transition with rising temperature. In this connection many cases are cited which conflict with the Ostwald rule.

(7) The nuclear hypothesis has been shown to afford a simple explanation of the phenomena described.

STANFORD UNIVERSITY, CAL., December 1905.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

ARSONIC AND ARSINIC ACIDS.

BY WILLIAM M. DEHN AND S. J. MCGRATH.

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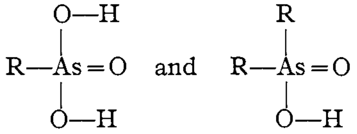
ARSONIC acids may be considered as derived from arsenic acid, $AsO(OH)_3$, by replacing one of the hydroxyl groups by a univalent hydrocarbon or substituted hydrocarbon radicle; thus the arsonic acids have the general formula $R—AsO(OH)_2$. Arsinic acids may be considered dialkyl or dialphyl substitution-products of arsenic acid and have the general formula RR′AsOOH, wherein R and R′ are any two univalent hydrocarbon radicles. All of the arsinic acids hitherto prepared have the two radicles identical, except phenyl-*p*-toluylcacodylic acid.[1] The arsinic acids are, of course, homologues of cacodylic acid and are therefore frequently termed cacodylic acids—for instance phenylarsinic acid is also known as phenylcacodylic acid.

The structural formulas usually assigned to the arsonic and arsinic acids are:



$$\begin{array}{c} O—H \\ | \\ R—As=O \\ | \\ O—H \end{array} \quad \text{and} \quad \begin{array}{c} R \\ | \\ R—As=O \\ | \\ O—H \end{array}$$

The best proof of the direct union[2] of the radicles with arsenic is seen in their reduction to the corresponding arsines,[3] which unquestionably contain the radicles in direct union with arsenic:

$$RAsO_3H_2 + 6H = RAsH_2 + 3H_2O$$
$$R_2AsOOH + 4H = R_2AsH + 2H_2O.$$

The possibility here of molecular rearrangement is precluded

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[1] Ann. 321, 157.

[2] Ibid. 107, 269.

[3] Ber. 27, 1378; Am. Ch. J. 33, 104.

by the fact that the arsines spontaneously reoxidize to the respective acids:[1]

$$RAsH_2 + 3O = RAsO(OH)_2$$
$$R_2AsH + 2O = R_2AsOOH.$$

Proof of the pentavalent condition of the arsenic atoms in the arsonic and arsinic acids is seen in their stability towards oxidizing agents, as for instance toward nitric acid[2] or the halogens.[3] Whereas all soluble arsenic compounds that are known to contain trivalent arsenic easily reduce nitric acid and decolorize bromine water, the arsonic acids and the arsinic acids are indifferent toward these reagents, therefore their arsenic atoms must be held in the pentavalent condition.

The remainder of the structure of the arsonic acids and the arsinic acids is established by their basicity. The arsonic acids are dibasic,[4] and the arsinic acids are monobasic; the former possess two hydroxyls and the latter, only one. All of the facts are therefore in accordance with the above-mentioned structural formulas.

According to some recent work of Hantzsch,[5] however, conductivity measurements of methylarsinic acid (cacodylic acid) tend to show that when treated with an excess of caustic alkali, it does not react strictly as a monobasic acid, but, at least in part, as the sodium salt of a tribasic acid. His data are as follows:

			$(CH_3)_2AsO_2Na+NaOH$.		
	$(CH_3)_2AsO_2Na$.	NaOH.	By addition.	Found.	Difference.
M_1..........	56.8	202.0	258.0	232.8	25.2
M_2..........	56.8	201.9	257.9	233.1	24.8

Hantzsch concluded that in the presence of one molecule of sodium hydroxide, cacodylic acid functionates as a monobasic acid,

$$(CH_3)_2AsO_2H + NaOH = (CH_3)_2AsO_2Na + H_2O,$$

but in the presence of an excess of sodium hydroxide it forms the molecular aggregate $(CH_3)_2As(OH)(ONa)_2$, and thus cacodylic acid functionates also in the tribasic form $(CH_3)_2As(OH)_3$. This effect is very slight, however, and disappears entirely in N/48 solution.

[1] Am. Ch. J. 33, 123; 35, 9.

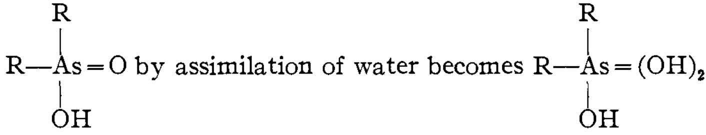
[2] Ann. 46, 9; Ibid. 208, 3, 32.

[3] Ibid. 201, 231.

[4] Ibid. 107, 290; 320, 277.

[5] Ber. 37, 1076.

This evidence is not at variance with, but is in confirmation of, the above-mentioned structural formula, that is, the formula



$\mathrm{R{-}}\underset{\substack{|\\ \mathrm{OH}}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{As}}}\mathrm{{=}O}$ by assimilation of water becomes $\mathrm{R{-}}\underset{\substack{|\\ \mathrm{OH}}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{As}}}\mathrm{{=}(OH)_2}$,

the former bearing to the latter the same relation that metaphosphoric acid does to orthophosphoric acid.

Methods of Preparation.—There is available at present only one good general method for the preparation of both arsonic and arsinic acids; *viz.*, the hydrolysis of the corresponding radicle-halogen compounds:

$$RAsCl_4 + 3H_2O = RAsO(OH)_2 + 4HCl$$
$$R_2AsCl_3 + 2H_2O = R_2AsOOH + 3HCl.$$

The first application of this general reaction was made by Baeyer in the preparation of cacodylic acid:[1]

$$(CH_3)_2AsCl_3 + 2H_2O = (CH_3)_2AsOOH + 3HCl.$$

The first application in the aromatic series was made by La-Coste and Michaelis[2] in the preparation of phenylarsonic acid:

$$C_6H_5AsCl_4 + 3H_2O = C_6H_5AsO(OH)_2 + 4HCl.$$

Modifications of the above general method are found in the oxidation of monomethylarsine dichloride by means of moist silver oxide,[3]

$$(CH_3)AsCl_2 + 2Ag_2O + H_2O = (CH_3)AsO(OH)_2 + 2AgCl + 2Ag;$$

the oxidation of *m*-xylylarsine dichloride by means of hydrogen peroxide,[4]

$$(C_8H_9)AsCl_2 + 2H_2O_2 = (C_8H_9)AsO(OH)_2 + 2HCl + O;$$

and the oxidation of primary[5] and secondary[6] arsines by atmospheric oxygen, etc.,

$$RAsH_2 + 3O = RAsO(OH)_2,$$
$$R_2AsH + 2O = RAsOOH.$$

The intermediate compounds in the preparation of arsonic and arsinic acids, *viz.*, the trivalent radicle-halogen compounds, are derived by two general reactions:

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[1] Ann. 107, 268.

[2] Ibid. 201, 202.

[3] Ibid. 107, 268.

[4] Ibid. 320, 333.

[5] Ber. 34, 3594; Am. Ch. J. 33, 124.

[6] Ber. 27, 1378; Am. Ch. J. 35, 9.

(1) The interaction of arsenic trihalides with mercury alkyl or mercury alphyl:

$$HgR_2 + 2AsCl_3 = HgCl_2 + 2RAsCl_2$$
$$HgR_2 + AsCl_3 = HgCl_2 + R_2AsCl.$$

(2) The condensation of arsenic trihalides and alkyl or alphyl monohalides by means of sodium:

$$RCl + AsCl_3 + 2Na = RAsCl_2 + 2NaCl$$
$$2RCl + AsCl_3 + 4Na = R_2AsCl + 4NaCl.$$

The first application of reaction (1) to the aromatic arsenic compounds was made by LaCoste and Michaelis[1] in the preparation of phenylarsine dichloride:

$$(C_6H_5)_2Hg + 2AsCl_3 = 2(C_6H_5)AsCl_2 + HgCl_2.$$

The first in the fatty series was made by LaCoste[2] in the preparation of ethylarsine dichloride:

$$(C_2H_5)_2Hg + 1AsCl_3 = C_2H_5AsCl_2 + C_2H_5HgCl.$$

The first application of reaction (2) to the aromatic series was made by Michaelis and Rees[3] in the preparation of triphenylarsine and its subsequent transformation to phenylarsine dichloride on heating with an excess of arsenic trichloride:

$$3C_6H_5Cl + AsCl_3 + 6Na = (C_6H_5)_3As + 6NaCl$$
$$(C_6H_5)_3As + 2AsCl_3 = 3(C_6H_5)AsCl_2.$$

The first application of reaction (2) to the fatty series was made by Dehn and Wilcox[4] in the preparation of mono- and diisoamylarsine chlorides:

$$C_5H_{11}Cl + AsCl_3 + 2Na = C_5H_{11}AsCl_2 + 2NaCl$$
$$2C_5H_{11}Cl + AsCl_3 + 4Na = (C_5H_{11})_2AsCl + 4NaCl.$$

Besides the above general methods for the preparation of arsonic and arsinic acids there are a number of special methods which are of great importance.

(1) The reaction of alkyl halides with alkali arsenites to form fatty arsonic acids:

$$As(ONa)_3 + RI = RAsO(ONa)_2 + NaI.$$

This reaction was first employed by Meyer,[5] was modified by Klinger and Kreutz[6] and was elaborated and extended by Dehn.

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[1] Ann. **201**, 196.

[2] Ibid. **208**, 33.

[3] Ber. **15**, 2876.

[4] Am. Ch. J. **35**, 48.

[5] Ber. **16**, 1440.

[6] Ann. **249**, 247.

[7] Am. Ch. J. **33**, 131.

(2) The preparation of cacodylic oxide by heating potassium acetate and arsenic trioxide:

$$4CH_3CH_2OK + As_2O_3 = ((CH_3)2As)_2O + 2CO_2 + 2K_2CO_3,$$

and its oxidation to cacodylic acid:

$$((CH_3)_2As)_2O + H_2O + 2O = 2(CH_3)_2AsOOH.$$

This reaction has not, however, yielded a single homologue of cacodylic acid.

The arsonic acids hitherto known and studied are as follows:

1. Methyl.[1]
2. Ethyl.[2]
3. Phenyl.[3]
4. Nitrophenyl.[4]
5. Dimethylaminophenyl.[5]
6. *p*-Anisyl.[6]
7. *p*-Phenetyl.[7]
8. *p*-Benz.[8]
9. *m*-Benz.[9]
10. Nitrobenz.[10]
11. *o*-Toluyl.[11]
12. *m*-Toluyl.[12]
13. *p*-Toluyl.[13]
14. Nitrotoluyl.[14]
15. Tertiary butylphenyl.[15]
16. *o*-Dimethylamino-*p*-tolyl.[10]
17. *m*-Xylyl.[16]
18. *p*-Xylyl.[17]
19. Monochlorxylyl.[18]
20. Dichlorxylyl.[18]
21. Nitroxylyl.[18]
22. *m*-Tolu.[19]
23. *p*-Tolu.[20]
24. Phthalo.[19]
25. Pseudocumyl.[21]
26. *p*-Cumyl.[21]
27. α-naphthyl.[22]
28. β-naphthyl.[23]

It will be seen that though some twenty-six arsonic acids of the aromatic series have been prepared only two of the fatty series have been prepared. We herein contribute two new fatty arsonic acids; *viz.*:

29. Propyl.
30. Isoamyl.

Also the aromatic arsonic acid,

31. Benzyl.

The arsinic acids hitherto prepared and studied are the following:

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[1] Ber. 16, 1440; Ann. 107, 263; 249, 149.
[2] Ann. 208, 34; Am. Ch. J. 33, 132.
[3] Ibid. 201, 203.
[4] Ber. 27, 265.
[5] Ann. 270, 139.
[6] Ber. 20, 51.
[7] Ann. 320, 300.
[8] Ibid. 208, 5.
Ibid. 320, 329.
[10] Ibid. 320, 325.
[11] Ibid. 201, 255.
[12] Ibid. 320, 328.
[13] Ibid. 201, 255.
[14] Ibid. 320, 321.
[15] Ibid. 320, 342.
[16] Ibid. 320, 333.
[17] Ibid. 320, 338.
[18] Ibid. 320, 334.
[19] Ibid. 320, 335.
[20] Ibid. 320, 339.
[21] Ibid. 320, 340.
[22] Ber. 11, 1503.
[23] Ann. 320, 344.

1. Methyl.[1]
2. Ethyl.[2]
3. Phenyl.[3]
4. Benzyl.[4]
5. *p*-Toluyl.[5]
6. Nitrophenyl.[6]
7. Benz.[7]
8. Phenyl-*p*-toluyl.[8]
9. Isoamyl.[9]

Normal Propylarsonic Acid.—This acid was prepared in the same manner as ethylarsonic acid.[10] To 275 grams of arsenic trioxide (1 mol.) and 460 grams of potassium hydroxide (6 mols.), sufficient water was added to cause complete solution. After cooling, alcohol was added to the point of incipient precipitation of potassium arsenite; then 460 grams of normal propyl iodide (2 mols.) were added and the mixture was shaken. Usually either some potassium arsenite or some propyl iodide precipitates at this stage, but a homogeneous solution may be produced by adding either water or alcohol; or, when the solution is too concentrated, both must be added. After keeping the mixture in tightly-stoppered bottles for a number of days, the following reaction:

$$\mathrm{As(OK)_3 + C_3H_7I = (C_3H_7)AsO(OK)_2 + KI},$$

and the unavoidable side-reaction:

$$\mathrm{C_2H_5OK + C_3H_7I = C_2H_5{-}O{-}C_3H_7 + KI},$$

were complete. The mixture was then subjected to distillation, to remove the alcohol and the ethylpropyl ether. Hydrochloric acid was added to the point of incipient precipitation; then a stream of chlorine was passed in until the pure white double salt[11] first formed was dissolved and all of the iodine was precipitated. The filtrate was treated in the cold with magnesium mixture to precipitate the arsenate; upon boiling the filtrate from the ammonium magnesium arsenate, with more magnesium mixture, the *magnesium salt of normal propylarsonic acid* was precipitated as pearly-white, soapy crystals. Yield, 42 per cent. The magnesium salt was dried and analyzed:

	Per cent. Mg.
Salt dried at 100°–105° for eight hours	11.93
Salt dried at 130°–140° for six hours	11.99
Salt dried at 135°–160° for four hours	12.09
Salt dried at 190°–200° for five hours	13.38
Theory for $(\mathrm{C_3H_7AsO_3Mg})_2\mathrm{H_2O}$	12.05
Theory for $\mathrm{C_3H_7AsO_3Mg}$	12.48

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[1] Ann. **46**, 2.

[2] Ibid. **92**, 365.

[3] Ibid. **201**, 231; **321**, 150.

[4] Ibid. **233**, 82.

[5] Ibid. **208**, 20.

[6] Ibid. **208**, 25.

[7] Ibid. **321**, 151.

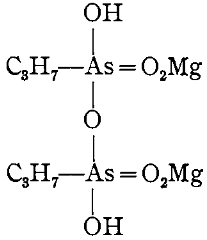
[8] Ibid. **321**, 157.

[9] Am. Ch. J. **35**, 52.

[10] Ibid. **33**, 132.

[11] Ibid. **33**, 141.

These analyses indicate that the magnesium propylarsonate, like magnesium ammonium arsenate[1] dried above 100°, contains one molecule of water of crystallization to two molecules of the anhydrous salt. Drying above 190° not only removed this water of crystallization from magnesium propylarsonate but also partially decomposed the salt. Its probable structural formula is:



$$\begin{array}{c} \mathrm{OH} \\ | \\ C_3H_7\text{—}\mathrm{As}=O_2\mathrm{Mg} \\ | \\ \mathrm{O} \\ | \\ C_3H_7\text{—}\mathrm{As}=O_2\mathrm{Mg} \\ | \\ \mathrm{OH} \end{array}$$

Free n-propylarsonic acid was prepared by treating the magnesium salt in the cold with the calculated quantity of concentrated sulphuric acid and then extracting with alcohol. Upon evaporating the alcoholic solution the acid was obtained as needle-form crystals.

The acid is very soluble in water; 100 parts of an aqueous solution at 26° contained 43 parts of acid. It is also very soluble in alcohol but is insoluble in ether.

n-Propylarsine Disulphide.—A quantity of the magnesium propylarsonate was dissolved in dilute hydrochloric acid and treated with hydrogen sulphide. A heavy, light yellow oil was slowly precipitated. It was extracted with carbon bisulphide, dried with calcium chloride and freed from the solvent by evaporation. The analysis gave 35.29 per cent. of S. Calculated for $C_3H_7AsS_2$, 35.16 per cent.

Therefore the reaction was:

$$C_3H_7AsO(OH)_2 + 2H_2S = C_3H_7AsS_2 + 3H_2O.$$

The density of the disulphide was found to be 1.8. It is a viscid oil that becomes a gummy mass below —10°.

Isoamylarsonic Acid.—This acid was prepared in a manner nearly identical with the manner of preparation of the *n*-propylarsonic acid. One molecule of arsenic trioxide (150 grams) was dissolved in six molecules of potassium hydroxide (254 grams) and treated with two molecules of isoamyl iodide (300 grams).

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[1] Z. anal. Chem. 10, 62.

The reaction mixture was permitted to stand for two or three days, when the alcohol was removed by distillation; the solution was then *carefully* neutralized and filtered from the double salt of $As_2O_3.2KI$. Upon acidifying, a mass of shining scale-like crystals separated, usually after some time; they were filtered off, washed, recrystallized, dried and analyzed. Calculated for $C_5H_{11}AsO(OH)_2$: C, 30.61; H, 6.84. Found: C, 30.21; H, 6.63.

The magnesium salt was easily prepared by boiling the acid with magnesium mixture. *Isoamylarsonic acid* is a pearly white crystalline substance that melts at 194°; 100 cc. of a saturated aqueous solution at 28° contains 0.820 gram; an equal quantity of a saturated alcoholic solution at 21° contains 2.2 grams. Like the other arsonic acids it is insoluble in ether.

Isoamylarsine Disulphide.—This sulphide was prepared as was the normal propyl disulphide. It is a viscid, light-yellow oil that will not solidify in a freezing-mixture and cannot be distilled without decomposition. The analysis gave 30.62 per cent. of S. Calculated for $C_5H_{11}AsS_2$, 30.48 per cent.

Benzylarsonic Acid.—Of all the arsonic acids, this is the most easily prepared. When quantities of the substances indicated by the equation,

$$2C_6H_5CH_2I + As_2O_3 + 6KOH = 2C_6H_5CH_2AsO(OK)_2 + 2KI + 3H_2O,$$

are dissolved in a mixture of alcohol and water in the manner previously described, freed from the alcohol by distillation, first neutralized and then carefully acidified with hydrochloric acid, a precipitation of *benzylarsonic acid* to the extent of 60 per cent. occurs.

Benzylethyl ether, equal to the loss of benzyl iodide not fixed by the arsenite, may be recovered from the alcohol removed by distillation[1]. Upon washing the free acid with water and recrystallizing once from water or alcohol it is easily obtained pure. The analysis gave: C, 38.65; H, 4.20. Calculated for $C_6H_5CH_2AsO(OH)_2$: C, 38.88; H, 4.16.

Benzylarsonic acid crystallizes in long, beautiful, white, glistening needles. It melts at 167°. It dissolves with difficulty in cold water but is quite easily soluble in hot water; 100 cc. of a saturated aqueous solution at 22.5° contains 0.34 gram; at 27°, 0.39 gram; and at 97° contains 3.50 grams of the acid. Its solubility in alcohol is indicated by the following data: 100 cc.

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[1] Am. Ch. J. 33, 142.

of a saturated alcoholic solution at 23° contains 0.87 gram of acid and at 70°, 5.91 grams of the acid. It is stable in the air, has no odor but has a peculiar bitter taste. It has an irritating effect upon the epidermis and the mucous membrane. An aqueous solution of the acid gives with silver nitrate a white precipitate of the silver salt, and with magnesium mixture on boiling, a white precipitate of the magnesium salt.

Benzylarsine Disulphide.—Treated with hydrogen sulphide benzylarsonic acid slowly precipitates the benzylarsine disulphide, $C_6H_5CH_2AsS_2$, which is very similar in properties to the arsine disulphides previously described. It is a heavy, bright-yellow oil that dissolves rapidly in nitric acid, liberating sulphur and oxides of nitrogen. On being heated alone it gives off hydrogen sulphide and forms arsenic trioxide and stilbene. The reaction is, probably:

$$2C_6H_5CH_2AsS_2 = C_6H_5CH{=}CHC_6H_5 + As_2O_3 + H_2S.$$

Decomposition of Benzylarsonic Acid by Heat.—Benzylarsonic acid on being heated yields the following decomposition products: Benzyl alcohol, benzaldehyde, stilbene, water and arsenic trioxide. Probably the most important reaction is:

$$2C_6H_5CH_2AsO(OH)_2 = C_6H_5CH_2OH + C_6H_5CHO + As_2O_3 + 3H_2O,$$

while stilbene is formed in smaller quantities according to the equation:

$$2C_6H_5CH_2AsO(OH)_2 = C_6H_5CH{=}CHC_6H_5 + As_2O_3 + 3H_2O.$$

Upon heating the corresponding arsinic acid, $(C_6H_5CH_2)_2AsOOH$, Michaelis and Paetow[1] found that it decomposed according to the following reaction:

$$2(C_6H_5CH_2)_2AsOOH = As_2 + 2H_2O + 2C_6H_5CHO + (C_6H_5CH_2)_2.$$

When 50 grams of benzylarsonic acid, containing some water of crystallization, were heated in a small flask attached to a condenser, an emulsion having the odor of benzaldehyde passed over. On standing, 15 grams of water separated. The oil was shaken with a concentrated aqueous solution of sodium bisulphite until the odor of benzaldehyde was discharged, and was then extracted with ether. On acidifying and distilling with steam, the aqueous solution was easily proved to contain benzaldehyde. The ether solution, after drying with calcium chloride, was distilled and gave a fraction which boiled largely between 200° and 210° (benzyl alcohol boils at 206°). This fraction was

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[1] Ann. 233, 83.

treated with acetyl chloride and benzoyl chloride and yielded benzyl acetate (106°) and benzyl benzoate (329°) respectively. The quantities of benzyl alcohol and benzaldehyde produced were approximately equal; therefore, the following reaction is established:

$$2C_6H_5CH_2AsO(OH)_2 = C_6H_5CH_2OH + C_6H_5CHO + As_2O_3 + H_2O.$$

A higher fraction boiling between 300° and 310° was obtained, (stilbene boils at 306° and dibenzyl boils at 284°). It was, however, too small in quantity to be purified by fractionation and it could not be crystallized by cooling in a freezing-mixture. A combustion gave:

	Substance.	Calculated for stilbene.	Calculated for dibenzyl.	Calculated for benzyl alcohol.
C	84.65	93.34	92.30	77.07
H	7.95	6.66	7.70	7.64

Evidently the higher fraction was a mixture of benzyl alcohol and stilbene rather than benzyl alcohol and dibenzyl. Further evidence for this conclusion is seen in its easy decolorization of bromine water. Therefore it may safely be held that a secondary decomposition of benzylarsonic acid by means of heat is:

$$2C_6H_5CH_2As(OH)_2 = C_6H_5CH{=}CHC_6H_5 + As_2O_3 + 3H_2O.$$

Decomposition of Benzylarsonic Acid by Acids.—Unlike its homologues and isologues, benzylarsonic acid is easily decomposed by mineral acids. Michaelis and Paetow[1] observed that concentrated hydrochloric acid completely decomposed dibenzylarsonic acid into arsenic trichloride, benzyl chloride and toluene, according to the equation:

$$(C_6H_5CH_2)_2AsOOH + 4HCl = C_6H_5CH_2Cl + C_6H_5CH_3 + AsCl_3 + 2H_2O.$$

With concentrated hydrochloric acid we find that benzylarsonic acid is decomposed into benzyl chloride and arsenious acid (no toluene was detected), therefore the reaction is:

$$2C_6H_5CH_2AsO(OH)_2 + 2HCl = 2C_6H_5CH_2Cl + As_2O_3 + 3H_2O.$$

With sulphuric acid we find that dibenzyl, benzaldehyde, and arsenious acid are the decomposition-products, therefore, the following reaction is probable:

$$4C_6H_5CH_2AsO(OH)_2 = (C_6H_5CH_2)_2 + 2C_6H_5CHO + 2As_2O_3 + 4H_2O.$$

The speed of the above reaction may be determined by titration with a standard iodine solution, free iodine having no effect on

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[1] Ann. 233, 84.

arsonic acids. The accompanying table shows the great speed of the decomposition:

Weight of benzyl-arsonic acid.	H_2O. cc.	H_2SO_4. cc.	Time. Minutes.	Temperature.	Decomposition. Per cent.
1.500	25	10	30	100°	100
1.500	25	10	15	100	100
1.318	25	5	5	100	99
1.318	25	5	5	100	99.4
1.172	25	1	10	100	92

The decomposition with sulphuric was much more rapid than with hydrochloric acid. When phenyl- and ethylarsonic acids were treated in the same manner only traces of arsenious acid were detected.

Decomposition of the Salts of Fatty Arsonic Acids by Heat.—It was found by Dehn[1] that heat decomposed magnesium ethylarsonate into magnesium oxide, metallic arsenic, water and a hydrocarbon gas.

A closer study of this decomposition was made by us and it was found that the hydrocarbon gas given off is a mixture of methane and ethylene. The unsaturated gas was separated from the methane by treatment with bromine water, and the ratio of their volumes was found in one case to be 42.5 per cent. of the former to 57.5 per cent. of the latter. A combustion of the residual gas gave the following data:

43.5 cc. of gas (corrected and equal to 0.0317 gram) gave 0.0863 gram of CO_2 and 0.0714 gram of H_2O.

	Calculated for CH_4.	Found.
Carbon	75.00	75.10
Hydrogen	25.00	24.04

An analysis of the saturated gas by the explosion method gave the following results:

	Vol. gas saturated.	Vol. CO_2 theory.	Vol. CO_2 found.	Vol. H_2O theory.	Vol. H_2O found.
I.	10.2	10.2	10.4	20.4	20.4
II.	12.0	12.0	11.8	24.0	24.2

Evidently, the saturated gas is methane.

An analysis of the mixture of saturated (57.5 per cent.) and unsaturated (42.5 per cent.) gases was made by the explosion method and gave the following data:

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[1] Am. Ch. J. 33, 133.

	Volume gas saturated and unsaturated.	Volume CO_2 calculated.	Volume CO_2 found.	Volume H_2O calculated.	Volume H_2O found.
1.	8.4	12.0	11.8	16.8	16.6
2.	9.0	12.0	12.8	18.0	18.2

This indicates that the unsaturated gas is ethylene. An equation proposed to represent the decomposition of magnesium ethylarsonate is as follows:

$$(C_2H_5AsO_3Mg)_2H_2O = 2CH_4 + C_2H_4 + Mg_2As_2O_7.$$

This, however, cannot represent the entire reaction, for water is formed as well as a larger quantity of ethylene than is indicated by the equation. As magnesium ethylarsonate is dehydrated and partially decomposed at 145–170°,[1] the following secondary reaction may occur:

$$2C_2H_5AsO_3Mg = C_2H_4 + H_2O + Mg_2As_2O_5.$$

Furthermore as carbon dioxide (10–18 per cent. of the evolved gases) and metallic arsenic are found among the end-products, other reactions are probably necessary to represent the complete decomposition.

Decomposition of Magnesium n-Propylarsonate by Heat.—When magnesium *n*-propylarsonate was heated in an apparatus filled with carbon dioxide, it yielded a gaseous product which, when freed from carbon dioxide, was soluble in bromine water to the extent of 40 per cent.; therefore this gaseous product consisted of 40 per cent. of an unsaturated hydrocarbon and 60 per cent. of a residual gas whose analysis indicated a mixture of hydrogen with methane. In the analysis given below, the gas in experiment (*a*) was obtained from the total evolved gas, while in experiment (*b*) the gas was obtained from that last evolved during the heating of the arsonate.

(*a*)	Volume gas.	Volume CO_2 found.	Volume H_2O found.	Volume H_2O calc. for H_2.	Volume H_2O calc. for CH_4.	Volume CO_2 calc. for CH_4.
1.	15.0	8.6	25.4	15.0	30.0	15.0
2.	11.5	6.2	18.6	11.5	23.0	11.5
3.	12.0	6.9	19.8	12.0	24.0	12.0

This experiment shows that the saturated gas consists of nearly equal parts of hydrogen and methane.

(*b*)	Volume gas.	Volume CO_2 found.	Volume H_2O found.	Volume H_2O calc. for H_2.	Volume H_2O calc. for CH_4.	Volume CO_2 calc. for CH_4.
1.	10.8	7.8	14.1	10.8	21.6	10.8
2.	10.2	7.0	13.2	10.2	20.4	10.2
3.	10.7	7.3	13.7	10.7	21.4	10.7

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[1] Am. Ch. J. 33, 133.

This experiment shows about 70 per cent. of methane and 30 per cent. of hydrogen.

When 40 grams of magnesium *n*-propylarsonate were heated so that the gaseous products were passed through bromine water, a quantity of halogen-olefine addition-product was obtained. Distillation of the oil yielded fractions that boiled near the boiling-points of ethylene bromide (129.5°) and propylene bromide (141°).

Analysis of the first fraction by the Carius method gave 85.35 per cent. Br; calculated for $C_2H_4Br_2$, 85.11 per cent.

The second fraction gave 78.42 per cent. Br; calculated for $C_2H_5BrCH_2Br$, 79.71 per cent.

The above experiments prove the presence of hydrogen, methane, ethylene, and propylene. However, at present, the evidence on the decomposition of magnesium *n*-propylarsonate is too slight to venture writing the equations involved.

Meyer's Reaction.—The above-described arsonic acids were prepared by Meyer's reaction, that is, by application of the following general reaction:

$$RX + K_3AsO_3 = K_2RAsO_3 + KX.$$

Evidence for their formation was obtained in preliminary experiments[1] by determination of the per cent. of transformation of arsenite. Other preliminary studies along this line are given below.

Haloid derivative.	Time. Hours.	Temperature.	Yield. Per cent.
Isobutyl iodide	2	25°	5
" "	4	25	9
" "	32	25	10
" "	100	25	10
" "	0.5	80	12
" "	3	80	12
Chloroform	1	25	1
"	4	25	1
"	45	25	4
"	98	25	4.8
Bromoform	1	25	5
"	42	25	15
"	53	25	23
"	96	25	30
"	216	25	30

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[1] Am. Ch. J. 33, 138.

Haloid derivative	Time. Hours.	Temperature.	Yield. Per cent.
Iodoform	26	23	35.4
"	40	23	50
"	51	23	52.9
"	94	23	79
"	114	23	81.5
"	210	23	92.2
"	0.5	80	50
"	1	80	51
"	2.5	80	54
"	15	80	86
p-Chlortoluene	1	25	.0
"	42	25	3
"	96	25	3
Allyl iodide	0.2	25	39
" "	0.5	25	45
" "	1	25	46
" "	26	25	51

These determinations were made by titrating the unchanged potassium arsenite with standard solutions of iodine, and thus determining by difference the quantity which had been transformed into the arsonic acid. The allyl iodide appeared to act abnormally, first a brown precipitate being formed, and then a yellow oil.

It is evident from these experiments that other arsonic acids besides those hitherto described may easily be prepared.

Properties of the Arsonic and Arsinic Acids.—All of these acids are beautiful white crystalline substances which are usually quite easily soluble in water and alcohol and are almost insoluble in ether.

Solubilities and melting-points as determined by us are given in the accompanying table:

Acid.	Solvent.	Temperature.	Soluble in 100 parts.	Melting-point.
Ethylarsonic.	Water.	27°	70.00	99.5°
" "	"	40	112.00	......
" "	Alcohol.[1]	25	39.40	......
Propylarsonic.	Water.	26	43.00	125.0
Isoamylarsonic.	"	28	0.82	194.0
" "	Alcohol.	21	2.20	......
Benzylarsonic.	"	23	0.87	167.0
" "	"	70	5.91	......
" "	Water.	22.5	0.34	......

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[1] The alcohol used in these experiments was of 95 per cent. concentration.

Acid.	Solvent.	Temperature.	Soluble in 100 parts.	Melting-point.
Benzylarsonic.	Water.	27	0.39	......
" "	"	97	3.50	......
Phenylarsonic.	"	28	3.25	158.0
" "	"	41	4.82	......
" "	"	52	8.52	......
" "	"	84	24.00	......
" "	Alcohol.	26	15.51	......
" "	"	68	55.40	......
Methylarsinic.	Water.	22	82.90	......
Phenylarsinic.	"	27	0.28	164.0
" "	Alcohol.	22	11.80	......
" "	"	55	57.70	......

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[CONTRIBUTION FROM THE MISCELLANEOUS LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

COPPER SALTS IN IRRIGATING WATERS.[1]

BY W. W. SKINNER.

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THE Miscellaneous Laboratory of the Bureau of Chemistry has for several years past been engaged in a study of the effect of certain waste products from manufacturing operations in regard to their injurious effect upon vegetation and agricultural crops. "The Injury to Vegetation by Smelter Fumes," by J. K. Haywood is the first of a series of bulletins upon this subject. Supplementing this work and as a logical sequence thereto, a study of other waste products from smelters, concentrating plants, and mining operations naturally follows. The data submitted in this paper relate only to copper operations, and the injurious effect upon vegetation from copper salts which, as a waste product from the mining and reduction of copper ores, are frequently carried into and contaminate water supplies which later are used for irrigation purposes.

Toxicity of Copper Salts.—The extremely toxic character of copper salts to plant life is a subject that has received considerable attention both in this country and by foreign investigators. Johnson[2] remarked years ago the injurious effect of salts of copper,

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[1] The second of a series of studies by the Miscellaneous Laboratory on trade wastes in their relation to agriculture. Read at the New Orleans Meeting of the American Chemical Society.

[2] "How Crops Grow," Johnson.