± 0·08 0·94*	1·02 ± 0·05 0·91*	—
HNO_3	24·75 ± 1·02 1·07*	—	7·75 ± 0·28 0·97*	—	5·38 ± 0·22 0·96*	8·41 ± 0·27 0·94*	—	—
H_2SO_4	(no extraction)	1·11 ± 0·05	0·135 ± 0·004	2·42 ± 0·33	0·135 ± 0·004	—	0·15 ± 0·004 1·01*	0·12 ± 0·004 1·03*

*Least squares slope.

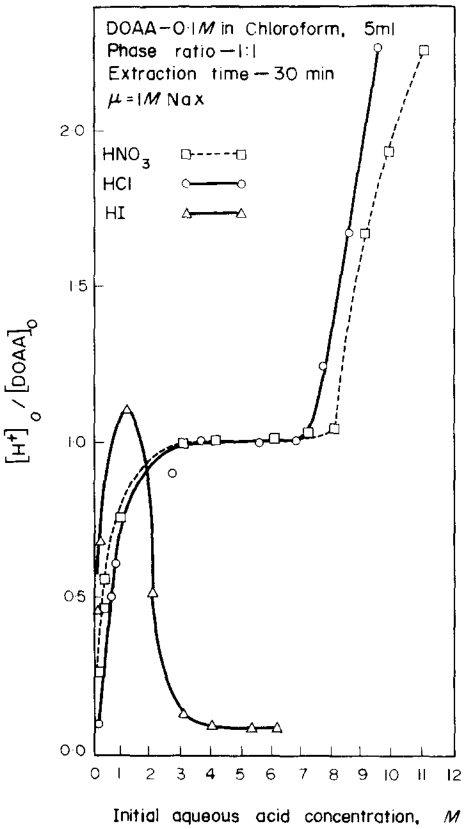

Fig. 3. Extraction of mineral acids by dioctylarsinic acid as a function of acid concentration.

and 5·0 *M* H_2SO_4) for the 2:2 complex. The trend in the K values for the 2:2 complex at mineral acid concentrations $\geqq$ 1·0 *M* indicates that at the lower concentrations the 2:2 complex is not the only species, but rather, that it is the predominant species.

$HClO_4$

The loading experiments with perchloric acid (Fig. 2) indicate that DOAA after equilibration with $HClO_4$ of initial concentrations from 5·0 to 9·0 *M* forms a dimeric specie $(DOAA{\cdot}HClO_4)_2$. With each mole of $HClO_4$ which entered the organic phase, 1·25, 0·5 and 0 mole of water were coextracted at 5·5, 7·7 and 9·0 *M* initial aqueous acid concentration, respectively. There is no evidence that $HClO_4$ reacts further with DOAA to form species with a $HClO_4$:DOAA ratio larger than one.

Reagent dependence studies using 0·1, 1·0, 2·0 and 3·0 *M* aqueous $HClO_4$ solutions and DOAA solutions less than 0·1 *M* showed a first power dependence of log $E_a{}^o$ (for the 2:1 adduct at 0·1 *M* $HClO_4$ concentration) and log $P_a{}^0$ (for the 2:2 adduct at higher concentrations) on the logarithm of uncomplexed dimeric $(DOAA)_2$ concentration (Fig. 4). The concentration equilibrium constants and the least squares slopes (Table 1) are in agreement with the adduct $(DOAA)_2 \cdot HClO_4$ at $0{\cdot}1\,M$ aqueous $HClO_4$ concentration and $(DOAA \cdot HClO_4)_2$ at concentrations greater than $1\,M$.

HCl, HBr, HNO_3 and H_2SO_4

The loading curves for HCl, HBr and HNO_3 obtained with $0{\cdot}1\,M$ DOAA solutions are similar to the curve for $HClO_4$ with well defined plateaus at 1:1 molar ratios of $[H^+]_o/[DOAA]_o$ in the range of initial aqueous acid concentration from about $3{\cdot}0$–$7{\cdot}0\,M$. Sulfuric acid does not extract well and its loading curve lacks the plateau characteristic of the other acids. The results of reagent dependence studies are summarized in Table 1.

Unlike $HClO_4$ the four acids HCl, HBr, HNO_3 and H_2SO_4 form adducts with ratios $[H^+]_o/[DOAA]_o$ greater than 1 at initial aqueous acid concentrations greater than $7\,M$. These higher ratios are caused by the presence of species containing more than one acid anion in the molecule. Reactions of arsinic acids with mineral acids to form R_2AsX_3 where X is Cl, Br, NO_3, ClO_4, etc. have been described in the literature[16–19].
The reaction (4) of DOAA with gaseous HCl was strongly exothermic[20].

$$R_2AsOOH \xrightarrow{HCl} R_2As(OH)_2Cl \xrightarrow{HCl} R_2As(OH)Cl_2 \xrightarrow[-H_2O]{+HCl} R_2AsCl_3 \qquad (4)$$

$$R_2AsCl_3 \xrightarrow{heat} RCl + RAsCl_2$$

The intermediate compounds which account for the higher acid to DOAA ratios in the extraction experiments were not isolated. Only the end products water, octyl chloride and octyldichloroarsine were identified.

HI

Only loading studies were performed with hydriodic acid. Increasing yellowish to brownish discoloration of both the aqueous and organic phases was observed upon equilibration of DOAA solutions with aqueous HI solutions of increasing concentration. The increasing discoloration[21, 22] with increasing HI concentration may be due to liberation of I_2 as is shown in reaction (3).

As is shown in Fig. 3, the ratio $[H^+]_o/[DOAA]_o$ increased to a value slightly larger than 1 at $1{\cdot}2\,M$ HI and dropped rapidly to low values at higher initial aqueous HI concentrations.

Structure of the adducts

It is reasonable to assume that the strongly hydrogen bonded $(DOAA)_2$ dimer[9] will remain hydrogen bonded in chloroform, a diluent of low dielectric

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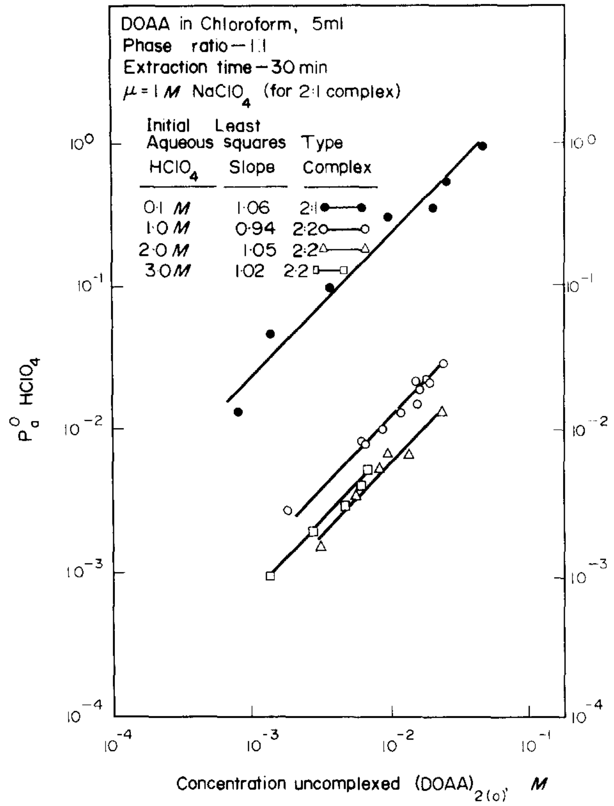
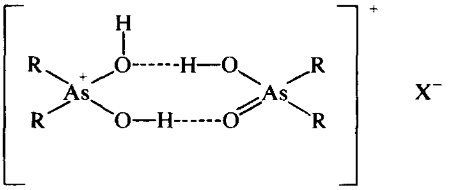
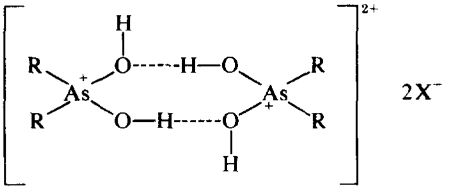


Fig. 4. Extraction of perchloric acid by dioctylarsinic acid as a function of the equilibrium concentration of uncomplexed $(\mathrm{DOAA})_{2(o)}$.

constant, even after complex formation. We propose the following structures for the 2:1 and 2:2 adducts. These adducts exist in chloroform solution probably





as ion pairs[23]. The possibility of covalent bond formation between the arsenic

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atom and the acid anion (especially in the case of the hydrochloric acid adduct) cannot be excluded. Such covalent bonding would stabilize the 2:2 adduct, which in the ionic formulation contains two positive arsonium centers in close proximity.

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