International Journal of Academic Research and Development
ISSN: 2455-4197
Impact Factor: RJIF 5.22
www.academicsjournal.com
Volume 3; Issue 3; May 2018; Page No. 231-233

Kinetic study of D [$(CH_3)_3Pb\text{-}CH_3$] by the Toluene carrier flow system

Arundendra Pandey[1], Priyanka Patel[2], Anita Tiwari[3], RP Pandey[4]

[1, 2] Department of Chemistry, Govt. Model Science College, Rewa, Madhya Pradesh, India
[3, 4] Professor, Department of Chemistry, Govt. Model Science College, Rewa, Madhya Pradesh, India

Abstract

Tepra methyl lead has been studies in a toluene carrier flow system over the term range 671-753°K. The reaction was followed by measuring the amount of, methane, ethane and Althyl benzene formed comparison of the extent of reaction based on product analysis and alkyl recovery indicate that approximately feure methyl radicals are relate for each molecule undergoing reaction $K_1 = 5.0 \times 10^{14}$ Exp (-49400 / RT) SB^1 with an estimated under certainly of ±1000 cal mol^{-1} in E_1. Under the conditions used E_1 should be a reasonable measure of D[$(CH_3)_3$ Pb-CH_3)].

Keywords: kinetic study, methane, ethane and althyl benzene

Introduction

The Kinetic study of the Pyrolysis of $Ph(CH_3)_4$ has been Previously studied by electron 1 with the very dilute stream of Pb(CH3)4 in at a total pressure of 0.4 mm he obtained $K_1 = 1.5 \times 10^{10}$ Exp (-28200/ RT)5^{-1} (400-700°C, Decomposition 600°C).

$$Pb\ (CH_3)_4 \Leftrightarrow Pb\ (CH_3)_3 + CH_3$$

Both the factor and activation energy are unreasonably low. A recent investigation (2) combined mass spectrometric data. Thermo chemistry to give $D(CH_3)_3Pb\text{-}CH_3] = 48.8$ K Cal Mol^{-1}, based on $\Delta H^0_{10}(CH_3, g) = 34.8$ K Cal Mol^{-1} (3). the present work was designed to obtain a revaluation of both A_1 and D_1.

Experimental

Material

a. Toluene from sulfonic acid was refluxed over sodium under vacuum and then degassed by bulb-to-bulb distillation.
b. Tetra methyl lead was obtained from the ethyl carporation as a blend containing 68% $Pb(CH_3)_4$ and 32% toluene. The $Pb(CH_3)_4$ was separated by a series of four successive fractional crystallizations in each stage of which approximately 50% of the solution was allowed to solidity and the remaining. Light was discarded the resulting product had a refractive index of 1.15120 at 20°C in agreement with the literature value (4). A small quantity of residual toluene was found by gas chromatographic analysis. A part from necessitating a small correction in the weight of alkyl used in a run the residual toluene was no significance as all experiments were carried out in a toluene carrier system.

Apparatus and procedure

Except for the substitution of an electron capture detector for the hydrogen flame detector when tests were made for possible lead containg products, all apparatus and procedures were identical to those used previously for $Sn(CH_3)_4$ (5)

Results and Discussion

Selected experimental results are given in tables 1-4.
They may be discussed in terms of the following mechanism.

1. $Pb(CH_3)_4 \quad \Leftrightarrow \quad Pb(CH_3)_3 + CH_3$
2. $Pb(CH_3)_3 \quad \Leftrightarrow \quad Pb(CH_3)_2 + CH_3$
3. $Pb(CH_3)_2 \quad \Leftrightarrow \quad PbCH_3 + CH_3$
4. $PbCH_3 \quad \Leftrightarrow \quad Pb + CH_3$

Table 1: Selected results for the Pyrolysis of tetramethyl lead.

T(k)	p(mm)	fc(S)	Alkyl used mol x 10^4	Products (mol x 10^4)			
				CH_4	C_2H_6	$C_6H_5C_2H_5$	$K_1(5^1)$
743	12.2	0.81	7.37	5.50	5.50	3.47	1.39
734	14.4	1.00	5.83	5.86	4.24	2.70	1.30
725	13.4	0.82	6.10	3.24	2.59	1.96	0.69
715	15.5	1.37	3.72	2.87	1.23	0.91	0.39
711	14.1	1.08	6.23	2.76	2.05	1.57	0.38
708	13.5	0.85	5.17	1.61	1.03	1.22	0.32
700	14.7	0.83	8.22	1.90	0.97	1.22	0.20

693	15.2	0.80	18.70	3.00	1.01	1.89	0.14
692	14.7	1.02	6.06	1.44	0.66	0.75	0.15
683	13.7	0.88	7.56	0.87	0.33	0.39	0.074
671	14.1	0.96	7.40	0.63	0.23	0.29	0.038

Table 2: Comparison of percent decomposition based on product analysis with that determent by residual alkyl analysis

T (°K)	**% decomposition**		
	Product analysis	**Alkyl recovery**	**CH_3 per $Pb(CH_3)_4$ undergoing reaction**
734*	73.7	76.5	3.86
728	63.6	64.7	3.93
724	63.6	63.7	3.99
714	46.2	45.7	4.04
712	44.5	43.7	4.06
711	41.6	44.0	3.80
711*	34.4	35.7	3.86
692*	15.4	15.7	3.92

Table 3: Effect of alkyl concentration

T (°K)	**Initial $Pb(CH_3)_4$ [(mol/cc) x 10^9]**	**Ki (5^{-1})**
720	0.76	0.53
	1.04	0.55
	2.58	0.54
714	2.17	0.38
	4.03	0.39
	4.25	0.39

Table 4: Effect of total pressure on K1

T (°K)	**Pressure (Cm.)**	**Ki (5^{-1})**
720	2.79	0.39
	1.62	0.40
	0.53	0.38

5. $CH_3 + C_6H_5CH_3 \Leftrightarrow CH_4 + C_6H_5\text{-}CH_3$
6. $2CH_3 + M \Leftrightarrow C_2H_6 + M$
7. $CH_3 + C_6H_5CH_2 \Leftrightarrow C_6H_5C_2H_5$

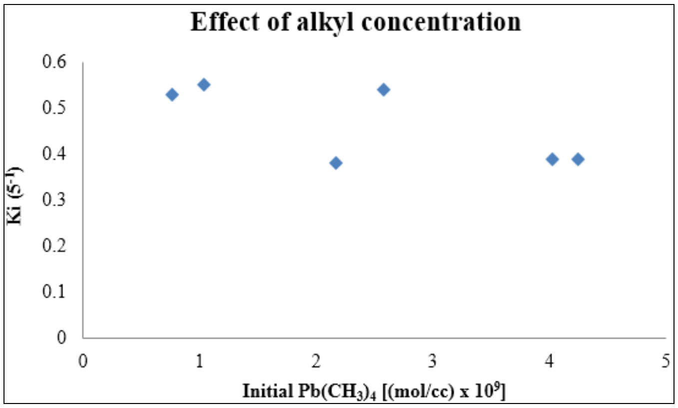

Fig 1

As shown by the product distribution in table 1. Reaction 5-7 are all major processes under the experimental conditions used (Toluene alkyl molar ratios 50-300 with the bulk of these between 65 and 100). In table 2 a comparison in make between the % decomposition based on product analysis.

8. $$\%\ decomp. = 100\left(\frac{Moles\left(CH_4 + C_6H_5C_2H_5\right) + 2(Moles\ C_2H_6)}{4(Moles\ Pb\ (CH_3)_4\ used}\right)$$

9. $$\%\ decomp. = 100\left(\frac{Moles\ Alkyl\ used - Moles\ alkyl\ recovered}{Moles\ Alkyl\ used}\right)$$

The agreement between these methods shows that essentially four methyl radicals are released for each molecules undergoing reaction 1 and indicates that no undetected major products were produced. Acid digestion of the deposit formed outside he reactor did indicate the formation of about 0.1% $(Pb\text{-}CH_3)n$ or some similar compound. Early results seemed to indicate the formation of a very small amount of a volatile lead containing product but this could not be confirmed.

The value of K_1 shown in table 1, 3 and 4 and used to obtained the arrhimius plot. Shown in fig. 1 have calculated form the usual first order equation,

$$K_1 = \frac{2.3}{tc}\log\frac{100}{100 - x}$$

where x, the present decomposition have been calculated eq.8. The result in table 3. Support the assumption of first order behavior and table 4 shown that as expect to significant molecular pressure effects are observed.

Least - squares analysis of the points in fig. gives

$$K_1 = 5.0 \times 10^{14} Exp.\left(\frac{49400}{RT}\right)5^{-1}$$

with an estimated uncertainty of ±1000 cal mol^{-1} in E_1. This results has been obtained at the high pressure limit and using flow conditions. Selected to minimize errors due to thermal equilibrium or diffusion problem (6, 7). The observed activation energy should therefore be a reasonable measure of $D[(CH_3)_3\ Pb\text{-}CH_3]$ comparison with the value of Lappert *et al.* (2), 48.8 K Cal Mol^{-1} indicated good agreement with

$$\Delta H^0_{1298}\left(CH_{3,g}\right) = 33.2\ K\ Cal\ Mol^{-1}\ \ (8)$$

and hy b

or at 0°K approx.. 142 K Cal Mol^{-1} this leads to an average bond dissociation energy for the four $Pb\text{-}CH_3$ bonds D = 35.7 K Cal Mol^{-1} compared to the value of 38.4 K Cal mol^{-1} used by Lappert at all (2). 0.8 K Cal mol^{-1} of the difference is the to different values accepted for $\Delta H^0_{10}\left(CH_{3,g}\right), 34.0\ K\ Cal\ mol^{-1}$ in the present work (8) and 34.8 by Lappert (3). The bulk of the remaining 1.9 K Cal mol^{-1} difference is due to an error in

Lappert's work caused by using $\Delta H_{10}^{0}(CH_{3,g}) and\ \Delta H_{10}^{0}$ (Pb, g) in conjunction with $\Delta H_{1298}^{0}(Pb(CH_3)_{4,g})$ therefore accepting E_1 as a reasonable measure of D_1 gives $D_2 + D_3 + D_7 = 93.5$-96.7 K cal mol-1 (depending) on the value chosen for $\Delta H_{10}^{0}(CH_{3}.g)$.

An estimated correction for the effect of pressure thus gives $E_2 + E_3 + E_4 =$ approximately 85-88 K Cal mol^{-1}. with any reasonable choice of A_2, A_3 and A_4 (5) it is obvious that value of E_2, E_3 and E_4 can be assigned which satisfy the relationship $K_1 >> K_2, K_3, K_4$. Decomposion by reactions 1-4 with reaction 1 rate controlling is therefore plausible.

References

1. Eltenton GCJ. Chem. Phys. 1947; 15:455.
2. Lappert MFd. Pedley TB. Simpson J, Spalding TR. J Organometal Chem. Phys¸ 1971; 29:195.
3. Chupka WA. J Chem. Phys. 1968; 48:2337.