The pyrolysis of trimethylarsine

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The pyrolysis of trimethylarsine has been studied in a toluene carrier flow system from 764 to 858 °K using total pressures from 6.35 to 35.5 mm. Contact times varied from 0.9 to 3.7 s and the amount of decomposition, from 1.2 to 73%. The progress of the reaction was followed by measuring the amount of methane, ethane, ethylene, and ethylbenzene formed. No heterogeneous reaction was detected and the first order rate constants appear to have been determined at approximately the high pressure limit. In seven runs the undecomposed alkyl was also measured. The quantity found was in agreement with the product analysis if three methyl radicals are released for each molecule undergoing reaction.

Least squares analysis of the results gives

$$\log_{10} k/\mathrm{s}^{-1} = 15.82 - (62\,800 \pm 800)/2.3RT$$

The activation energy should be a good approximation to $D[(CH_3)_2As—CH_3]$. The product analysis and the values of $k_4/k_5^{1/2}$ are consistent with the simple consecutive release of three methyl radicals but thermodynamic and kinetic considerations may preclude this possibility.

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Introduction

The pyrolysis of trimethylarsine in a static system has been reported by Ayscough and Emeleus (1). They found the reaction to be homogeneous and of the first order with an activation energy of 54.6 ± 1.8 kcal/mole ($\log_{10} k = 12.77 - 54\,600/2.3RT$). It was assumed that the eventual fate of $(CH_3)_2AsCH_2$ had no appreciable effect on the observed rate and the activation energy was associated with $D[(CH_3)_2As—CH_3]$.

The present toluene carrier work was undertaken to study the pyrolysis of trimethylarsine under conditions such that no significant attack by methyl radicals on the parent alkyl should occur.

Experimental

Materials

(*a*) Trimethylarsine was prepared by the reaction of CH_3MgI in butyl ether with $AsCl_3$. The complex formed was decomposed by gradually heating to 120–150 °C (2). The fraction boiling at 50–52 °C was separated, refractionated, and degassed. Vapor pressure data for the final product over the temperature range −14 to 20 °C may be represented by $\log P/\mathrm{mm} = -1574/T + 7.749$. This equation gives an extrapolated standard boiling point of 50.2 °C, in excellent agreement with literature values of 50.1–50.3° (1) and 50.4° (3).

(*b*) Toluene from sulfuric acid (Eastman Organic X325) was used. Gas chromatographic analysis detected traces of higher hydrocarbons (xylenes, ethylbenzene). These were reduced to less than 40 p.p.m. by a fractional distillation in which a large tail fraction was discarded. Prior to use, the toluene was dried by refluxing over sodium metal for 24 h and then degassed by bulb-to-bulb distillation.

Apparatus and Procedure

The experiments were carried out in a system similar to that used in previous work (4). The reaction vessel had a volume of 156 cc. To test for surface effects a vessel was packed with small quartz tubes. This vessel had a volume of 117 cc and a surface to volume ratio 18 times that of the unpacked vessel. Both vessels were treated with hot concentrated nitric acid before use. The residual acid was baked out under vacuum after the vessels were installed in the reaction system.

The gaseous products were analyzed using a Perkin–Elmer model 154 gas chromatograph equipped with a 1/4 in. × 6 ft silica gel column. The column was maintained at 80 °C, and a helium flow rate of 20 cm³ per min was used.

The liquid products which condensed along with the toluene in an acetone – Dry Ice trap were analyzed using a Perkin-Elmer model 800 gas chromatograph equipped with a 150 ft × 0.02 in. i.d. Golay column coated with poly(propylene glycol). (Isothermal operation at 60 °C, inlet pressure of nitrogen carrier was 7 lb.)

After a number of runs, the grey deposit at the outlet of the reaction zone was dissolved in nitric acid and analyzed for arsenic by titration with iodine (5). The results indicated that this deposit is essentially pure arsenic (98.4% As found).

Results and Discussion

The experimental results are given in Tables 1 and 2. They may be discussed in terms of the following mechanism

[1] $As(CH_3)_3 \rightarrow As(CH_3)_2 + CH_3$

[2] $As(CH_3)_2 \rightarrow AsCH_3 + CH_3$

[2*a*] $2As(CH_3)_2 \rightarrow As(CH_3)_3 + AsCH_3$

[3] $AsCH_3 \rightarrow As + CH_3$

[3*a*] $2As(CH_3) \rightarrow As(CH_3)_2 + As$

TABLE 1

Experimental data for pyrolysis of $As(CH_3)_3$

T (°K)	t_c (s)	P (mm)	T/A* ratio	$As(CH_3)_3$ used	CH_4	C_2H_6	C_2H_4	Ethyl-benzene	k_1 (s^{-1})
				(moles × 10^4)					
858.0	1.94	24.7	61.3	3.549	5.028	0.179	0.111	2.132	0.668
858.0	1.71	26.5	49.9	5.282	7.490	0.345	0.172	2.267	0.667
858.0	1.18	24.8	64.5	5.606	6.362	0.264	0.140	1.782	0.643
858.2	0.99	21.2	61.8	5.940	6.225	0.284	0.124	1.654	0.674
852.6	1.47	22.3	112.5	7.064	9.594	0.261	0.131	1.092	0.530
852.7	1.59	21.0	60.0	3.807	4.491	0.198	0.095	1.445	0.533
852.7	1.46	25.2	52.8	5.606	6.764	0.295	0.138	1.646	0.548
852.7	1.52	20.9	51.0	6.964	8.092	0.386	0.180	2.278	0.527
852.6	2.16	23.2	32.0	5.690	8.131	0.434	0.201	2.362	0.541
840.6†	1.06	23.4	56.4	5.140	3.328	0.107	0.071	0.650	0.311
836.5	3.47	35.5	17.1	9.989	13.202	0.861	0.391	2.501	0.270
835.4	1.66	24.5	32.4	7.889	5.281	0.302	0.132	1.495	0.234
836.1	2.02	20.4	112.4	3.190	2.941	0.071	0.045	0.703	0.256
836.5	3.70	20.1	15.3	5.856	7.040	0.561	0.277	2.145	0.260
836.5	1.25	13.1	55.2	3.349	1.925	0.085	0.037	0.578	0.255
836.4	1.33	11.6	39.5	3.849	1.941	0.121	0.047	0.607	0.215
836.5	1.82	6.3	33.6	10.814	6.272	0.439	0.190	1.958	0.190
811.5	1.70	26.0	35.1	11.697	3.575	0.137	0.044	0.863	0.0863
811.5	1.74	24.9	33.1	11.613	3.553	0.145	0.043	0.779	0.0834
810.5	1.31	21.5	58.5	5.107	1.215	0.031	0.003	0.223	0.0792
810.3	1.36	22.8	35.5	8.506	1.942	0.065	0.012	0.386	0.0752
804.7†	1.21	19.8	55.9	4.032	0.718	0.017	0.005	0.091	0.0606
804.7†	1.25	19.8	51.5	4.223	0.801	0.019	0.005	0.092	0.0617
782.1†	1.33	19.4	68.5	3.015	0.192	0.002	0.001	0.038	0.0199
774.3	1.84	23.6	30.7	11.788	0.735	0.012	0.001	0.117	0.0137
774.1	1.84	23.9	29.7	12.305	0.685	0.013	0.002	0.123	0.0125
764.6	1.85	24.3	31.9	11.747	0.391	0.005	0.000	0.066	0.00722
764.5	1.84	21.4	26.2	12.580	0.406	0.008	0.000	0.061	0.00697
764.5	1.89	22.3	23.9	18.645	0.661	0.011	0.000	0.086	0.00735
764.3	1.85	24.5	31.4	12.047	0.403	0.005	0.000	0.046	0.00690

*Molar ratio of toluene to $As(CH_3)_3$ at the inlet of the reaction vessel. Initial concentrations may be calculated from this figure, the total pressure (P) and the temperature of the reaction zone (T).

†Packed vessel runs.

[4] $CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2$

[5] $2CH_3 \rightarrow C_2H_6$

[6] $CH_3 + C_6H_5CH_2 \rightarrow C_6H_5C_2H_5$

plus the usual reactions leading to small quantities of ethylene and traces of xylenes and styrene. Values of k_1 were calculated from the usual first order equation

$$k = \frac{2.303}{t_c} \log \frac{1}{1 - x}$$

where t_c is the average residence time in the reaction zone and the fraction decomposed, x, is given by

$$x = \frac{\text{moles } CH_4 + \text{moles ethylbenzene} + 2(\text{moles } C_2H_6 + \text{moles } C_2H_4)}{3(\text{moles } As(CH_3)_3)\text{ used}}$$

The only volatile arsenic containing compound that could be found by either flame or electron capture gas chromatography following a run was the parent alkyl. The only involatile products were dibenzyl and a grey deposit at the outlet of the furnace which, as previously mentioned, was 98.4% arsenic. These facts, coupled with the distribution of products shown in Table 1 and the agreement shown in Table 2 between the percent decomposition calculated from product analysis and from the differences between the quantity of alkyl used and the residual alkyl, indicate that reaction 1 is the rate controlling step in a sequence of reactions that produces three methyl radicals and free arsenic. The simple linear nature of the Arrhenius plot of $k_4/k_5{}^{1/2}$ shown in Fig. 1 is further supporting evidence (6).

All contact times used should be such that

TABLE 2

Percent decomposition by product analysis and alkyl recovery

T (°K)	Percent decomposition Product analysis	 Alkyl recovery*
858.0	72.7	67.1
852.7	55.2	53.8
852.6	54.1	53.4
840.6	28.1	27.4
836.5	60.8	63.0
836.4	25.0	20.1
774.3	2.5	1.6

*From gas chromatographic analysis of the toluene trapped at the outlet of the reaction vessel in a trap cooled by acetone – Dry Ice. Conditions used were the same as those for ethylbenzene analysis. Analyses were carried out immediately following the run and fresh standard solutions were used. The solutions have limited stability and care must be taken to avoid loss of alkyl by evaporation.

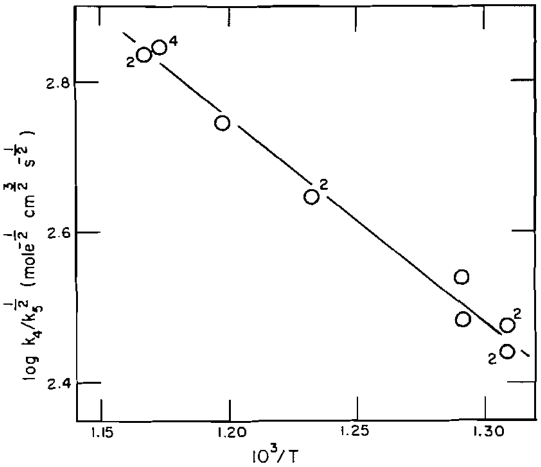

FIG. 1. Arrhenius plot of $k_4/k_5^{1/2}$. Numerals denote the number of runs averaged to obtain the given point. Total pressure 21–26 mm.

thermal equilibrium and diffusion problems should not be significant (7). The experimental results at 858 °K support this conclusion.

The negligible effect on k_1 of a variation by a factor of 3.7 in concentration at 852 °K and by a factor of 7.2 at 836 °K indicates that the decomposition is first order. The agreement in Fig. 2 between the four experiments in the packed vessel and those in the unpacked vessel shows that no detectable surface reactions are occurring. Least squares analysis of the points used to obtain this plot gives

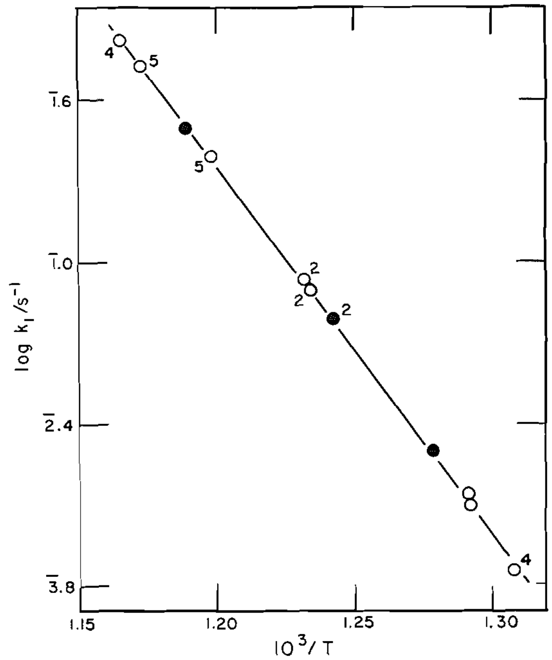

FIG. 2. Arrhenius plot for k_1. Numerals denote the number of runs averaged to obtain the given point. ○, runs in unpacked reaction vessel; ●, runs in packed reaction vessel.

$$\log k_1/\text{s}^{-1} = 15.82 - (62\,800 \pm 800)2.3RT$$

From the runs at 836 °K it is apparent that above approximately 13 mm total pressure the values of k_1 are essentially the high pressure limiting values. The observed activation energy should therefore be a reasonable measure of $D[(CH_3)_2\text{-}As\text{—}CH_3]$.

From $\Delta H_f{}^\circ{}_{298}$ [$As(CH_3)_{3,g}$] = 3.7 kcal mole^{-1} (3), $\Delta H_f{}^\circ{}_{298}$ [$CH_{3,g}$] = 33.2 kcal mole^{-1} (8), and $\Delta H_f{}^\circ{}_{298}$ [As, g] = 72.3 kcal mole^{-1} (8) the sum of the dissociation energies for reactions 1, 2, and 3 should be approximately 168 kcal mole^{-1}. Therefore, with D_1 = 63 kcal mole^{-1}, $D_2 + D_3$ = 105 kcal mole^{-1}. At the temperatures and pressures used, the A factor for reaction 2 should have a maximum value of about 10^{15} and, in all likelihood, would be considerably lower. If reaction 1 is to be rate controlling, k_1 must be significantly smaller than k_2. Taking the rather conservative estimate that k_2 must be at least twice k_1 leads to what should probably be considered an absolute maximum value of D_2 = 59 kcal mole^{-1}. This then requires that $D_3 \geqslant$ 46 kcal mole^{-1} and for $k_3 = 2k_2$ the minimum value of A_3 would be about 10^{12} s^{-1}, a value which is probably at least a power of ten greater than that expected (6).

Obviously the preceding discussion does not rule out completely the possibility that reactions 2 and 3 occur and, in fact, based on experience with other alkyls, reaction 2 is probably much more likely than reaction 2*a*. The regeneration of $As(CH_3)_3$ by either reaction 2*a* or by recombination of CH_3 with $As(CH_3)_2$ is probably negligible. To the extent that it does occur, the reported value of $D[(CH_3)_2As—CH_3]$ may be slightly low. There does seem to be a distinct possibility that the decomposition of methylarsine must occur largely by reaction 3*a* or some other similar process.

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1. P. B. AYSCOUGH and H. J. EMELEUS. J. Chem. Soc. 3381 (1954).
2. R. A. ZINGDRO and A. MERIJANIAN. Inorg. Chem. **3**, 580 (1964).
3. L. H. LONG and J. F. SACKMAN. Trans. Faraday Soc. **52**, 1201 (1956).
4. M. KRECH and S. J. PRICE. Can. J. Chem. **41**, 224 (1963).
5. A. VOGEL. Quantitative inorganic analysis. 3rd ed. Longmans. 1961.
6. M. G. JACKO and S. J. W. PRICE. Can. J. Chem. **42**, 1198 (1964).
7. M. F. R. MULCAHY and M. R. PETHARD. Aust. J. Chem. **16**, 527 (1961).
8. Selected values of chemical thermodynamic properties. Natl. Bur. Std. U.S. Tech. Notes, No. 270-3. 1968.