

"surface" paramagnetism. A number of writers⁴ have postulated the existence of a paramagnetic layer on the surface of many if not all solids. This postulate has been introduced to account for the small but measurable ortho-para hydrogen conversion on solids ordinarily considered to be diamagnetic. Although small, such conversion is greater than can be accounted for by the influence of nuclear spins. The reason why the surface layer of atoms should be paramagnetic has never been explained, nor has any direct relationship been reported between the surface of a powder and its supposed paramagnetism. The present experiments establish that relationship in a qualitative way because the crystalline lanthanum sulfate has obviously much less surface than either the oxides or the oxalate. The sulfate shows the smallest temperature coefficient of susceptibility. A possible mechanism for the effect may be the dropping of an electron back into the 4f shell in the surface atoms only. It seems not impossible that the high electric dissymmetry of the surface could achieve what ordinary chemical reducing agents cannot. A somewhat parallel effect has been observed¹⁰ in the case of zinc oxide. This compound has a slight temperature coefficient of susceptibility which disappears on sintering, that is, reducing the surface. The implication is clear,

(10) Turkevich and Selwood, unpublished.

therefore, that the effect described here is associated with transition group elements, but is actually observable only with the diamagnetic elements at the beginning or end of a transition group. This will be true because the "surface" paramagnetism is at best small, and will be completely masked by the large normal paramagnetism of those elements actually members of a transition group. The effect should be shown by compounds of the following elements, besides those already named: cadmium, mercury, scandium, yttrium, and lutecium. Sufficiently accurate data on these elements are not yet available for an adequate test of this prediction.

Summary

Accurate measurements of magnetic susceptibility at 20 and -150° have been made on the compounds $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, and La_2O_3 , the last-named being prepared in two different ways. A slight residual paramagnetism was observed in all cases. The possible causes of this phenomenon are examined. It is suggested that this work constitutes direct observation of the so-called "surface" paramagnetism which has been postulated to explain the small ortho-para hydrogen conversion on supposedly diamagnetic surfaces.

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Arsonium Compounds. II^{1,2}

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Some time ago the discovery was made by one of us (H. H. W.) that tetraphenylarsonium chloride³ is a unique and very valuable analytical reagent. It serves for the quantitative precipitation of perrhenate, periodate, perchlorate, permanganate and other anions. As far as the authors are aware tetraphenylarsonium permanganate is the only insoluble permanganate known. Tetraphenylarsonium chloride is useful also in the determination of zinc, cadmium, mercury, gold, platinum and other metals.^{4,5}

(1) Paper I, Blicke and Cataline, *THIS JOURNAL*, **60**, 423 (1938).

(2) This investigation was made possible by a grant from the Faculty Research Fund of the University of Michigan.

(3) Blicke and Monroe, *THIS JOURNAL*, **57**, 722 (1935).

(4) A full account of the analytical applications of the arsonium chloride will be published soon by Willard and Smith.

(5) Other organic arsenicals which have found application in

The preparation of tetraphenylarsonium chloride,⁶ while not especially difficult, is more labori-

analytical chemistry are arsonic acids. Thus, phenylarsonic acid has been used for the determination of zirconium and thorium by Rice, Fogg and James [*THIS JOURNAL*, **48**, 895 (1928)]; for zirconium by Klinger and Schliessmann [*Arch. Eisenhüttenw.*, **7**, 113 (1933)] and for tin by Knapper, Craig and Chandlee [*THIS JOURNAL*, **55**, 3945 (1933)]. Tougarinoff [*Bull. soc. chim. Belg.*, **45**, 542 (1936)] used nitrophenylarsonic acid for the estimation of tin. Iron has been determined with the aid of *p-n*-butylphenylarsonic acid by Craig and Chandlee [*THIS JOURNAL*, **56**, 1278 (1934)]; Arnold and Chandlee [*ibid.*, **57**, 8 (1935)], as well as Geist and Chandlee [*Ind. Eng. Chem., Anal. Ed.*, **9**, 169 (1937)], have used *n*-propylarsonic acid for zirconium; see also Chandlee, *THIS JOURNAL*, **57**, 591 (1935). Recently the use of *p*-hydroxyphenylarsonic acid as a reagent for titanium and zirconium has been described by Simpson and Chandlee [*Ind. Eng. Chem., Anal. Ed.*, **10**, 642 (1938)]. Feigl, Krumholz and Rajmann [*Mikrochemie*, **9**, 395 (1931)] have used *p*-dimethylaminoazophenylarsonic acid for the detection of zirconium and Bullard [*J. Chem. Education*, **14**, 312 (1937)] described the use of phenylarsonic acid in the qualitative test for tin.

(6) This reagent can be purchased from Merck and Company.

TABLE I
 ARSONIUM HALIDES AND NITRATES

	Arsonium halide	Prepared from	M. p., °C.	Formula	% As		% Halogen		
					Calcd.	Found	Calcd.	Found	
1	Allyltriphenylarsonium bromide	Triphenylarsine and allyl bromide	180-181	C ₂₁ H ₃₀ AsBr	17.56	17.29	Br	18.73	
2	Allyltriphenylarsonium iodide	Allyltriphenylarsonium bromide and potassium iodide	163-164	C ₂₁ H ₃₀ AsI	15.82	15.86	I	26.77	
3	<i>p</i> -Nitrobenzyltriphenylarsonium bromide	Triphenylarsine and <i>p</i> -nitrobenzyl bromide	160-162	C ₂₅ H ₂₇ O ₂ NAsBr	14.36	14.35	Br	15.32	
4	<i>p</i> -Bromophenacyltriphenylarsonium bromide	Triphenylarsine and <i>p</i> -bromophenacyl bromide	170-171	C ₂₆ H ₂₅ OAsBr ₂	12.84	12.95	Br	27.39	
5	Triphenylbromoarsonium malonic ester	Triphenylarsine and ethyl bromomalonate	169-171	C ₂₃ H ₂₆ O ₄ AsBr	13.76	13.34	Br	14.68	
6	Benzyltriphenylarsonium iodide	Triphenylarsine and benzyl iodide	156-157	C ₂₅ H ₂₈ AsI	14.31	14.58	I	24.22	
7	Benzyltriphenylarsonium chloride	Benzyltriphenylarsonium iodide and silver chloride	180-181	C ₂₅ H ₂₈ AsCl	17.34	17.52	Cl	8.20	
8	Allyltriphenylarsonium bromide	Triphenylarsine ^e and allyl bromide	180-182	C ₂₆ H ₂₆ AsBr	15.99	16.08	
9	Benzylidiphenyl- α -naphthylarsonium iodide	Diphenyl- α -naphthylarsine ^b and benzyl iodide	171-172	C ₂₆ H ₂₄ AsI	13.07	13.45	I	22.11	
10	Allyltriphenylarsonium bromide	Triphenylarsine ^e and allyl bromide	264-266	C ₂₆ H ₂₆ AsBr	11.45	11.15	Br	12.21	
Arsonium nitrate									
11	Tetraphenyl	Tetraphenylarsonium bromide ^d and nitric acid	259-261 ^f	C ₂₄ H ₂₀ O ₄ NAs	16.83	16.59	
12	Iodomethyltriphenyl	Iodomethyltriphenylarsonium iodide ^e and nitric acid	189-190	C ₁₉ H ₁₇ O ₃ NAsI	14.73	14.53	I	24.93	
13	Benzyltriphenyl	Benzyltriphenylarsonium iodide and nitric acid	178-180	C ₂₅ H ₂₂ O ₃ NAs	16.34	16.77	
14	Methyltriphenyl	Methyltriphenylarsonium iodide ^e and nitric acid	131-133 ^g	C ₁₉ H ₁₈ O ₂ NAs	19.58	19.76	
15	β -Hydroxyethyltriphenyl	β -Hydroxyethyltriphenylarsonium chloride ^e and silver nitrate	138-140	C ₂₀ H ₂₆ O ₄ NAs	18.16	17.77	
16	Allyltriphenyl	Allyltriphenylarsonium bromide and silver nitrate	140-148	C ₂₁ H ₃₀ O ₂ NAs	18.33	18.42	

^a Michaelis and Paetow, *Ber.*, **18**, 41 (1885). ^b Blicke and Cataline, *Trans* different method Blicke and Cataline [*Trans* JOURNAL, **60**, 423 (1938)] found 260-260-
 JOURNAL, **60**, 421 (1938). ^c Worrall, *ibid.*, **52**, 665 (1930). ^d Blicke and Monroe, 262°. ^e Michaelis [*Ann.*, **321**, 169 (1902)] obtained this nitrate by a different
^f *ibid.*, **57**, 721 (1935). ^g Michaelis, *Ann.*, **321**, 166-174 (1902). ^h Prepared by a procedure but did not report a melting point.

ous than that of a number of alkyltriphenylarsonium halides which can be obtained merely by allowing triphenylarsine and an alkyl halide to react at an elevated temperature. Consequently, it was considered advisable to determine whether or not any arsonium compounds of the alkyltriphenyl type could serve as satisfactory analytical reagents.

An investigation of the following compounds—iodomethyltriphenylarsonium chloride,⁷ phenacyltriphenylarsonium chloride,⁷ allyltriphenylarsonium bromide, β -hydroxyethyltriphenylarsonium chloride,⁷ methyltriphenylarsonium chloride,⁷ and carboxymethyltriphenylarsonium chloride⁷ showed that although, in general, the reactions are somewhat similar to those of tetraphenylarsonium chloride, none of these compounds reacted quantitatively with iodine or with the perchlorate, perrhenate or chlorocadmiate ions.

A number of new arsonium halides and nitrates which have been prepared are listed in Table I. The nitrates were obtained by warming a mixture of the arsonium bromide or iodide with concentrated nitric acid until all of the liberated halogen had been volatilized or by treatment of an aqueous solution of the arsonium chloride or bromide with a solution of silver nitrate.

By means of simple modifications we have been able to shorten the procedure described previously⁸ for tetraphenylarsonium chloride and have improved the yield.

Experimental Part

Arsonium Halides.—The arsine was heated with two to three times

(7) Michaelis, *Ann.*, **321**, 168-179 (1902).

the calculated amount of the required halogen compound for at least twenty-four hours on a steam-bath and the cold product then washed with ether. If the materials were solids which did not melt below steam-bath temperature absolute ether was used as a solvent; in this case the arsonium compound separated, gradually, from the solution.

Allyltriphenylarsonium iodide precipitated when potassium iodide solution was added to 1 g. of allyltriphenylarsonium bromide dissolved in 25 cc. of water.

To obtain benzyltriphenylarsonium chloride 10 g. of the corresponding arsonium iodide, 20 g. of freshly precipitated silver chloride and 400 cc. of water were refluxed for twenty-four hours, the mixture filtered and the filtrate evaporated to dryness on a steam-bath.

In order to purify the arsonium halides and nitrates the products were dissolved in the least possible amount of absolute alcohol and precipitated by the addition of absolute ether.

Arsonium Nitrates.—The procedures used are illustrated below.

Three grams of iodomethyltriphenylarsonium iodide was warmed with 10 cc. of concd. nitric acid until all of the iodine had been evolved. The solution was then heated to dryness on a steam-bath, the crystalline residue dissolved in the smallest possible amount of absolute alcohol and absolute ether added until the iodomethyltriphenylarsonium nitrate began to precipitate.

Ten grams of allyltriphenylarsonium bromide dissolved in 300 cc. of warm water was stirred and 3.5 g. of silver nitrate, dissolved in 100 cc. of the same solvent, was added slowly. The mixture was heated for a short time and then silver nitrate solution added, dropwise, until no more silver bromide precipitated. The mixture was filtered and the filtrate evaporated to dryness.

Tetraphenylarsonium Chloride.—Phenylmagnesium bromide was prepared from 30 g. of magnesium, 135 cc. of bromobenzene and 600 cc. of ether in a 5-liter three-necked flask fitted with a reflux condenser and a stirrer which passed through a mercury seal.

After 1 liter of dry benzene had been poured into the solution of the Grignard reagent, 120 g. of thoroughly dry triphenylarsine oxide was added, in four portions, during the course of four hours and the viscous mass on the bottom

of the flask was *stirred thoroughly* until all of the oxide had disappeared; this usually required about three hours.

The ether-benzene layer was decanted from the viscous oil, the latter washed with 200 cc. of benzene and 1 liter of water was then added, slowly, while the oil was stirred with a stirring rod. After thorough trituration hydrochloric acid (about 300 cc.) was added until all of the white solid, which had formed upon addition of the water, had disappeared. The small amount of benzene-ether usually present was removed and the mixture cooled, whereupon the oily product gradually became crystalline; it was filtered and dried; yield 128 g.

The aqueous, acidic filtrate was treated with sodium hydroxide until it was only slightly acidic and any tetraphenylarsonium halide which precipitated at this stage was removed by filtration. The solution, the volume of which was about 2 liters, was boiled with charcoal, filtered and enough solid sodium chloride added to almost saturate the boiling solution; about 300 g. was required. A small amount of the arsonium chloride, usually about 10 g., precipitated when the solution was cooled and the container scratched.

In order to purify the crude arsonium chloride, which contained some bromide, it was dissolved in approximately 1600 cc. of hot water, solid sodium chloride added (about 300 g.) until the hot solution was almost saturated and the solution then cooled; total yield 138 g. or 86% of the calcd. amount; m. p. 255–257°.⁸

Summary

A number of new arsonium halides and nitrates have been described. It has been found that alkyltriphenylarsonium halides, as far as they have been investigated by us, are not satisfactory substitutes for the valuable analytical reagent tetraphenylarsonium chloride.

An improved procedure has been described for the preparation of tetraphenylarsonium chloride.

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(8) Ref. 3. The melting point reported is 256–257°.