METAL-CARBON BONDS

PART 3.—THE PYROLYSES OF TRIMETHYL BISMUTH, TRIMETHYL ANTIMONY AND DIMETHYL TIN DICHLORIDE

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The thermal decompositions of trimethyl bismuth, trimethyl antimony and dimethyl tin dichloride have been studied by the toluene carrier technique between 346° and 584°, 475° and 664°, and 554° and 688°C respectively. The reactions were followed by measuring the hydrogen, methane, ethylene and ethane formed. The unchanged trimethyl bismuth and the amount of antimony deposited in the reaction vessel were also determined. The rate constant for the decomposition reaction

$$Bi(CH_3)_3 = Bi(CH_3)_2 + CH_3$$

is given by

$$\log_{10} k/\text{sec}^{-1} = (14{\cdot}02 \pm 0{\cdot}01) - (44030 \pm 25/2{\cdot}303\boldsymbol{RT})$$

at 16·1 mm. The interpretation of the results with trimethyl antimony is not straightforward. The rate of fission of the first bond is probably given by

$$\log_{10} k/\text{sec}^{-1} = 15{\cdot}2 - (57{,}000/2{\cdot}303\boldsymbol{RT}) \text{ at } 16{\cdot}5 \text{ mm.}$$

The rate constant of the overall reaction

$$(CH_3)_2SnCl_2 = SnCl_2 + 2CH_3$$

is given by

$$\log_{10} k/\text{sec}^{-1} = (13{\cdot}52 \pm 0{\cdot}01) - (56{,}100 \pm 40/2{\cdot}303\boldsymbol{RT}) \text{ at } 16{\cdot}1 \text{ mm.}$$

The first two papers[1, 2] in this series described the thermal decomposition of dimethyl mercury, cadmium and zinc. The energy required to break the first metal-carbon bond was found to be considerably greater for each of these alkyls than that required to break the second. This finding confirmed the suggestion of Skinner[3] that such a disparity should exist for the compounds of these metals. The work on dimethyl mercury was in good agreement with that of Gowenlock, Polanyi and Warhurst[4] who first tested Skinner's suggestion as it applied to the metallic alkyls. The primary object of the present work was to measure the strengths of the bonds in trimethyl bismuth and trimethyl antimony. No kinetic studies of the decompositions of these alkyls have been reported, though Ayscough and Emeleus[5] have investigated the decompositions of trimethyl arsenic, and trifluoromethyl arsenic and antimony.

The original intention was to follow the study of the group 5 alkyls by a study of the methyl derivatives of group 4, but it was felt that the same difficulties that were found with trimethyl antimony might recur in a more severe form with tetramethyl compounds. The only investigations that have been reported were carried out in static systems and there was considerable evidence of complexity.[6-9] The reactions of tetramethyl tin might have been cleaner in the presence of excess toluene, but the study of the equally interesting dimethyl tin dichloride offered a better hope that definite information on the bond strengths would be obtained. No pyrolysis of this type of compound has been investigated, although Carter, Chappell and Warhurst[10] have measured the rates of pyrolysis of phenyl mercuric chloride and bromide. They found that the pyrolysis of *n*-propyl mercuric chloride was complex.

EXPERIMENTAL

MATERIALS

TRIMETHYL BISMUTH was prepared by the action of anhydrous bismuth trichloride on methyl magnesium iodide.[11] The excess Grignard reagent was destroyed with aqueous ammonium chloride and the ether solution dried with sodium sulphate. The crude product was twice fractionated and the fraction distilling at 55-56°C at 120 mm was stored under vacuum at − 196°C (vapour pressure 21·6 mm at 16°C).

TRIMETHYL ANTIMONY was prepared by heating antimony powder with dimethyl mercury using mercuric chloride as a catalyst.[12] After fractionation the product was stored under vacuum at − 196°C (vapour pressure 72 mm at 17°C, 30·5 mm at 0°C).

DIMETHYL TIN DICHLORIDE was prepared by bubbling methyl chloride through molten tin containing 10 % of fine copper powder as a catalyst.[13] The metal mixture was heated to 350°C and any oxides reduced by passing hydrogen for 1 h. The temperature was then raised to 375°C and the flow of methyl chloride initiated. After 30 min the temperature was reduced to 315°C. About 10 g, m.p. 106°C, were obtained in 18 h.

PROCEDURE

The apparatus and procedure were essentially the same as those previously employed,[1] but were modified for the involatile tin alkyl. Before the run began, a quantity of the alkyl was distilled from a weighed storage tube into a U-tube. The toluene stream was saturated with alkyl vapour as it flowed through the U-tube which was maintained at a convenient temperature. At the end of the run the remaining alkyl was distilled back into the storage tube and the amount used determined by weighing.

In three runs with trimethyl bismuth, the undecomposed alkyl was determined. The alkyl was destroyed by passing a very slow stream of oxygen through the toluene solution removed from the CO_2 + alcohol trap. The toluene was distilled off, and the bismuth determined by a colorimetric estimation employing potassium iodide.[14]

In a number of experiments with trimethyl antimony, the amount of antimony remaining in the reaction vessel was determined. At the end of a run, all the antimony and involatile antimony compounds deposited in the reaction vessel were converted into a mixture of antimony trichloride and pentachloride by the action of chlorine. The chlorides were distilled out, dissolved in hydrochloric acid and reduced to the trivalent state by boiling with sodium sulphite. The antimony was then titrated with standard potassium bromate using methyl red as an indicator.[15]

RESULTS AND DISCUSSION

Selected experimental results are given in tables 1, 2 and 3.

DIMETHYL TIN DICHLORIDE

The behaviour of the tin compound was most straightforward and will be discussed first. The results can be satisfactorily interpreted in terms of the following simple reaction scheme.

$$(CH_3)_2SnCl_2 = CH_3SnCl_2 + CH_3 \tag{1}$$

$$CH_3SnCl_2 = SnCl_2 + CH_3 \tag{2}$$

$$CH_3 + C_6H_5CH_3 = CH_4 + C_6H_5CH_2 \tag{3}$$

$$2CH_3 = C_2H_6 \tag{4}$$

$$2C_6H_5CH_2 = (C_6H_5CH_2)_2 \tag{5}$$

If the amount of ethane formed plus half the amount of methane is used as a measure of the amount of dimethyl tin dichloride decomposed, it is found that 96·8 and 98·0 % decomposition occurred in runs 1 and 2, respectively. This is good evidence that two methyls are released each time a molecule decomposes. Accordingly the first-order rate constants were calculated on this basis.

The results of runs 10, 11 and 25 at 588° and of runs 20 and 26 at 567° show that the decomposition is homogeneous. Those of runs 3, 4, 5 and 6 show that the rate constant is independent of variations of the alkyl concentration between

TABLE 1.—THE PYROLYSIS OF DIMETHYL TIN DICHLORIDE

run no.	temp. °C	toluene (mm)	t (sec)	CH_4	C_2H_6	Me_2SnCl_2*	k_1 (sec^{-1})
				10^{-4} mole			
2*b*	688	16·1	3·22	5·54	0·328	3·16	—
1*c*	637	16·1	3·38	3·94	0·220	2·26	1·02
18	637	16·1	1·12	7·14	0·133	5·18	1·13
19	636	16·1	1·10	6·41	0·108	4·68	1·13
23	589	16·1	3·21	3·54	0·100	3·73	0·216
10	588	16·1	1·19	2·50	0·049	5·81	0·213
25*a*	588	16·1	0·98	2·36	0·050	6·50	0·213
11	588	16·1	1·22	2·41	0·053	5·61	0·208
24	587	16·1	0·66	1·59	0·017	6·32	0·210
7	575	6·0	1.87	1·76	0·104	7·07	0·080
9	575	9·5	1·43	1·11	0·029	4·50	0·097
5	575	16·1	1·22	0·63	0·008	2·32	0·121
4	574	16·1	1·27	0·96	0·010	3·56	0·116
3	574	16·1	1·27	1·30	0·031	4·87	0·118
6	575	16·1	1·26	2·60	0·059	9·65	0·120
8	575	25·0	1·09	1·22	0·008	4·69	0·130
26*a*	567	16·1	1·00	0·95	0·026	5·91	0·088
20	567	16·1	1·19	0·823	0·013	4·35	0·087
21	554	16·1	1·17	0·536	0·006	4·72	0·051
22	554	16·1	1·21	0·596	0·006	5·15	0·050

a, runs in packed vessel; *b*, 12 μmole H_2; *c*, 4 μmole H_2.
* amount of alkyl fed into the reaction vessel.
The results of runs 12-17 may be found in the *Ph.D. Thesis* of S. J. W. Price, Edinburgh, 1958.

1·01 × 10^{-9} and 4·36 × 10^{-9} mole cm^{-3}, and those of runs 10, 11, 23 and 24 show that it is independent of variations in the contact time from 0·66 to 3·21 sec.

The rate constants depend slightly on the overall pressure of toluene as is shown by the following results, all obtained at 514·4°C.

run	7	9	3	8
toluene pressure/mm	6·0	9·5	16·1	25·0
k/sec^{-1}	0·0795	0·0965	0·118	0·130

Accordingly, all the results obtained at about 16·1 mm are adjusted to this pressure.

The rate constants for the overall decomposition obtained at 16·1 mm pressure have been fitted to the Arrhenius equation by the method of least squares. Hence

$$\log k/\text{sec}^{-1} = (13{\cdot}52 \pm 0{\cdot}01) - (56100 \pm 40/2{\cdot}303\,\boldsymbol{R}T).$$

The errors are most probable errors found by the normal statistical methods. The results are clearly very reproducible but it is likely that normal systematic errors which may be considerable are also involved. Unfortunately they cannot be satisfactorily estimated.

The overall rate constant may be assumed to be equal to the rate constant k_1 for the fission of the first bond in the alkyl. Hence $D(CH_3—CH_3SnCl_2)$ is equal to the activation energy, 56·1 kcal mole^{-1}. This dissociation energy is probably close to but more than the mean bond energy for the Sn—C bonds in tetramethyl tin, which have been reported to be 53·5 ± 3 kcal mole^{-1}.[16] This finding is in keeping with the observation that the redistribution of stannic halides with stannic alkyls is exothermic.[16, 17] The metal-alkyl bonds in the alkyl mercuric halides are also considerably stronger than the bonds in the corresponding dialkyls.[18]

TRIMETHYL BISMUTH

The results obtained in the pyrolysis of trimethyl bismuth may be satisfactorily interpreted by the following reaction scheme:

$$Bi(CH_3)_3 = Bi(CH_3)_2 + CH_3 \qquad (6)$$

$$Bi(CH_3)_2 = BiCH_3 + CH_3 \qquad (7)$$

$$BiCH_3 = Bi + CH_3 \qquad (8)$$

followed by reactions (3), (4) and (5).

TABLE 2.—THE PYROLYSIS OF TRIMETHYL BISMUTH

run no.	temp. °C	toluene (mm)	t (sec)	CH_4	C_2H_6	$BiMe_3$*	k_6 (sec^{-1})
				10^{-4} mole			
E*a*	584	16·1	1·16	7·22	18·70	14·90	—
C*ac*	548	16·1	1·26	7·10	18·20	14·50	—
B*ad*	526	16·1	1·29	7·95	17·50	14·40	—
A′	429	16·1	3·25	7·45	14·30	12·05	—
C′*e*	409	16·1	3·78	6·12	10·90	9·25	·820
16	409	16·1	1·67	7·47	11·20	13·60	·795
4*a*	409	16·1	1·42	6·15	9·26	12·10	·800
18	403	16·1	1·75	4·02	4·02	6·20	·597
17	402	16·1	1·78	6·10	8·85	12·20	·578
B′*b*	395	16·1	3·86	5·13	8·65	9·40	·410
12	392	16·1	1·77	4·72	7·77	14·10	·368
13	392	6·3	3·14	2·06	5·54	6·60	·347
27	392	16·1	1·80	4·36	5·50	10·70	·364
11	390	10·6	2·18	3·29	6·30	10·40	·327
10	389	11·0	2·12	3·04	5·35	9·70	·302
8	388	16·1	1·72	4·72	6·15	14·20	·296
3*a*	387	16·1	1·54	3·45	5·15	12·80	·280
33	387	16·1	0·69	2·32	1·83	11·20	·278
6	386	16·1	1·77	2·74	2·34	6·60	·264
7	386	16·1	1·71	1·44	0·77	2·73	·264
5	383	16·1	1·76	3·41	4·34	12·40	·222
30	382	25·0	1·53	3·18	2·24	9·1	·217
31	382	6·3	3·14	2·78	8·55	14·20	·200
32	382	16·1	4·04	3·94	5·86	8·95	·217
2*a*	369	16·1	1·56	1·80	2·41	13·50	·114
22	367	16·1	1·95	1·90	2·10	11·70	·0972

Duration of all runs 30 min.

* amount of alkyl fed into the reaction vessel.
a, runs in packed reaction vessels;
b, colorimetric estimation of the products yields $k_6/sec^{-1} = 0{\cdot}405$;
c, approx. 20 μmole of ethylene and 7 μmole of hydrogen formed;
d, no C_3 or C_4 gases detectable;
e, k_6 based on measurement of the undecomposed alkyl identical with that calculated from gaseous products. Complete details of runs 1-33 may be found in the *Ph.D. Thesis* of S. J. W. Price, Edinburgh, 1958.

Runs B, C, E and A′ were all carried out at high temperatures, where the observed decomposition is close to 100 % as measured both by the volume of methane and ethane produced, and by the quantity of undecomposed alkyl. It is thus established that three methyl radicals are released each time a molecule undergoes reaction (6). The analysis of the gaseous products of runs B and C shows that the amounts of hydrogen, ethylene and C_3 hydrocarbons formed are negligible. The conclusion that the quantity of gas produced is a satisfactory measure of the progress of the decomposition is further supported by run B′.

Hence the first-order rate constant k_6 may be calculated from the amounts of methane and ethane in the products.

Runs 3 and 33 at 387°C and runs 32, 5 (0·216) and 30 at 382°C show that the calculated rate constant is independent of the contact time. (The value in parenthesis is the observed value of k_6 adjusted to the temperature of the other two runs.) Runs 17 and 18 (0·580) at 402°C and 3, 6 and 7 at 386°C show that k_6 is independent of the concentration of the alkyl. Runs 4 and 16 at 408·5°C, 3 (0·295) and 8 at 388°C, and 2 (0·103) and 22 at 367°C show that k_6 is also independent of a change in the surface volume ratio of the reaction vessel of a factor of six. k_6 is independent of pressure above about 10 mm as is shown by the two series of runs 12, 27, 10, 11, 13 and 30, 5, 32, 31.

The experiments may therefore be accepted as a measure of the rate of fission of the $(CH_3)_2Bi—CH_3$ bond. The activation energy given by the equation:

$$\log_{10} k_6/\text{sec}^{-1} = 14{\cdot}02 \pm 0{\cdot}01 - (44030 \pm 25/2{\cdot}303\, RT),$$

which has been obtained by the method of least squares, is then equal to the strength of the bond.

The average $Bi—CH_3$ bond energy in trimethyl bismuth is 33·8 ± 0·6 kcal mole^{-1} if $D(CH_3—H) = 102{\cdot}5$ kcal mole^{-1}.[11] The probable error of ± 0·6 kcal mole^{-1} is derived solely from the statistical uncertainty in the thermochemical measurements. The bond energy is based on a heat of formation of bismuth atoms (49·7 kcal mole^{-1}) that may well be low and should be regarded as a minimum.[19] Hence the minimum value for the sum $(D_2 + D_3)$ of the strengths of the second and third bonds is 57·8 kcal mole^{-1}.

It is possible to make some tentative deductions about D_2 and D_3. In part 2 it was found that the rate of decomposition of zinc methyl was given by

$$\log_{10} k/\text{sec}^{-1} = 6{\cdot}8 - (D/2{\cdot}303\, RT) \text{ at 16 mm.}$$

k was found to be proportional to the overall pressure. Hence if it was assumed that toluene molecules established an energetic equilibrium on each collision with zinc methyl, the results could be expressed as

$$\log_{10} k/\text{mole}^{-1}\,\text{cm}^3\,\text{sec}^{-1} = 13{\cdot}36 - (D/2{\cdot}303\, RT)$$

This A factor is very close to that which would be expected for the decomposition of a diatomic molecule in a region in which its rate is proportional to the pressure. It is therefore reasonable to assume that A_8 for the decomposition of methyl bismuth is also 13·36 mole^{-1} cm^3 sec^{-1}.

Now at 389°C, $\log_{10} k_6 = -0{\cdot}5$. Since there is no evidence that any of the methyl bismuth fails to decompose, $\log_{10} k_3$ must be $> 0{\cdot}5$. If $A_8 = 13{\cdot}36$ mole^{-1} cm^3 sec^{-1}, then $E_8 = D_3 \leqslant 19{\cdot}2$ kcal mole^{-1}. Hence $D_2 \geqslant 38{\cdot}6$ kcal mole^{-1}. If D_2 were substantially greater than 38·6 kcal mole^{-1}, k_7 would be less than k_6 for A_6 is reasonably high. It is therefore likely that $\Delta H_f(\text{Bi})g$ is not much greater than 49·7 kcal mole^{-1}.

TRIMETHYL ANTIMONY

The results obtained show that the pyrolysis of trimethyl antimony is homogeneous (32, 49), but otherwise the decomposition is not simple. Even at the highest temperatures the yield of methane and ethane falls far below the amount that would be expected if all the alkyl decomposed. For instance, in run 29, only 73·6 % of the possible gases were produced, but amounts of antimony corresponding to 98·5 % decomposition were deposited in the reaction vessel. The discrepancy is not due to the formation of substances such as hydrogen, ethylene or propylene, for negligible quantities of these gases are produced. Nevertheless, for the purpose of further discussion it will be convenient to assume that each trimethyl antimony molecule that undergoes reaction (9) yields three methyl radicals and an atom of antimony. The first-order rate constants given in the table derived from measurements of the gases, k_g, and the metal, k_m, are based on this assumption. The calculated rate constants are independent of the contact time.

TABLE 3.—THE PYROLYSIS OF TRIMETHYL ANTIMONY

run no.	temp. °C	toluene (mm)	t (sec)	CH_4	C_2H_6	$SbMe_3$*	k_g	k_m
				10^{-4} mole			(sec^{-1})	
29	603	16·5	1·33	20·7	6·40	15·2	1·00	3·16
36	569	16·5	1·43	22·2	4·90	14·9	0·885	1·78
35	558	16·5	1·44	20·7	4·00	13·9	0·814	1·47
37	541	16·5	1·47	11·2	1·47	7·80	0·612	0·890
41	519	16·5	1·55	6·11	0·670	7·55	0·258	0·332
48	518	16·5	0·55	5·86	0·920	21·2	0·232	0·291
49*a*	518	16·5	1·29	8·06	1·28	14·1	0·220	0·260
32	517	16·5	1·49	8·84	1·42	14·4	0·210	0·248
47	518	6·3	2·59	5·02	2·20	11·6	0·121	0·142
44	516	16·5	1·63	12·0	2·78	24·6	0·164	0·182
46*b*	519	29·0	1·22	19·7	2·99	33·2	0·245	0·282
42	519	16·5	1·53	13·4	3·28	27·9	0·179	0·215
14*c*	518	17·0	1·67	7·91	1·89	16·7	0·160	
23	518	16·5	3·52	12·7	3·16	14·8	0·158	
33	496	15·5	1·59	4·40	0·600	17·3	0·073	0·083
34	475	16·5	1·58	1·72	0·145	14·4	0·030	0·034

Duration of runs 30 min, unless otherwise stated.

* amount of alkyl fed into the reaction vessel.
a, run in packed reaction vessel;
b, approx. 20 μmole of ethylene formed;
c, duration of run 17 min.

Complete results for all runs from 1 to 49, except for run 45 which was spoilt, may be found in S. J. W. Price's *Ph.D. Thesis*, Edinburgh, 1958.

It can be seen from runs 44, 46 and 47 that k_m and k_g are dependent upon the pressure of toluene. The dependence is very similar to that shown by the dimethyl derivatives of the group 2 metals as can be seen from the following figures for the rate constants at 6 and 24 mm pressure of toluene.

alkyl	$Zn(CH_3)_2$	$Cd(CH_3)_2$	$Hg(CH_3)_2$	$Sb(CH_3)_3$
temp. °C	597	552	543	518
$k_{24}k_6$	2·0	2·0	1·9	2·1

This dependence is presumably due to the limiting effect of the rate of energy transfer. The greater complexity of trimethyl antimony is offset by its higher *A* factor. Hereinafter only those runs in which the toluene pressure was close to 16 mm will be considered.

The apparent loss of methyl radicals in the products which is illustrated by the figures below is most simply interpreted by supposing that a polymer of the type (SbMe) is produced.

run	29	36	37	48	32	34
temp. °C	603	569	541	518	517	475
$\frac{\%\ \text{decomposition (gas)}}{\%\ \text{decomposition (metal)}}$	·75	·78	·82	·81	·87	·91

It is simplest to suppose that the polymer is formed from $SbCH_3$ radicals by a reaction of higher order than the first. This would explain the greater formation of the polymer at the higher temperatures, although the activation energy of (12) is probably very low, because the radical concentration would then be highest. We may therefore tentatively write

$$\mathrm{Sb(CH_3)_3 = Sb(CH_3)_2 + CH_3} \tag{9}$$

$$\mathrm{Sb(CH_3)_2 = SbCH_3 + CH_3} \tag{10}$$

$$\mathrm{SbCH_3 = Sb + CH_3} \tag{11}$$

$$n\mathrm{SbCH_3 = (SbCH_3)}_n \tag{12}$$

followed by the usual reactions of methyl with toluene.

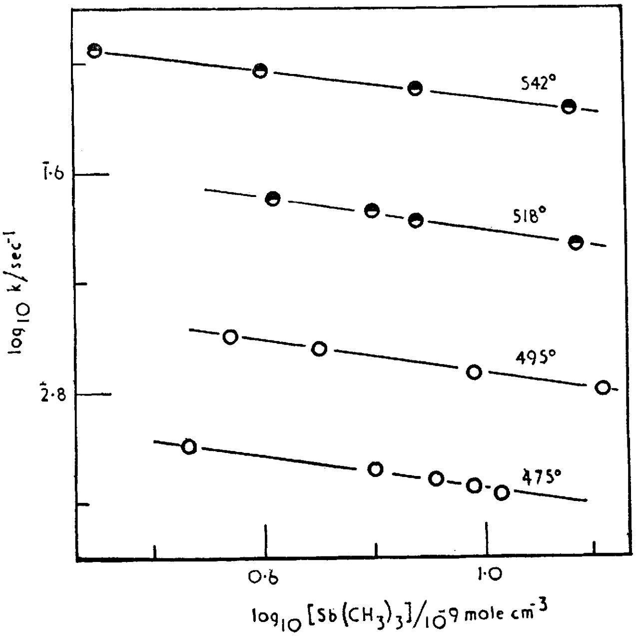

FIG. 1.—The variation of the first-order rate constant for the decomposition of trimethyl antimony with alkyl concentration.

● k_ms based on metal analysis. ○ k_gs based on gas analysis.

This mechanism does not explain the dependence of the overall rate constant, measured either by the gas produced or the metal deposited, on the initial concentration of the alkyl. The effect is illustrated in fig. 1. It is difficult to see how reaction (9) could be less than first order; accordingly we must suppose that the trimethyl can be regenerated. This may be done by the disproportionation reaction (13) with low activation energy.

$$\mathrm{2Sb(CH_3)_2 = Sb(CH_3)_3 + SbCH_3} \tag{13}$$

At a given temperature the concentration of dimethyl antimony will be roughly proportional to a fractional power of the concentration of trimethyl antimony admitted to the system. The regeneration will probably be proportional to a power of the initial alkyl concentration higher than the first but lower than the second. This mechanism accounts qualitatively for the observed effects. The complexities introduced by the flow conditions and the limited precision of the results makes it impractical to apply a detailed quantitative treatment.

If this mechanism is correct, values of k_9 should be obtained by measurements of the rate of metal production at zero alkyl pressure. Unfortunately the results do not lend themselves well to extrapolation to zero alkyl pressure. However, it can be seen that the plots of $\log_{10} k$ against $\log_{10}$ alkyl concentration at the different temperatures are nearly parallel. We may therefore be reasonably confident that the values of $\log k_9$ at zero alkyl concentration will run closely parallel to the values at a concentration of $7{\cdot}6 \times 10^{-9}$ mole cm^{-3}. The Arrhenius equations derived from metal and gas analyses are:

$$\log_{10} k_9/\text{sec}^{-1} = 15{\cdot}2 - (57000/2{\cdot}303\,RT)\ \text{(metal)},$$

and

$$\log_{10} k_9/\text{sec}^{-1} = 14{\cdot}1 - (53500/2{\cdot}303\,RT)\ \text{(gas)},$$

respectively.

It seems reasonable to assume that the observed activation energy based on the metal analysis for the decomposition of trimethyl antimony is very close to $D((CH_3)_2Sb—CH_3)$. By making similar assumptions to those employed when discussing the second and third bonds in trimethyl bismuth, it may be shown that $D(Sb—CH_3)$ is unlikely to be greater than 27 kcal mole^{-1}. The minimum value of 46 kcal mole^{-1} currently accepted [19] for the heat of formation of antimony atoms corresponds to a value of 135 kcal mole^{-1} for the sum of the three bonds of trimethyl antimony.[12] Hence $D(CH_3Sb—CH_3)$ is at least 51 kcal mole^{-1}. The observed kinetics would not obtain if D_2 were substantially greater. Accordingly, the present work supports a low value for $\Delta H°(Sb)g$.

The pyrolysis of trimethyl antimony is so complex, even when studied by this toluene carrier technique, that it is difficult to believe that the pyrolysis of trimethyl arsenic in a static system is straightforward. Hence, in our view, little reliance can be placed on the suggestion of Ayscough and Emeleus [5] that the overall activation energy observed by them is equal to the strength of the $(CH_3)_2As—CH_3$ bond.

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