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THE THERMAL ANALYSIS OF ALKYLARSONIC ACIDS

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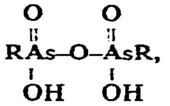
ABSTRACT

The behavior of a series of alkylarsonic acids, $C_nH_{2n+1}AsO_3H_2$ ($n = 1$–20), has been studied by thermogravimetry (TG). At atmospheric pressure the compounds have been observed to undergo dehydration to the pyroarsonic acids,



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{As}}}}}\text{–O–}\overset{\mathrm{O}}{\overset{\|}{\underset{\mathrm{OH}}{\underset{|}{\mathrm{As}}}}}\mathrm{R},$$

which on further heating decomposed into arsenic trioxide, the alkanol, and gases which could not be trapped in CCl_4 at -20 to $-30°$. At 10 mm Hg, TG curves showed that the arsonic acids lost 1 mole of H_2O per mole of acid. The insoluble polymeric anhydrides which were produced decomposed on further heating into arsenic trioxide and the alkanols. These anhydrides are hygroscopic and were easily converted to the parent acids by moisture.

INTRODUCTION

There are several reports in the literature concerning the dehydration of arsonic acids, $RAsO(OH)_2$. Methylarsonic acid kept at 130–140° has been found to lose one mole of water per two moles of acid. At 180° it decomposes to methanol and arsenic trioxide[1]. Trifluoromethylarsonic acid has been dehydrated stepwise in vacuum to give first the pyroarsonic acid and then the anhydride[2]. Morgan[3], found that aromatic arsonic acids formed anhydrides when they were heated in the conventional manner to the melting temperature. The melting points of the acids could be obtained only by inserting the samples into a bath preheated to the melting temperature.

Alkylarsonic acids having alkyl chains ranging from butyl to eicosyl have recently been prepared[4], completing the series of the n-alkylarsonic acids from C_1 to C_{20}. The melting points of these acids in capillary tubes were in agreement with those given for previously reported arsonic acids[5]. When the acids were heated on the Fisher–Johns melting point apparatus, some melted at the melting temperatures

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observed in capillary tubes and then resolidified, with the resulting solid melting at a higher temperature. Others (C_8, C_{10}, C_{17}) did not melt at the lower temperature, but appeared instead to undergo a change in crystalline form followed by melting at a higher temperature. The phenomenon of melting, solidification and remelting was never observed in capillary tubes. Preliminary experiments with hexyl- and dodecylarsonic acids suggested that at 150° one mole of water per two moles of acid is lost[4].

The thermal behavior of alkylarsonic acids has not been investigated in detail. Therefore, differential thermal analysis (DTA) and thermogravimetry have been carried out with this series of compounds.

EXPERIMENTAL

Alkylarsonic acids. — Disodium methylarsonate, donated by the Vineland Chemical Company, was converted to the free acid by passing its aqueous solution through a Dowex 50 W-x8 cation exchange column. The eluate was evaporated and the methylarsonic acid recrystallized twice from water. The other alkylarsonic acids, $C_nH_{2n+1}AsO_3H_2$, were prepared according to published procedures (Ref. 5, $n = 2,3$; Ref. 4, $n = 4$–20).

Alkylarsonic acid anhydrides (*$RAsO_2$*). — The appropriate acid was placed into a small tube with a constricted neck and heated at a pressure of 0.5 mm Hg in an Abderhalden vacuum-drying apparatus for 24 h at 110° (refluxing toluene). The sample tubes were then flame-sealed under vacuum.

Chemical analysis of $RAsO_2$. — Calc. for C_6H_{13}: C, 37.89; H, 6.96; As, 39.34. Found: C, 37.72; H, 6.81; As, 39.21. Calc. for C_8H_{17}: C, 43.51; H, 7.86; As, 34.34. Found: C, 43.85; H, 7.82; As, 34.19. Calc. for $C_{13}H_{27}$: C, 53.75; H, 9.19; As, 26.03. Found: C, 53.98; H, 9.41; As, 25.90.

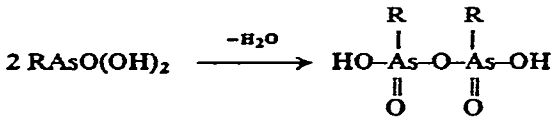
Thermal analysis. — All TG curves were obtained on an R. L. Stone Model No. TGA-3C controlled atmosphere thermogravimetric analysis apparatus with a Model Fl-C furnace. The reference thermocouple was Pt/Pt–10% Rh located slightly above and to the left of the sample holder. The heating rate was 3–5°/min. Small sample holders were made from Pyrex glass. These holders did not have a frit in the bottom. In this way loss of material by dripping after melting was avoided. Analyses were carried out in a dynamic atmosphere by passing nitrogen over the samples. Samples weighing 20–200 mg (see Table I) were placed into the holder, from which small wire weights were hung to obtain the required total balance-load. It was therefore unnecessary to use an Al_2O_3 filler.

The operating parameters for the DTA experiments have been previously described[4,6].

Decomposition of hexylarsonic acid. — Hexylarsonic acid (0.5 g) was placed in a small flask, which was flushed with a stream of dry nitrogen. The exit gas was passed through CCl_4 contained in a test tube which was cooled by a Dry Ice–isopropanol bath at -20 to -30°. At 200°, the acid underwent complete decomposition in 40 min. Hexanol and As_2O_3, identified by i.r. spectroscopy, were collected in the traps. The same results were obtained when the acid or its anhydride, $(RAsO_2)_n$ were decomposed at 180–190° in a vacuum.

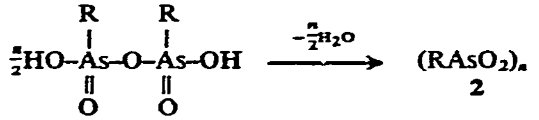
RESULTS AND DISCUSSION

Thermogravimetry (TG) was carried out on the alkylarsonic acids, $C_nH_{2n+1}AsO(OH)_2$ ($n = 1$–20), at atmospheric pressure and at approximately 10 mm Hg. The TG curves show that the first step involves dehydration, followed by the decomposition of the sample, and complete volatilization of the decomposition product. Arsonic acids, bearing two hydroxyl groups, can lose one mole of water intermolecularly (Eqn. 1) forming $[RAsO(OH)]_2O$ (**1**). The pyroarsonic acid (**1**) can then in a second dehydration step condense linearly to a polymeric arsonic acid anhydride (**2**) (Eqn. 2).



$$2\,RAsO(OH)_2 \xrightarrow{-H_2O} HO\text{–}\underset{\underset{O}{\|}}{\overset{\overset{R}{|}}{As}}\text{–}O\text{–}\underset{\underset{O}{\|}}{\overset{\overset{R}{|}}{As}}\text{–}OH \quad (1)$$

1



$$\tfrac{n}{2}HO\text{–}\underset{\underset{O}{\|}}{\overset{\overset{R}{|}}{As}}\text{–}O\text{–}\underset{\underset{O}{\|}}{\overset{\overset{R}{|}}{As}}\text{–}OH \xrightarrow{-\frac{n}{2}H_2O} \underset{\mathbf{2}}{(RAsO_2)_n} \quad (2)$$

$$n\,RAsO(OH)_2 \xrightarrow{-nH_2O} (RAsO_2)_n \quad (3)$$

There exists also the possibility that the arsonic acids are directly converted to **2** without prior formation of any large quantity of **1** (Eqn. 3).

The vacuum TG runs show a consistency in the thermal behavior of most of the members of this series of alkylarsonic acids. Typical vacuum TG curves are shown for the C_1 and C_{12} acids in Fig. 1 and for the C_5 acid in Fig. 2. The initial weight loss corresponds to the elimination of one mole of water per mole of acid. The remainder of the sample decomposed to give a curve which shows a continuous loss in weight. This behavior was observed for all compounds except for the C_1–C_4 and the C_8 compounds, which produced only changes in slopes or ill-defined plateaus (Fig. 1). The results of the TG studies are summarized in Table I.

The dehydration of these compounds in vacuum is probably best represented by Eqn. 3. It was observed, however, that the vacuum TG curves for the C_1, C_6 and C_{20} acids exhibited a change in slope of the weight loss curve, which indicates the formation of a pyroarsonic acid according to Eqn.1. Attempts to obtain a better defined plateau by variations of heating rate and chart speed were unsuccessful and caused the weight loss, in several cases, to appear to be continuous.

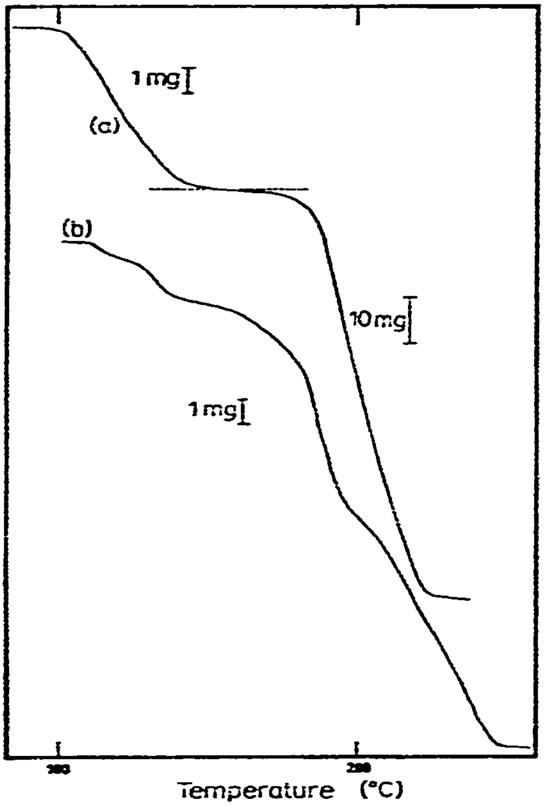


Fig. 1. Vacuum TG curves for dodecyl- and methylarsonic acids. (a) $C_{12}H_{25}AsO_3H_2$, 99.3 mg; heating rate, 3°/min; pressure 11 mm Hg. (b) $CH_3AsO_3H_2$, 21.0 mg; heating rate 2.5°/min; pressure 10 mm Hg.

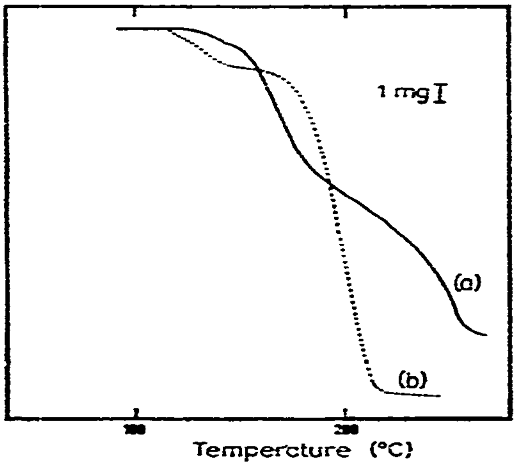


Fig. 2. TG curves for pentylarsonic acid ($C_5H_{11}AsO_3H_2$) at atmospheric pressure (curve (a), 17.5 mg), and in vacuum (curve (b), 11 mm Hg, 20.2 mg). Heating rate, 3°/min.

TABLE I

TG RESULTS OF THE DEHYDRATION OF THE n-ALKYLARSONIC ACIDS AT ATMOSPHERIC AND REDUCED PRESSURE

	Atmospheric pressure			*Reduced pressure*			
n-R	*Sample weight (mg)*	*Weight loss (%) found (calc.[a])*	*Temperature range of weight loss (°C)*	*Sample weight (mg)*	*Pressure (mm Hg)*	*Weight loss (%) found (calc.[b])*	*Temperature range of weight loss (°C)*
CH_3	19.4	6.0 (6.5)	126–150	21.0	10	12.4 (13.0)	114–150
C_2H_5				19.6	10	Continuous weight loss	80–[c]
C_3H_7	19.4	6.7 (5.4)	114–150	18.6	4	10.2 (10.8)	105–160
C_4H_9	141.0	5.3 (5.0)	118–150	150.5	8	9.1 (10.0)	105–150
C_5H_{11}	17.5	4.5 (4.6)	124–150	20.2	11	9.5 (9.2)	116–160
C_6H_{13}	171.9	4.2 (4.3)	130–160	163.4	10	8.6 (8.6)	117–150
C_7H_{15}	18.0	4.3 (4.0)	132–150				
C_8H_{17}	21.7	5.6 (3.8)	117–150	149.7	10	7.6 (7.6)	103–150
C_9H_{19}	100.4	3.3 (3.6)	110–165	100.4	14	7.2 (7.2)	98–145
$C_{10}H_{21}$	20.0	4.5 (3.4)	114–130	151.1	12	6.6 (6.8)	95–140
$C_{11}H_{23}$	49.7	3.4 (3.2)	116–150	200.3	8	5.9 (6.4)	98–155
$C_{12}H_{25}$	100.9	3.1 (3.1)	108–150	99.3	11	6.1 (6.2)	98–155
$C_{13}H_{27}$	19.8	3.0 (2.9)	118–145	99.8	8	5.7 (5.8)	93–140
$C_{14}H_{29}$	50.7	2.5 (2.8)	118–140	48.2	10	5.2 (5.6)	77–110
$C_{15}H_{31}$	20.0	2.9 (2.7)	110–130	99.1	15	5.5 (5.4)	95–135
$C_{16}H_{33}$	100.5	2.1 (2.6)	105–150	19.9	20	5.4 (5.2)	98–125
$C_{17}H_{35}$	50.0	2.8 (2.5)	110–140	49.8	17	5.0 (5.0)	102–125
$C_{18}H_{37}$	49.5	2.4 (2.4)	110–130	50.5	20	5.1 (4.8)	85–125
$C_{19}H_{39}$	49.9	2.0 (2.3)	120–140	50.3	10	4.6 (4.6)	88–120
$C_{20}H_{41}$	52.1	1.9 (2.2)	116–140	55.5	8	4.4 (4.5)	100–115

[a] Calculated for the loss of ½ mole of water per mole of acid. [b] Calculated for the loss of 1 mole of water per mole of acid. [c] No discernible plateau in the weight-loss curve.

The temperature at which dehydration commenced varied, beginning at 114° for C_1, falling sharply to ~80° for C_2, then increasing to 105° for C_3 and C_4, falling to a minimum of 77° for C_{14}, and finally increasing to 100° for the C_{20} acid (see Table I). The final products of the dehydration reactions are polymeric anhydrides, $(RAsO_2)_x$. Several of these anhydrides were prepared by heating the corresponding acids at the reflux temperature of toluene for 24 h at a pressure of 0.5 mm Hg. Attempts to obtain the molecular mass of $C_6H_{13}AsO_2$ were unsuccessful due to its insolubility in benzene, chloroform, carbon tetrachloride, acetone, methanol, ethyl acetate, tetrahydrofuran, dimethylformamide, methyl ethyl ketone, dioxane and *N,N*-dimethylacetoacetamide. The stoichiometric composition of the C_6, C_8 and C_{13} compounds was verified by elemental analyses. Weighed samples of several arsonic acid anhydrides (C_6, C_9, C_{11}, C_{15}, C_{18}) were allowed to stand under nitrogen saturated with water. After three hours, the compounds had gained the weight calculated for the uptake of one mole of water per gram formula of anhydride. The compounds which formed were identified as the parent acids by their melting points, by i.r. spectroscopy, and by thermogravimetric analysis.

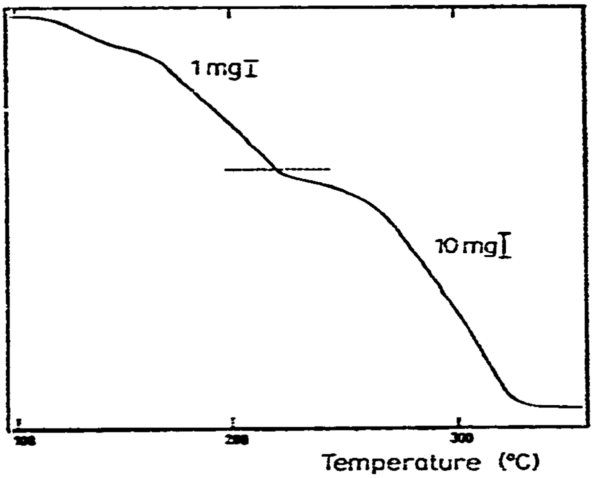


Fig. 3. TG curve for hexadecylarsonic acid ($C_{16}H_{33}AsO_3H_2$, 100.5 mg) at atmospheric pressure. Heating rate, 3°/min.

The shape of the TG curves at atmospheric pressure (Figs. 2(a) and 3) differ from the vacuum TG runs in several respects. The initial weight loss at atmospheric pressure occurs at higher temperatures and involves only half the weight loss observed in the vacuum analysis. The decomposition and volatilization of the remaining substance is slower. The weight loss curve in this region shows several changes in slope not seen in the vacuum curve. At atmospheric pressure, the arsonic acids first form pyroarsonic acids (I, Eqn. 1). There are no indications in the TG curves that the pyroarsonic acids are then dehydrated to $(RAsO_2)_n$. The agreement of the experi-

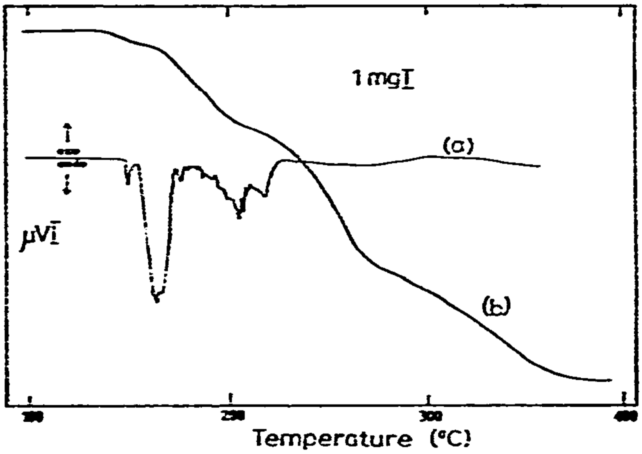


Fig. 4. DTA (curve (a), 8.0 mg) and TG (curve (b), 19.4 mg) curves for methylarsonic acid ($CH_3AsO_3H_2$) at atmospheric pressure.

mental weight loss with the calculated value for the loss of one mole of water per two moles of acid was, in most cases, within the limits of accuracy of the TG instrument (see Table I). In some cases (C_3, C_8, C_{10}) the agreement was not as good as expected. Attempts to obtain better results by varying sample size, heating rate and particle size were unsuccessful. Recrystallization of the analytically pure compounds[4] from ethanol–water mixtures also had no noticeable effect. The temperature at which the pyroarsonic acids begin to form was observed to vary from 108° (C_8, C_{16}) to 130° (C_3) (Table II). From the DTA curves (Table II, Fig. 4(a)), it appears that the formation of pyroarsonic acids occurs just prior to melting or, in the case of the C_3–C_{20} compounds, simultaneously with melting.

TABLE II

DTA AND TG OF THE n-ALKYLARSONIC ACIDS AT ATMOSPHERIC PRESSURE

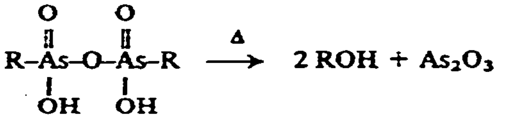
n-R	*DTA Peak (°C)*	*Relative size^a and sign^b of ΔH^a*	*TG (°C) (range)*	*Probable cause of weight loss and DTA peak*	*Weight loss (%)*
CH_3	125–160	+L B	126–145	Dehydration	6.0
	160–220	+ VB	145–210	Decomposition	~23
	220–280	+ VB	210–280	Decomposition	~36
			280–360	Decomposition	~35
C_3H_7			114–150	Dehydration	6.7
			150–225	Decomposition	~39
			225–250	Decomposition	~14
			250–290	Decomposition	~40
C_4H_9	114–150	+M S	118–150	Dehydration	5.3
	150–210	+ VB	150–210	Decomposition	~62
	210–	+ VB	210–270	Decomposition	~35
C_5H_{11}	125–150	+M S	125–150	Dehydration	4.5
	150–172	+ VB	152–173	Decomposition	~45
	185–195	−S B	173–250	Decomposition	~50
C_6H_{13}	132–157	+L S	130–160	Dehydration	4.2
	157–200	+ VB	160–200	Decomposition	~25
	200–225	−M B	200–250	Decomposition	~70
C_7H_{15}	120–150	+L S	132–150	Dehydration	4.3
	150–200	+ VB	150–200	Decomposition	~57
	200–230	−M B	200–265	Decomposition	~38
C_8H_{17}	108–155	+L B	117–150	Dehydration	5.6
	185–210	+M B	175–230	Decomposition	~65
	220–225	+L S	230–260	Decomposition	~30
C_9H_{19}	120–150	+L B	110–165	Dehydration	3.3
	170–180	−S B			
	180–230	+ VB	165–310	Decomposition	96.7
	230–260	+ VB			

TABLE II *(continued)*

n-R	*DTA Peak* (°C)	*Relative size*[a] *and sign*[b] *of* ΔH[a]	*TG* (°C) (*range*)	*Probable cause of weight loss and DTA peak*	*Weight loss* (%)
$C_{10}H_{21}$	122–145	+L B	114–130	Dehydration	4.5
	165–180	+M B	170–260	Decomposition	95.5
	185–240	+ VB			
$C_{11}H_{23}$	124–150	+L S	116–150	Dehydration	3.4
	150–250	+ VB	150–290	Decomposition	96.6
$C_{12}H_{25}$	121–138	+L B	108–150	Dehydration	3.1
	160–175	+M B			
	175–185	−Sm B	150–305	Decomposition	96.9
	185–	+ VB			
$C_{13}H_{27}$	125–145	+L B	118–145	Dehydration	3.0
	180–250	+ VB	170–270	Decomposition	97.0
$C_{14}H_{29}$	108–140	+M B	118–140	Dehydration	2.5
	170–270	+ VB	138–300	Decomposition	97.5
$C_{15}H_{31}$	125–140	+L S	110–130	Dehydration	2.9
	170–270	+ VB	180–310	Decomposition	97.1
$C_{16}H_{33}$	110–135	+L B	105–150	Dehydration	2.1
	170–220	+ VB	150–350	Decomposition	97.9
$C_{17}H_{35}$	115–135	+M B	110–140	Dehydration	2.8
	175–245	+ VB	150–300	Decomposition	97.2
$C_{18}H_{37}$			110–130	Dehydration	2.4
			150–300	Decomposition	97.6
$C_{19}H_{39}$	115–135	+M B	120–140	Dehydration	2.0
	165–240	+ VB	150–310	Decomposition	98.0
$C_{20}H_{41}$	115–138	+M B	116–140	Dehydration	1.9
	150–220	+ VB	160–310	Decomposition	98.1

[a] Peak area: L, large; M, medium; Sm, small. Peak Shape: S, sharp; B, broad; VB, very broad.
[b] +, endothermic; −, exothermic.

The second weight loss probably involves the decomposition of the pyroarsonic acid into arsenic trioxide and alkanol (Eqn. 4). Gases not retained in CCl_4 at −20 to −30° were also detected.



$$\text{R--}\underset{\text{OH}}{\overset{\text{O}}{\overset{\|}{\underset{|}{\text{As}}}}}\text{--O--}\underset{\text{OH}}{\overset{\text{O}}{\overset{\|}{\underset{|}{\text{As}}}}}\text{--R} \xrightarrow{\Delta} 2\,\text{ROH} + As_2O_3 \qquad (4)$$

Such a decomposition was observed for methylarsonic acid by Baud[1]. The plateaus in the TG curves corresponding to the loss of alkanol are not well defined. While the experimental weight losses agree within a few percent with the calculated values, based on Eqn. 4, for the C_1, C_3, C_5 and C_7 derivatives, the other compounds show changes in slopes, or plateaus, which cannot be correlated with the loss of any reasonable molecular entity. The difference in the appearance of the decomposition of the TG curves for the lower (C_1–C_8, Fig. 2) and higher acids (C_9–C_{20}, Fig. 3) can be explained by the temperatures and rates of volatilization of the decomposition products. In the higher acids, the volatility of the alkanol (b.p. of $C_8H_{17}OH = 194°$) is similar to that of arsenic trioxide (begins to sublime at 193°), preventing the appearance of a distinct plateau in the TG curve. A synthetic mixture of octanol and arsenic trioxide in a 2:1 molar ratio gave a TG trace which showed only changes of slope, but no plateaus.

To obtain additional proof that alkanols are formed as decomposition products, hexylarsonic acid was heated to 200° in a stream of dry nitrogen. The decomposition gases were trapped in CCl_4 at -20 to $-30°$. The white solid found in the traps was identified as arsenic trioxide. The i.r. spectrum of the CCl_4 solution was identical with that of hexanol in CCl_4. A significant amount of the decomposition products passed through the trap. The gases fumed on contact with air and they decolorized $KMnO_4$ and $K_2Cr_2O_7$ solutions. This suggests the formation of arsines.

The anhydrides, $(RAsO_2)_n$, obtained in the vacuum TG experiments, decomposed on further heating and yielded a continuous weight loss curve. To obtain information about the nature of these decomposition products a sample of $(C_6H_{13}AsO_2)_n$ was heated at 180–190° at 1 mm Hg pressure. The top portion of the flask above the oil bath was cool enough so that most of the products remained in the flask. After the completion of decomposition the residue was extracted with CCl_4. Arsenic trioxide remained undissolved. The solution gave an i.r. spectrum identical with that of hexanol in CCl_4.

The isolation of hexanol as a decomposition product of the anhydride in vacuum was somewhat unexpected, since OH groups are not available in the anhydride. Free alkyl radicals formed during decomposition are the likely source of hydrogen atoms for the OH group. The mechanism of this decomposition reaction has not been investigated.

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