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INTER-OFFICE CORRESPONDENCE

June 8, 1938.

Dr. Robert A. Kehoe
College of Medicine
University of Cincinnati
Cincinnati, Ohio

Dear Bob:

I am sending you herewith a copy of our Report LTD 38-25 on the mechanism of decomposition of triethyllead bromide by steam distillation. As I told you during your last visit, we are pursuing those studies, and I will send you reports from time to time on the other alkyl lead salts.

Very truly yours,

George Calingaert

GC:AMC
Encl.

LTD #38-25
O.E.Kurt
F.J.Dykstra
263-XP-15, pp 41-51
May 23, 1938.

STEAM DISTILLATION OF LEAD TRIETHYL BROMIDE

PURPOSE

This study is part of the problem of determining the volatility of lead ethyl salts and their decomposition products. The run reported here was made by Mr. Dykstra in order to verify the results of previous runs (230-XP-19 and 230-XP-22 reported in LTD #37-28 and 230-XP-23 reported in LTD #38-1) and in order to acquire technique for subsequent runs on other lead alkyl salts.

CONCLUSIONS

The decomposition of $PbEt_3Br$ proceeds as follows, these results confirming those of previous runs:

	230XP22	230XP23	This Run
$2\ PbEt_3Br = PbEt_4 + PbEt_2Br_2$			
$2\ PbEt_2Br_2 = PbEt_3Br + PbBr_2 + EtBr$	63%	84%	83
$PbEt_2Br_2 = PbBr_2 + 2\ Et$	37	16	17
Percent decomposed at 100° C	89	81	72
Time of Run	210	160	160

SUMMARY

Very good yields of pure EtBr and $PbEt_4$ were obtained.

The composition of the hydrocarbon products was not established because gas analysis results were unsatisfactory. The yield of gas, though measured more accurately than previously, is still much lower than theoretical.

The relative extent of the two decomposition reactions of $PbEt_2Br_2$ was calculated from the data for $PbEt_3Br$, $PbEt_4$, $PbBr_2$ and EtBr, which are in good agreement with each other.

All of the lead was accounted for except 2.5 percent, which loss can be ascribed to handling.

DETAILS

The apparatus and procedure were similar to those of runs 230-XP-22 and 230-XP-23. Several modifications were made which improved the products and reduced the work required. A 500 cc. 3-neck round-bottom flask was used as a boiler. One side neck was fitted with a stopcocked inlet for nitrogen. The other side neck was connected to the reflux condenser and $PbEt_4$ trap. The $PbEt_4$ trap was fitted with a water return tube which worked satisfactorily. No beads were used in the distilling column or in the condenser. The condenser was cooled with cold tap water at approximately 15°C. A small tube connected the upper end of the condenser to a trap kept in a dry-ice acetone bath and then led to the gas burette. The apparatus is sketched in the attached blueprint.

The $PbEt_3Br$ was freshly recrystallized from dry mixed hexane. 300 cos distilled water was placed in the boiling flask, the air in the apparatus was replaced by nitrogen, the water was boiled until equilibrium was reached, then a filter paper thimble filled with $PbEt_3Br$ was placed in the flask through the central neck. Consequently the increase in the gas volume in the apparatus, which is measured by the gas which passes into the burette, is all due to gas generated and not partly due to thermal expansion of the nitrogen as in previous runs. The gas was drawn into evacuated 100 cc. pipettes after being measured in the burette. The run was stopped after 160 minutes. The system was flushed with nitrogen to collect the gas in the system.

The initial material and the products were analyzed to obtain the results presented in the attached table. Analysis of the initial material gave two values for % Pb and one value for % Br equal within experimental error to those of pure $PbEt_4Br$. The other % Br seems unreliable in view of the method of purification so the most probable composition to accept is that of pure $PbEt_3Br$.

The $PbEt_4$ layer of the distillate had a specific gravity so close to that of pure $PbEt_4$ that it was not considered necessary to give it any further treatment. It was assumed to contain 1% EtBr. Analysis for Pb showed it to be quite pure, but the % Pb was used to calculate the mols of $PbEt_4$.

The material which condensed in the dry ice trap was quite pure EtBr according to the specific gravity and refractive index measurements. There was considerably larger amount than was obtained in previous runs, even after including the EtBr found condensed in the $PbEt_4$ layer in previous runs.

The water solution left in the boiler deposited beautiful crystals on cooling, presumably of $PbBr_2$. It was reheated to put the $PbBr_2$ and undecomposed $PbEt_3Br$ into solution, the flask was washed and an aliquot portion of the solution analyzed. A residue remained in the flask which was molten in hot water and solid at room temperature. All except a small portion of it and the residue on the filter paper were put into solution with ether. The residue was dissolved in nitric acid and analyzed for lead.

The gas was collected in three 100 cc. pipettes. The analyses were mostly unsatisfactory. The results on the first pipette did not check each other. The results on the second pipette gave an H/C ratio of 2.38. The contents of the third pipette were not analyzed. The molecular weight calculated from the weight of the gas in the pipettes, which is mostly nitrogen, indicate that the hydrocarbon gas may be C_2H_4 and C_2H_6. 63.3 cos. of evolved gas at 25°C and 760 mm. would be .00259 mols. If the gas were C_2H_4 and C_2H_6 this would account for .00259 mol Et. Some Et might have polymerized to form higher hydrocarbons but then some of these should be found in the dry ice trap with the EtBr. The missing Et calculated from the other products, 0.00345 mol equals 0.100 gm., is small enough so that it might easily be lost in the EtBr, the $PbEt_4$, or absorbed in the rubber connections.

The missing Pb is assumed to be $PbEt_4$, which has either been volatilized or held up in the condenser, or decomposed to Pb in the $PbEt_4$ trap. It is also partly due to experimental errors in analysis.

The relative extent of the two $PbEt_2Br_2$ decomposition reactions are calculated from the data for $PbEt_3Br$, $PbBr_2$ and $PbEt_4$ in the attached table. It will be noted that the sum of equations (4) and (5) necessarily equals (3) because all the Pb has been accounted for by assigning the missing Pb to equation(4). Consequently there are really only two equations for solving for the two unknowns, a and b. The only check on the results lies in the fact that experimentally the Pb balance is quite good. Even so the 2.5% of missing Pb is a large enough amount to cause a high uncertainty in the values of a and b except for the fact that we can ascribe the missing Pb quite definitely to $PbEt_4$. A high uncertainty could occur in the analytical results, so it is recommended that the technique be improved to recover all of the Pb.

STEAM DISTILLATION OF $PbEt_3Br$ - 263-XP-15

		ANALYSIS		COMPOSITION - Gm.Mo
Initial $PbEt_3Br$	14.955 gm.	55.34% Pb	20.80% Br	0.03996 $PbEt_3Br$
		55.44	21.43	
	Theoretical:	55.37	21.36	
Distillate - $PbEt_4$ layer	3.40 cc @ 25°	Sp.Gr. 1.645, 1.643 (cf. 1.6528)		0.01712 $PbEt_4$
		63.40% Pb		.00051 EtBr
		63.55		
	Theoretical:	64.06		
Dry ice trap	0.35 cc @-70°	Sp.Gr.@ 23.5°, 1.445, 1.467 (cf. 1.450)		0.00528 EtBr
		R.I. 1.4233 (cf. 1.4239)		
Still residue -water soln.		0.01846 mol Pb, 0.028817 mol Br		0.01036 $PbBr_2$
" " ether extract		.00312 mol Pb, .00311 mol Br		.00810 $PbEt_3Br$
" " residue		.00023 Pb		.00311 $PbEt_3Br$
				.00023 ($PbBr_2$?
Volatile gas	63.3 ccs.	#1 ml.wt. 27.85	16.6% combustible	.00259 Et_x
		#2 " 27.95	12.7 "	H/C = 2.38
		#3 " 27.95	not analyzed	
Missing Pb				.00104 $PbEt_4$

3a $PbEt_3Br$ = 2 $PbEt_4$ + $PbBr_2$ + EtBr — 3a = 0.02271 (1)

2b $PbEt_3Br$ = $PbEt_4$ + $PbBr_2$ + 2 Et — 2b = 0.00604 (2)

$PbEt_3Br$ = 3a + 2b = .03996 - (.00810 + .00311) = .02875 (3)

$PbEt_4$ = 2a + b = .01712 + .00104 = .01816 (4)

$PbBr_2$ = a + b = .01036 + .00023 = .01059 (5)

a = 0.00757 b = 0.00302

EtBr = a = .00757, Recovered: .00051 + .00528 = .00529, Missing = .00228 (6)

Et_x = 2b = .00604, Recovered .00259, Missing = .00345 (7)

CEK