Thermal Decomposition of Trimethylarsine

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Abstract—The thermal decomposition of trimethylarsine was studied under static conditions at 352–409°C and a concentration of 8.7×10^{-3} mol/l. The temperature dependence of the rate constant of thermal decomposition is described by the equation $\log k = 13.6 \pm 0.7 - (224 \pm 4) \times 10^3/2.3RT$.

Alkyl derivatives of arsenic are widely used for the production of A_3B_5 compound semiconductors. Studies of the kinetics and mechanism of thermal decomposition of individual compounds are of importance for these applications.

Thermal decomposition of trimethylarsine has been studied by a number of authors [1–4]. In [1–3], the investigations were carried out in a flow reactor in the presence of toluene [1], helium, or deuterium [2], that is, substances that influence essentially the mechanism of thermal decomposition. The mechanism of thermal decomposition and the influence of hydrogen were studied in detail in [2]. In [3], the study was carried out in a quartz reactor. It was found that decomposition leads to the formation of a polymeric material, and a carbon film remains as arsenic is evaporated from this material.

The study under static conditions was carried out in [4]. In this work, a diaphragm zero manometer was used. The composition of gaseous decomposition products was determined, and the activation energy of the process was calculated to be 240 kJ/mol. This value is consistent with the As–C bond energy. However, the calculation carried out using the reported rate constants showed that their temperature dependence in the $\ln k$–T^{-1} coordinates is not linear, and the activation energies calculated from the initial and final portions of the plot varied from 173 to 263 kJ/mol. Therefore, in this work, we studied the thermal decomposition of trimethylarsine under batch conditions in order to refine the kinetic parameters and the mechanism of the process.

Trimethylarsine of 99.9 mol % purity was used in this work. The study was carried out in a batch reactor with a diaphragm zero manometer. The sampling, the filling of zero manometers, the analysis of hydrocarbon products, and the determination of hydrogen were performed as described in [5].

The errors in [4] could result from instability in the concentration of trimethylarsine in the membrane chamber, because this concentration can be different at the same initial pressure if temperature is not constant. Therefore, we studied the effect of trimethylarsine concentration on the rate of thermal decomposition. We carried out three experiments at 386°C and at initial concentrations of 4.3×10^{-3}, 6.7×10^{-3}, and 8.7×10^{-3} mol/l.

Kinetic curves plotted in the α–$f(t)$ coordinates practically coincide (the degree of decomposition α was calculated as the ratio of an increase in pressure at the point t in time to the total increase in pressure). Thus, in this concentration range, concentration did not influence the degree of decomposition as a function of time. Therefore, the process is of the first order.

The influence of temperature on the rate of thermal decomposition was studied at an initial concentration of trimethylarsine equal to 8.7×10^{-3} mol/l in a temperature range of 352–409°C. The kinetic curves are presented in Fig. 1.

The curves were described by a kinetic equation of the first order up to the degree of decomposition of 70–80% (Fig. 2). These curves were fitted with this equation using the least-squares method. The calculated rate constants are presented below.

t, °C	352.0	368.0	386.0	409.0
$k \times 10^5$, s^{-1}	0.82	3.01	6.88	33.4

The treatment of these rate constants as a function of temperature with the use of the Arrhenius equation gave the equation

$$\log k = 13.6 \pm 0.7 - (224 \pm 4) \times 10^3/2.3RT. \quad (1)$$

The cooling of zero manometers down to the temperature of liquid nitrogen showed that hydrogen was practically absent from the products of thermal decomposition. Table 1 presents the composition of hydrocarbon products of thermal decomposition, as determined by gas–liquid chromatography.

The analytical results are in a good agreement with published data [4]. At the same time, it is necessary to note that the main product of thermal decomposition is methane. In the case of free-radical decomposition [4], ethane would be formed as a result of methyl radical recombination. However, its yield is insignificant. The yield of propane and unsaturated hydrocarbons is even
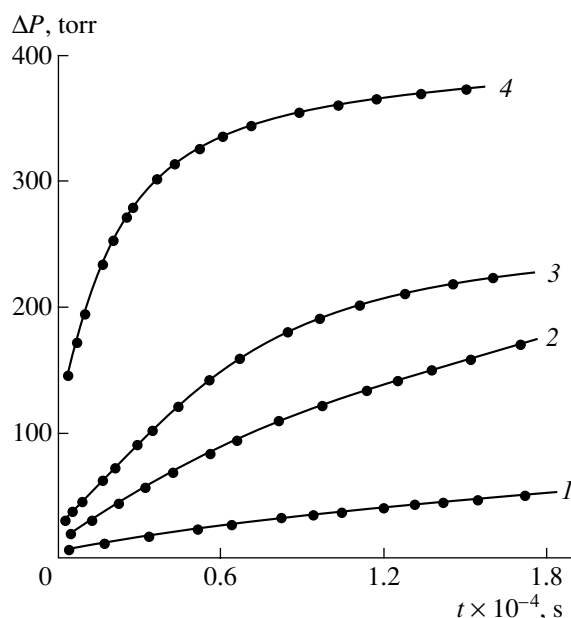
Fig. 1. Kinetic curves of the thermal decomposition of AsMe$_3$ at (*1*) 352.0, (*2*) 368.0, (*3*) 386.0, and (*4*) 409.0°C.
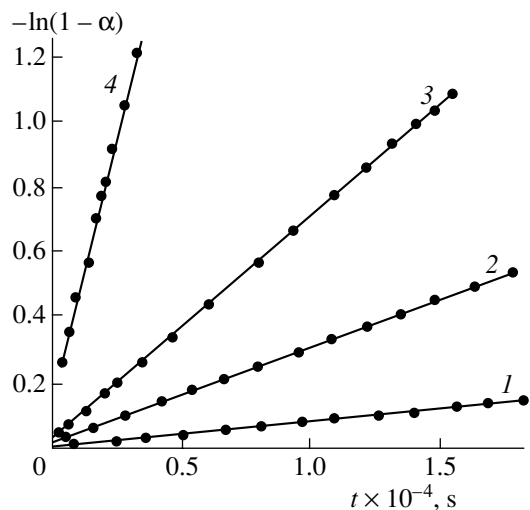

Fig. 2. Kinetic curves of the thermal decomposition of AsMe$_3$ plotted in the –ln(1 – α)–t coordinates at (*1*) 352.0, (*2*) 368.0, (*3*) 386.0, and (*4*) 409.0°C.

lower. Note that the kinetic parameters obtained are lower than the values obtained in [1] by the toluene method, and they probably exhibit a complex character.

A grey deposit was formed on the walls upon the decomposition of trimethylarsine. The deposit consisted of arsenic and a hydrocarbon polymer. This agrees with the results of [3]. To refine the composition of this polymeric deposit, we calculated a material balance of the process from the data on the initial pressure of trimethylarsine, the pressures of final products, and

the composition of a gas phase. The material balance equation has the form

$$As(CH_3)_3 = a(bCH_4 + cC_2H_4 + dC_2H_6 + eC_3H_6 + fC_3H_8 + gC_4H_8 + hC_4H_{10}) + C_xH_y, \quad (2)$$
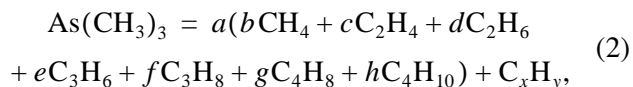
where a is the ratio of the pressure of products of thermal decomposition to the initial pressure of trimethylarsine; b, c, d, e, f, g, and h characterize the composition of a gas phase as molar fractions.

The material balances on carbon and hydrogen were calculated separately. We found that 22% of the carbon atoms and 1.4% of the hydrogen atoms passed into a condensed phase. The carbon-to-hydrogen ratio in the hydrocarbon film was 5 : 1.

Thus, by now, the thermal decomposition of a number of organoarsenic compounds (trimethylarsine, triethylarsine [6], tripropylarsine [7], diethylarsine [8], and triisopropylarsine) has been studied with the use of the same procedure. Therefore, a comparison can be made.

Table 2 summarizes the kinetic parameters of thermal decomposition and the composition of condensation products. The consideration of the homologous series of trialkylarsines with substituents of the normal structure shows a decrease in activation energies and preexponential factors on going from trimethylarsine to tripropylarsine. This could be explained by a decrease in the As–C bond energy. However, the activation energy of thermal decomposition of triisopropylarsine is higher than the activation energy of triethylarsine, and the preexponential factor is higher than that of trimethylarsine. The thermal decomposition of diethylarsine, in contrast to trialkyl analogs, takes place with considerable self-deceleration. Kinetic parameters of this process are considerably higher than the parameters of triethylarsine.

Therefore, the obtained kinetic parameters cannot be adequately explained in terms of As–C bond energies. This is related to the chain-radical mechanism of the thermal decomposition of alkylarsines and, hence, to the complex character of the kinetic parameters.

The reactions of H transfer play an important role in the development of a chain process. Note that, as the length and the degree of branching of the alkyl radical increase, the strength of the As–C bond decreases simultaneously with a decrease in the activity toward H-transfer reaction because this activity is proportional to the strength of newly formed R–H bonds. Thus, an increase in the length and the degree of branching of alkyl radical leads to an increase in the contribution from a nonchain mechanism of alkylarsine decomposition. This is particularly important in the case of triisopropylarsine. It is most likely that the kinetic parameters of diethylarsine are related to the reaction stoichiometry, which is different from that in trialkylarsines.

The yield and the composition of nonvolatile carbon-containing products depend on the processes of

Table 1. Composition (mol %) of the products of the thermal decomposition of $AsMe_3$ as a function of temperature

T, °C	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	ΣC_4H_8	$iso\text{-}C_4H_{10}$	C_4H_{10}
352.0	93.02	0.56	4.11	0.15	1.80	0.05	0.06	0.36
368.0	93.34	0.69	3.69	0.19	1.70	0.04	0.06	0.31
386.0	93.56	0.68	3.02	0.19	1.50	0.05	0.04	0.32
409.0	94.15	0.88	2.86	0.34	1.40	0.04	0.04	0.31

Table 2. Kinetic parameters and the yield of condensation products in the thermal decomposition of alkyl derivatives of arsenic

Compound	E, J/mol	A, s^{-1}	C, %	Atomic ratio H/C
$AsMe_3$	223 500	13.6	22.0	5/1
$AsEt_3$	167 300	13.0	14.4	3.1/1
$AsHEt_2$	228 000	11.9	–	–
$As(n\text{-}Pr)_3$	147 800	8.6	16.8	2.6/1
$As(iso\text{-}Pr)_3$	186 900	13.8	18.8	1.4/1

radical polymerization, as well as the H-transfer reactions. The relative yield of carbon in these products is maximal for trimethylarsine. With increasing chain length of trialkylarsines, this yield initially decreased and then somewhat increased. In this case, the hydrogen content of condensation products increased. In the case of diethylarsine, nonvolatile polymeric products were almost not formed.

The formation of semiconductor films is usually performed under dynamic conditions in a hydrogen flow at reduced pressures. This is favorable for a decrease in the carbon yield. However, it is difficult to completely exclude its formation. The carbon content of a film cannot be exactly predicted based on the results obtained in a study of thermal decomposition under static conditions. However, these results show that primary trialkylarsines are most prone to the formation of nonvolatile carbon-containing products. The yield of carbon decreases with a decrease in the number of alkyl groups and with an increase in the degree of branching.

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