On the Mechanism of the Reaction of Sodium-Lead Alloys with Ethyl Halides

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The reactivities of ethyl halides with active lead or sodium were investigated. The reactivities of ethyl halides with sodium-lead alloys were quite analogous to those of ethyl halides with sodium. The analysis of the gases produced in the reaction of sodium-lead alloys with ethyl halides revealed the presence of ethane, somewhat smaller amounts of ethylene and propane, *etc.* In the reaction of a sodium-lead alloy with ethyl halide in the presence of isopropylbenzene, 2, 3-dimethyl-2, 3-diphenylbutane was formed. In the reaction of ethyl bromide or ethyl iodide with sodium dispersed in isopropylbenzene, 2, 3-dimethyl-2, 3-diphenylbutane was also formed. On the basis of these results, it may be concluded that, in the reaction of sodium-lead alloys with ethyl halides, the initial step in the reaction is the formation of ethyl radicals by the reaction of ethyl halides with sodium in the alloys; then these radicals are combined with lead.

The mechanism of the reaction of sodium-lead alloys with ethyl halides is as yet unknown.[1,2] According to Groggins,[3] the reaction of monosodium-lead alloy with ethyl chloride is represented by:

$$4 \, PbNa + 4 \, C_2H_5Cl =$$
$$Pb(C_2H_5)_4 + 3 \, Pb + 4 \, NaCl$$
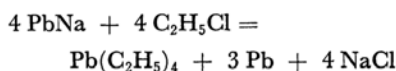
Marsh *et al.*[4] have stated, in a paper dealing with the crystal structures of monosodium-lead alloys, that the initial step in the formation of tetraethyllead is the production of free alkyl radicals by the action of sodium atoms on alkyl halides; however, no experimental evidence has been given.

The reactivities of sodium-lead alloys with ethyl halides are influenced to a great extent by both the sodium contents of the alloys and the kinds of halides. The present author[5] has investigated systematically the differences in these reactivities; he has concluded that, in order for the reaction to proceed efficiently, ethyl halides need to penetrate into the alloys and that the differences in the reactivities are to be ascribed to the penetration abilities of the ethyl halides.

In this paper, in an attempt to find out whether ethyl halide reacts in the first step with lead or with sodium in sodium-lead alloy, the correlation between the reactivities of ethyl halides with lead or with sodium and those of ethyl halides

with sodium-lead alloys was investigated. In order to find the free radicals produced in the reaction, the evolving gas was analyzed by gas chromatography; further, the formation of 2, 3-dimethyl-2, 3-diphenylbutane in the presence of isopropylbenzene was established. 2, 3-Dimethyl-2, 3-diphenylbutane was also produced in the reaction of sodium dispersed in the isopropylbenzene with ethyl bromide and iodide. On the basis of these results, the initial step of the formation mechanism of tetraethyllead will be discussed.

Results and Discussion

The yields of lead halides from ethyl chloride or bromide were poor. These results indicate that neither of the addition products, namely, ethyllead halides or tetraethyllead, is formed in any substantial amounts in the reaction of lead with ethyl halides. On the basis of this and other previously-reported results,[5,6] it may be considered that, in the absence of catalysts such as iodine, the reactivity of lead with ethyl halides is quite low.

The yields of sodium halides in the reaction of sodium with ethyl halides are shown in Table 1. The reactivities of sodium-lead alloys with ethyl halides in the presence or in the absence of any added compounds such as ethyl alcohol have previously been reported.[2,5,7-9] These reactivities are quite analogous to those of sodium with ethyl chloride or ethyl bromide; this suggests a

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7) W. S. Calcott, U. S. Pat 1559405 (1853); K. P. Monroe, U. S. Pat. 1661809 (1928).
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TABLE 1. YIELDS OF SODIUM HALIDES BY THE REACTION OF SODIUM WITH ETHYL HALIDES

Ethyl halide	Vol. of ethyl halide ml	Wt. of sodium g	Added compound ml	Reaction temp. °C	Reaction time hr	Yield %
EtCl	500	20	None	60	5	4.3
EtCl	500	20	None	70—80	5	2.8
EtCl	500	20	None	100	5	10.5
EtCl	500	20	None	120—130	5	89.2
EtCl	10	0.5	Ethyl alcohol 5	2	2	51.5
EtBr	10	0.5	None	36.5—37	2.5	2.3
EtBr	100	5	None	74—86	2.5	6.8
EtBr	100	5	None	120	2.5	23.9
EtBr	10	0.5	Water 5	37—38	2	13.3
EtBr	10	0.5	Ethyl alcohol 5	37—38	2	100.
EtBr	10	0.5	Ethyl alcohol 5	37—38	2	58.5
EtBr	10	0.5	Dimethylaniline 5	37—38	2	15.9
EtI	100	5	None	60	2	5.2
EtI	100	5	None	80	2	18.2
EtI	100	5	None	100	2	50.8
EtI	100	5	None	120	2	65.9

TABLE 2. GAS CHROMATOGRAPHICAL ANALYSES* FOR REACTION GAS OF SODIUM-LEAD ALLOYS WITH ETHYL HALIDES

Experiment No.		(1)	(2)	(3)	(4)	(5)	(6)
Reaction Material		$PbNa$ C_2H_5Cl	$PbNa$ C_2H_5Cl	$PbNa$ C_2H_5Br	$PbNa$ C_2H_5Cl Cumene	$PbNa$ C_2H_5Cl Cumene	$PbNa$ C_2H_5Cl Cumene
Reaction temp., °C		80	60	100	100	80	60
	Name						
Peak No. 1	Ethane	52.5%**	11.0	51.9	38.0	63.2	49.9
2	Ethylene	37.2	6.4	36.7	7.8	26.3	19.1
3	Propane	0.2	0.3	0.1	trace	0.2	0.1
4	Carbon dioxide	0.1	—	—	0.5	0.4	0.1
5	Propylene	0.1	—	—	trace	0.1	0.1
6	Isobutane	0.1	—	—	trace	—	0.1
7	n-Butane	6.5	79.9	6.2	49.8	9.4	30.8
8	Butene-1	0.8	0.2	0.1	0.1	0.2	0.1
9	Isobutene	1.6	—	—	—	—	—
10	trans-2-Butene	0.4	—	0.2	1.2	0.1	—
11	cis-2-Butene	0.3	—	0.1	2.6	—	—
12	Butadiene	0.2	2.2	—	—	·-	—

* Column: Squalane 0.75 m + DMF 9.75 m, 0°C. Carrier gas: He 100 ml/min.
** Relative ratio of area (nitrogen, oxygen and ethyl halides have bee leaved out).

similar mechanism for these reactions. However, ethyl iodide did not react with sodium-lead alloy in the absence of any added compounds, though it reacted quite efficiently with sodium. As has been discussed in a previous paper,[5] this result may be explained in terms of a suggested mechanism by which, in the reaction of sodium-lead alloy with ethyl halides, the reaction proceeds by means of the penetration of ethyl halides into the alloys; the degree of penetration may be influenced very much by the molecular size of the ethyl halides and by the vapor pressure as well as by the properties of the alloys. The ability of ethyl iodide to penetrate may be quite low. From the above discussion it may be concluded that ethyl halides react in the first step with sodium in sodium-lead alloys in the absence of any added compounds such as ethyl alcohol.

The results of the gas-chromatographic analysis of the reaction gas of monosodium-lead alloys with

ethyl chloride at 80 and 60°C and with ethyl bromide at 100°C are shown in (1), (2) and (3) of Table 2, which shows the formation of ethane and ethylene. These hydrocarbons may be formed by the disproportionation of ethyl radicals. At lower temperatures, the volume of *n*-butane increased; hence, the dimerization of ethyl radicals may take place predominantly. At higher reaction temperatures, propane, propylene and other hydrocarbons were formed; they may be formed *via* the fission of free ethyl radicals, for example:

$$\cdot CH_2CH_3 \rightarrow :CH_2 + \cdot CH_3$$

$$\cdot CH_3 + \cdot C_2H_5 \rightarrow CH_3CH_2CH_3$$
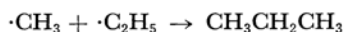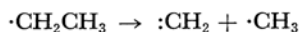
In the reaction of monosodium-lead alloy with ethyl chloride in the presence of isopropylbenzene as a detector of free radicals, the yields of 2, 3-dimethyl-2, 3-diphenylbutane (based on isopropylbenzene) at 100, 80 and 60°C were *ca.* 4.3, 3.3 and 1.0% respectively. This may be assumed to be due to the following reaction:

$$2\ C_6H_5CHMe_2 + 2\cdot C_2H_5 \rightarrow$$

$$C_6H_5\cdot CMe_2\cdot CMe_2\cdot C_6H_5 + 2C_2H_6$$
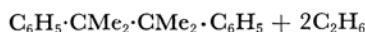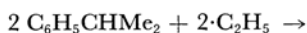
As to the Wurz reaction, the possibility of heterolysis or homolysis has hitherto been much discussed,[10] and recently Bennet *et al.*[11] have detected free radicals by an ESR technique. The reaction of sodium dispersed in isopropylbenzene with ethyl bromide and iodide in an autoclave at 120°C gave 2, 3-dimethyl-2, 3-diphenylbutane (4.8 and 9.5%, respectively). The results of the gas-chromatographic analysis of the reaction gas are given in Table 3. Except in the case of ethyl chloride, ethane is predominant over ethylene. Propane and other hydrocarbons, including methane, were also detected. The presence of propane or methane may be supposed to be produced *via* the fission of free ethyl radicals, as has been discussed in the case of sodium-lead alloys. These results make the presence of free radicals in the reaction apparent.

The thermal decomposition of tetraethyllead mixed with isopropylbenzene at 236—286°C in an autoclave gave only a small quantity of an oily product and no 2, 3-dimethyl-2, 3-diphenylbutane in spite of the fact that the thermal decomposition of tetraethyllead in the liquid state can give the

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11) J. E. Bennet and H. Thomas, *Nature*, **145**, 995 (1962).
12) G. A. Razuvaev, N. S. Vyazankin and N. N. Vyshinskii, *Zhur. Obshchei Khim.*, **29**, 3662 (1950); R. N. Meinert, *J. Am. Chem. Soc.*, **55**, 979 (1933); P. L. Gramer, *ibid.*, **56**, 1234 (1934); F. Paneth and W. Lautsh, *Ber.*, **64**, 2702 (1931).

TABLE 3. GAS CHROMATOGRAPHICAL ANALYSIS* FOR REACTION GAS OF SODIUM WITH ETHYL HALIDES IN THE PRESENCE OF CUMENE

Experiment No.		(7)	(8)	(9)
Reaction Materials		Na C_2H_5Br Cumene	Na C_2H_5I Cumene	Na C_2H_5Cl Cumene
Reaction temp., °C		120	120	60—150
	Name			
Peak No. 1	Ethane	44.4%**	71.0	42.2
2	Ethylene	22.2	17.1	33.7
3	Propane	0.3	0.1	0.1
4	Carbon dioxide	—	0.3	0.1
5	Propylene	—	0.1	trace
6	Isobutane	—	—	trace
7	*n*-Butane	25.9	6.4	23.80
8	Butene-1	1.2	3.2	0.2
9	Isobutene	2.3	—	—
10	*trans*-2-Butene	0.6	0.5	trace
11	*cis*-2-Butene	0.5	0.7	trace
12	Butadiene	2.6	—	—

* Similar to Table 2 ** Similar to Table 2

ethyl radical.[12] No 2, 3-dimethyl-2, 3-diphenylbutane was obtained in the reaction of ethyl chloride with sodium dispersed in isopropylbenzene. Some other reaction may be more dominant than the dimerization of isopropylbenzene radicals in these cases where the reaction proceeds violently. Probably the sudden increase in the concentration of free ethyl radicals in these reactions may be expedient for the disproportionation and the dimerization of ethyl radicals and for some other reactions.

The free radicals might be due to the decomposition of tetraethyllead or some intermediates of the reaction. Tetraethyllead, however, does not decompose, at least below 140°C. The tetraethyllead formed in the reaction can not be considered to decompose at the reaction temperature of 80—100°C. Thus the free radicals would be formed principally as follows:

$$C_2H_5X + Na \rightarrow \cdot C_2H_5 + NaX$$

Experimental

Materials. Commercial ethyl chloride was used. It was found to be 99.98% pure by gas chromatography. Ethyl bromide, ethyl iodide and isopropylbenzene were used after the rectification of commercial products. Their purities were 99.90, 99.69 and 99.60% respectively.

The Reaction of Lead with Ethyl Halides. Lead (110 g), after it had been deoxidized in a stream of hydrogen for 15 hr at 350°C, was reacted with ethyl chloride (500 m*l*) in an autoclave with agitation at 80—120°C for 2.5—5 hr. After the reactions had been completed, the ethyl chloride was driven off and the

residue was dissolved in nitric acid and heated; the chloride content was then determined by the $AgNO_3$-KCNO method. Deoxidized lead (4 g) was reacted at 37—40°C for 2 hr with ethyl bromide (20 m*l*) in a 100-m*l* flask equipped with a reflux condenser. The same tests were performed in the presence of dimethyl-aniline, diethyl ether, and other substances. The yields of the lead halides were less than 1% (based on lead) in every case.

The Reaction of Metallic Sodium with Ethyl Halides. Ethyl chloride (500 m*l*) was reacted at 15—130°C for 5 hr with metallic sodium (17—20 g) in a 1000-m*l* autoclave equipped with an internal agitator. After a liquid part had been separated from the reaction product, a solid residue was dried and dissolved in water; the sodium chloride in the product was then determined by the $AgNO_3$-KCNO method. Ethyl halide (10 m*l*) was reacted with sodium (0.5 g), while ethyl alcohol (5 m*l*) was poured into a 100-m*l* flask equipped with a reflux condenser. After the reaction had been completed, the sodium chloride formed was analyzed. Ethyl bromide was reacted with metallic sodium, and the sodium bromide formed was determined. The same tests were performed in the presence of water, ethyl alcohol, ethyl acetate, dimethyl aniline, and ethyl ether. A 100-m*l* flask was used for the reaction at 37—38°C, while a 100-m*l* autoclave was used in the case of 80 and 120°C; the reaction of sodium with ethyl iodide was carried out similarly.

Gas Chromatography of the Gas Formed in the Reaction of Sodium-Lead Alloys with Ethyl Halides. A sodium-lead alloy (100 g) containing *ca.* 10% sodium was reacted with ethyl halides (200 m*l*) by external heating in a 500-m*l* autoclave equipped with an internal agitator for 3 hr, at 80 and 60°C in the case of ethyl chloride and at 100°C in the case of ethyl bromide; after the reaction had been completed, the reaction gas was analyzed by gas chromatography.

The Reaction of Sodium-Lead Alloy with Ethyl Chloride in the Presence of Isopropylbenzene. A typical reaction was as follows: monosodium-lead alloy (100 g), ethyl chloride (120 m*l*), and isopropyl-benzene (30.3 g) were reacted at 80°C for 4 hr in a 500-m*l* autoclave equipped with an agitator. After the reaction had been completed, the reaction gas was analyzed by gas chromatography. The results are shown in (4), (5) and (6) of Table 2. The excess ethyl chloride was then evaporated and a liquid part of the product was extracted with ethyl ether. The extract was distilled at 42—77°C/12 mmHg, and the distillate was analyzed by gas chromatography; the tetraethyllead content was 21.2 g (15.1% based on lead). The residue

was a yellowish white solid, *ca.* 1.0 g (3.3% based on iso-propylbenzene); recrystallization from ethyl alcohol gave colorless crystals, mp 116.4—116.8°C.

Found: C, 89.75; H, 9.04%. Calcd for $C_{18}H_{22}$: C, 90.75; H, 9.25%.

The Reaction of Sodium Dispersed in Isopropylbenzene with Ethyl Halides. A typical run was as follows; sodium (8.75 g) dispersed in isopropyl-benzene (56.3 g) was reacted as above with ethyl bromide (120 m*l*) at 120°C for 5 hr. The organic materials in the reaction products were then extracted with ethyl ether and filtered. The filtrate was then distilled at 32—68°C/7 mmHg. The residue was colorless crystals (2.1 g) (4.8% yield based on the converted sodium). It was recrystallized from ethyl alcohol, mp 116.5—117.0°C.

Found: C, 90.00; H, 9.05%. Calcd for $C_{18}H_{22}$: C, 90.75; H, 9.25%.

The reaction of ethyl chloride with sodium in the presence of isopropylbenzene was very violent. The product was treated in the same way as above, and a small amount of a reddish-brown, viscous, oily material was obtained.

Thermal Decomposition of Tetraethyllead. Tetraethyllead (10 g) was heated gradually in a tube equipped with a thermometer and immersed in an oil bath. The liquid became slightly muddy at around 85°C. At around 120°C a small amount of a brown material floated on the upper layer of the liquid. At 150°C the brown precipitates turned black and the liquid boiled vigorously and began to decompose, evolving gas. At around 165°C it decomposed violently and the temperature suddenly rose as much as 20—30°C.

Thermal Decomposition of Tetraethyllead in the Liquid State in the Presence of Isopropylbenzene. Tetraethyllead (7.0 g) and isopropyl-benzene (20.5 g) were mixed in a 45-m*l* tube placed in a 100-m*l* autoclave. After the air in the autoclave had been replaced by nitrogen, the decomposition was carried out, keeping the reaction temperature at 236—286°C for about 3 hr. The product was then extracted with ethyl ether, and, after the extract had been filtered, it was distilled at 46—105°C/15 mmHg. The residue was 1.1 g of a yellowish oily material, from which no 2, 3-dimethyl-2, 3-diphenylbutane was isolated. Propane, propylene, methane, and other ingredients were detected by gas chromatography.