Diethyl lead dinitrate

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The reaction, at 0 °C, between tetra-ethyl lead and dinitrogen tetroxide in both nitromethane and diethyl ether as solvents has been studied. The product in both solvents is always diethyl lead dinitrate, the properties of which have been investigated and compared with both dimethyl tin dinitrate and triethyl lead nitrate. The infrared spectrum is consistent with covalent unidentate nitrate groups, while molecular weight and conductivity measurements indicate that the compound behaves essentially as a 1:2 electrolyte in water and dimethyl sulfoxide. Decomposition of diethyl lead dinitrate in solution and in the solid state is discussed with the aid of ultraviolet spectroscopy and thermogravimetric analysis.

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Following the work on $Me_2Sn(NO_3)_2$ (1), it was of interest to us to investigate the organonitrate chemistry of lead, where it might be expected that the organic groups would be more easily replaced, possibly giving $Pb(NO_3)_4$ as a final product. The reaction between tetraethyl lead and dinitrogen tetroxide though vigorous (and sometimes explosive), always stops at the diethyl lead dinitrate stage. Further replacement of ethyl groups was not possible even when the product was treated with dinitrogen pentoxide.

We have consistently been unable to repeat the work of Hetnarski and Urbański (2), who claim that the product of the reaction when carried out in diethyl ether as solvent at 0 °C is $[(NO)_2PbEt_4]^{2+}(NO_3)_2^{-}$, with no replacement of the ethyl groups. Under these conditions we find the product to be the same as in nitromethane solution, namely, diethyl lead dinitrate.

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Diethyl lead dinitrate has been previously made by Hurd and Austin (3) by the reaction of nitric acid on tetra-ethyl lead in hot chloroform, but they did not investigate its properties in detail. They did note that triethyl lead nitrate and lead(II) nitrate were present in the reaction mixture and our investigation shows that these products are the result of decomposition of diethyl lead dinitrate in solution.

This paper discusses the properties of diethyl lead dinitrate and in particular the decomposition reactions which it undergoes.

Results and Discussion

Diethyl lead dinitrate is a white amorphous solid and is non-deliquescent. On heating in a bunsen flame the compound explodes. The compound is only stable at temperatures below 0 °C. At room temperature significant decomposition occurs within two weeks and the compound turns progressively reddish brown in color, presumably due to lead dioxide, while the infrared (i.r.) spectrum of the solid indicates the formation of ionic nitrate.

Diethyl lead dinitrate is appreciably soluble in cold water and polar organic solvents but is insoluble in non-polar solvents.

Infrared Spectrum

The total i.r. spectrum observed for $Et_2Pb-(NO_3)_2$ is, in cm⁻¹, as follows: 1495 s,sp; 1450 vw,sh; 1421 m; 1380 w,sh; 1309 s,sp; 1259 s,sp; 1169 s,sp; 1032 m,sp; 1018 s,sp; 972 w; 809 m,sp; 745 w; 731 s,sp; 714 m,sp; 498 w; and 430 vw (where s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, sp = sharp).

In order to assign bands associated with the ethyl groups, the spectrum of Et_2PbCl_2 was taken, and by direct comparison, the following bands can definitely be assigned to vibrations of the nitrato groups: 1495, 1421, asymmetric NO₂ stretch; 1309, 1259, symmetric NO₂ stretch; 1032, 1018, NO stretch; and 809 cm⁻¹, NO₃ out-of-plane rock.

As was found with the spectrum of $Me_2Sn(NO_3)_2$ (1), the observed splitting of the (NO) and (NO₂) stretching modes is consistent with a tetrahedral structure for $Et_2Pb(NO_3)_2$ containing two unidentate nitrato groups. The smaller value of the splitting between the (NO₂) asymmetric and symmetric stretching frequencies and the higher frequency of the (NO) stretches as compared to $Me_2Sn(NO_3)_2$ is consistent with a less covalent metal-nitrato bond in the lead

CANADIAN JOURNAL OF CHEMISTRY, VOL. 47, 1969 TABLE I

Molar conductivities of aqueous solutions of diethyl lead dinitrate			
Molar concentration	Molar conductivity (Ω^{-1} cm ²)		
	Fresh solution, 25 °C	Solution, boiled 5 min	Solution, boiled 2 days
0.0010	222	328	218
0.0025	217 209	324 318	214 208
0.0075 0.0100	202 194	311 305	201 195

compound. The bands at 498 and 430 cm^{-1} are assigned to the two Pb—C stretching modes and are also in agreement with a tetrahedral model.

Infrared Spectrum of Et₃PbNO₃

A pure sample of Et_3PbNO_3 was prepared by the action of AgNO₃ on Et_3PbCl in methyl cyanide, and its i.r. spectrum is as follows: 1455 sh; 1438 m; 1420 m; 1375 m; 1280 s,b; 1225 m,sp; 1158 s,sp; 1039 m,sp; 1030 m,sp; 970 w; 952 w; 815 m,sp; 720 w,sp; 690 s,sp; 475 m; and 445 cm⁻¹ vw.

By comparison with the spectrum observed for Et₃PbCl the following bands can be assigned to vibrations of the nitrato group: 1438, asymmetric NO₂ stretch; 1280, symmetric NO₂ stretch; 1039, NO stretch; and 815 cm⁻¹, NO₃ out-of-plane rock. The bands at 475 and 445 cm⁻¹ are assigned to Pb—C stretching modes indicating a non-planar structure for the Et₃Pb group. The nitrate bands are consistent with a unidentate nitrato group, and as was the case with Me₃Sn-NO₃ (1), the nitrato group is less covalently bound to the lead atom than in Et₂Pb(NO₃)₂.

Molecular Weights

Using Analar lead nitrate as a reference 1:2 electrolyte in water, it was found that over the concentration range 0.01-0.06 M at 25 °C, a fresh solution of diethyl lead dinitrate behaves as a 1:2 electrolyte and is consistent with a molecular weight of 389.3.

Conductivities

Molar conductivities for solutions of diethyl lead dinitrate in water and dimethyl sulfoxide are given in Table I and Table II respectively. A fresh aqueous solution has values nearly consistent with a 1:2 electrolyte in water (ca. $240 \ \Omega^{-1} \ \text{cm}^2$, at 0.001 *M*), and on boiling under reflux for 5 min these conductivities rise

 TABLE II

 Molar conductivities of solutions of diethyl lead dinitrate in dimethyl sulfoxide at 25 °C

Molar concentration	Molar conductivity (Ω^{-1} cm ²)		
	Fresh solution	Solution 24 h old	
0.0025	64.3	66.8	
0.0050	61.5	61.5	
0.0075	58.3	58.3	
0.0100	56.5	56.5	
0.0125	55.0	55.0	

sharply to around 330 Ω^{-1} cm²; on prolonged boiling under reflux the conductivity drops to the initial value of the fresh cold solution.

In dimethyl sulfoxide a fresh solution also has values consistent with a 1:2 electrolyte in this



FIG. 1. Ultraviolet spectra of solutions of diethyl lead dinitrate in water: A, fresh solution at 25 °C; B, solution on standing 12 h at 25 °C; C, fresh solution boiled for 5 min.

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solvent (1) and no change in conductivity was observed even upon standing for 24 h at 25 °C.

Ultraviolet Spectra

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The spectrum of a freshly prepared aqueous solution of diethyl lead dinitrate at 25 °C is shown in Fig. 1, curve A.

The observed peak at 300 m μ ($\epsilon = 18.76$) is consistent with the presence of two nitrate ions per mole. By comparison, the spectrum of lead nitrate in water at 25 °C has a peak at 300 m μ ($\epsilon = 16.50$).

The solution is virtually unchanged on standing at 25 °C for a period of 12 h (Fig. 1, curve B). On refluxing a fresh solution for only 5 min the spectrum is that of curve C in Fig. 1. The appearance of an intense charge transfer band completely obscures the nitrate ion spectrum.



FIG. 2. Ultraviolet spectra of solutions of diethyl lead dinitrate in dimethyl sulfoxide: A, fresh solution at 25 °C; B, solution on standing 12 h at 25 °C.

A freshly prepared solution of diethyl lead dinitrate in dimethyl sulfoxide at 25 °C has the spectrum shown in Fig. 2, curve A. The nitrate ion in this solvent absorbs at 312 m μ (4). Curve A shows only an inflection at this wavelength, and on standing for 12 h at 25 °C the solution has the spectrum shown in Fig. 2, curve B.

Figure 3 shows the spectra obtained for solutions of diethyl lead dinitrate in methyl cyanide. Curve A is a fresh solution at 25 °C and shows a peak at 290 mµ ($\varepsilon = 22.4$); curve B shows the solution on standing for 12 h at 25 °C with a peak at 285 mµ ($\varepsilon = 29.0$), and this solution had



Frg. 3. Ultraviolet spectra of solutions of diethyl lead dinitrate in methyl cyanide: A, fresh solution at 25 °C; B, solution on standing 12 h at 25 °C; C, fresh solution boiled for 5 min.



FIG. 4. Ultraviolet spectra of solutions of diethyl lead dinitrate in methyl alcohol: A, fresh solution at 25 °C; B, solution on standing 12 h at at 25 °C; C, fresh solution boiled for 5 min.

by then deposited crystals of lead(II) nitrate. Curve C is the fresh solution refluxed for 5 min and this solution immediately deposited a large amount of lead(II) nitrate.

Figure 4 shows similar spectra for solutions in

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methyl alcohol. Curve A has a peak at 294 mµ ($\varepsilon = 21.9$), curve B is the spectrum on standing for 12 h, and curve C that of a fresh solution refluxed for 5 min.

While ionization is obviously occurring in fresh cold solutions of diethyl lead dinitrate in methyl alcohol and methyl cyanide, the wavelengths of the peak maxima indicate (1, 4) some degree of covalent metal nitrate interaction though not as much as for many metal nitrates in these solvents. The inflection observed in the fresh cold solution in dimethyl sulfoxide is not, however, consistent with simple dissociation into diethyl lead and nitrate ions, and a charge transfer spectrum is already evident. Discussion of the refluxed solutions and those obtained upon standing at 25 °C for 12 h will be deferred until the next section.

A diffuse reflectance spectrum of solid diethyl lead dinitrate has a peak maximum at 277 m μ which is consistent with covalent metal nitrate interaction.

Reactions in Solution

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A fresh aqueous solution at 25 °C is neutral and on treatment with hydrogen sulfide yields a cream precipitate characteristic of the diethyl lead ion (5). On refluxing for 5 min the solution becomes quite acidic (pH = 3.5), thus explaining the high conductivities observed. This acidity probably results from hydrolysis of the diethyl lead ion following initial ionization

 $\begin{array}{l} (C_{2}H_{5})_{2}Pb(NO_{3})_{2} + 2H_{2}O \\ \rightleftharpoons (C_{2}H_{5})_{2}Pb(H_{2}O)_{n}^{2+} + 2NO_{3}^{-} \\ (C_{2}H_{5})_{2}Pb(H_{2}O)_{n}^{2+} \end{array}$

 $\rightleftharpoons (C_2H_5)_2Pb(H_2O)_{n-1}(OH)^+ + H^+$

It should be noted that this hydrolysis only occurs on refluxing, as compared to the more acidic $(CH_3)_2Sn^{2+}$ ion which undergoes hydrolysis in cold solution (1).

On treating the refluxed solution with hydrogen sulfide, it became apparent that hydrolysis was not the only process occurring, since a black precipitate of lead(II) sulfide was obtained. On buffering the supernatant liquid (5), a noncharacteristic brownish precipitate occurred, which is probably a mixture of organolead and lead(II) sulfides. After refluxing the solution 2 days, it finally became neutral again, and the conductivity dropped to that of the original cold solution. Treatment of this solution with hydrogen sulfide yielded a black precipitate of lead(II) sulfide, and the supernatant liquid upon buffering yielded a pure white precipitate, characteristic of the Et_3Pb^+ ion (5). It is known (5) that aqueous solutions of dialkyl lead salts tend to decompose into trialkyl lead salts and lead(II) salts, particularly upon heating. Such a decomposition can be represented by the equation

$$2Et_2Pb(NO_3)_2 \rightarrow Et_3PbNO_3 + EtNO_3 + Pb(NO_3)_2$$

It is also known (6) that trialkyl lead salts have a charge transfer spectrum which is continuous over the 200–350 mµ region. In keeping with this we found that a solution of triethyl lead nitrate in water had such a spectrum, in contrast to the diethyl lead dinitrate which does not. Thus the charge transfer spectrum observed in curve C of Fig. 1 can be attributed to the presence of some triethyl lead nitrate in solution. Complete decomposition of the diethyl lead species in aqueous solution obviously requires prolonged refluxing for two reasons. Firstly, we found that even a refluxed solution of triethyl lead nitrate, lead(II) nitrate, and ethyl nitrate is not acidic and yet the solution of diethyl lead dinitrate required 2 days refluxing before the acidity due to the hydrolysis products disappeared. Secondly, the conductivity of the diethyl lead dinitrate remained high for the same period before dropping to values consistent with the decomposition products.

The charge transfer spectra observed in curves B and C for both methyl alcohol and methyl cyanide and curves A and B for dimethyl sulfoxide (DMSO) can likewise be assigned to the formation of triethyl lead nitrate in solution. While it is not difficult to understand a rise in temperature effecting some decomposition of the diethyl lead dinitrate in the solvents after only 5 min, the behavior on standing at 25 °C does not follow a regular pattern. The rate of decomposition of fresh solutions at 25 °C as measured by the appearance of charge transfer bands, is in the decreasing order

$DMSO >> MeOH > MeCN >>> H_2O$

which follows the order of increasing dielectric constant with the exception of dimethyl sulfoxide in which the rate is by far the fastest. One might expect the mechanism of decomposition to involve the transfer of a charged ethyl species as has been suggested (5), and this process will be slowest in media of high dielectric constant due to extensive non-specific solvation (7). By

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contrast dimethyl sulfoxide will enter into strong specific interaction (7) with the diethyl lead ion and presumably will thus facilitate the rupture of a lead-carbon bond.

Attempts to analyze quantitatively the decomposition products in the refluxed aqueous solution proved difficult due to separation of the products in this medium. However, the results in methyl cyanide proved much more conclusive. A solution of diethyl lead dinitrate in methyl cyanide was refluxed on a water bath for 30 min. During this period crystalline lead(II) nitrate was deposited quantitatively according to the proposed mechanism. The supernatant liquid was removed under vacuum and passed through a gas chromatograph showing only the presence of solvent and ethyl nitrate. The residual yellow solid analyzed as follows:

Anal. Calcd. for Et₃PbNO₃: C, 20.20; NO₃⁻, 17.40. Found: C, 19.08; NO₃⁻, 18.33.

A solution of this residual solid in water had a charge transfer ultraviolet spectrum and when treated with hydrogen sulfide gave a characteristic white precipitate of the Et_3Pb^+ ion. The i.r. spectrum was also identical with that obtained for Et_3PbNO_3 prepared as mentioned previously.

Pyrolysis

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A sample of diethyl lead dinitrate was heated under a vacuum of 10^{-2} mm to 200 °C. During this period the sample remained white and did not melt. The residual solid had an i.r. spectrum identical with that of lead(II) nitrate and a nitrate analysis was as follows:

Anal. Calcd. for Pb(NO₃)₂: NO₃⁻, 37.5. Found: NO₃⁻, 36.8.

An aqueous solution of the residue gave only a black precipitate when treated with hydrogen sulfide. A colorless oil was collected in a liquid nitrogen trap during the period in which the sample was heated, but no oxides of nitrogen were observed. This oil had an i.r. spectrum identical to that of a mixture of tetra-ethyl lead and ethyl nitrate with the latter component predominant.

By comparison, when a sample of triethyl lead nitrate was similarly heated, the original yellow solid melted to a yellow liquid at 100 °C and resolidified to a white solid at 150 °C. During the liquid stage the sample spluttered considerably, leaving a residue of lead(II) nitrate.

The residual solid was identified as lead(II) nitrate and a colorless oil was again collected in



Fig. 5. Thermogravimetric analysis of diethyl lead dinitrate.

the cold trap. This oil was also a mixture of tetra-ethyl lead and ethyl nitrate, as identified by its i.r. spectrum, but now the former component was predominant.

The spluttering of the liquid in the triethyl case precluded an investigation by thermogravimetric analysis, but this was done for diethyl lead dinitrate and is shown in Fig. 5. The weight loss observed is consistent with the decomposition

$3Et_2Pb(NO_3)_2 \rightarrow 2Pb(NO_3)_2 + Et_4Pb + 2EtNO_3$

and no intermediate stable product is detectable, such as the triethyl lead nitrate which is produced in the solution decompositions observed.

A possible equation for the decomposition of triethyl lead nitrate is

$3Et_3PbNO_3 \rightarrow Pb(NO_3)_2 + 2Et_4Pb + EtNO_3$

which results in relative concentrations of tetraethyl lead and ethyl nitrate which are the reverse of those obtained from the diethyl lead dinitrate. The observed i.r. spectra of the two oils produced qualitatively confirm this.

Finally, it is interesting to note that we found that triethyl lead chloride sublimes unchanged at 60 °C under vacuum, while diethyl lead dichloride decomposes to triethyl lead chloride and lead(II) chloride.

Experimental

Diethyl Lead Dinitrate

Tetra-ethyl lead (5 ml) was placed in a 250 ml twonecked flask fitted with a P_2O_5 guard tube and a dropping funnel. Dry nitromethane (15 ml) was added to the flask, forming a separate layer above the tetra-ethyl lead. Dinitrogen tetroxide (20 ml) was mixed with 25 ml of dry nitromethane and placed in the dropping funnel. The flask was cooled in an acetone – dry ice bath and the $N_2O_4 - CH_3NO_2$ mixture added a few drops at a time. Between each addition the flask was allowed to warm to about 0 °C. A white solid formed immediately above the tetra-ethyl lead layer, the solution became green, and much

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gas was evolved. After the reaction was complete, an excess of dinitrogen tetroxide was added, and the product was filtered and washed with fresh dinitrogen tetroxide. The product was dried under vacuum to remove solvent traces and was isolated as a white amorphous powder, yield 7.33 g.

The reaction using diethyl ether as solvent was carried out following the procedure described (2).

Analyses for nitrate were done with nitron, for carbon by the Van Slyke wet oxidation technique, and for lead by evaporation to dryness with concentrated nitric acid followed by chromate determination.

Anal. Calcd. for Et₂Pb(NO₃)₂: C, 12.3; NO₃⁻, 31.9; Pb, 53.2. Found: C, 12.3; NO₃⁻, 31.5; Pb, 52.6.

Triethyl Lead Nitrate

A 1:1 mole ratio of triethyl lead chloride and silver nitrate was dissolved in dry methyl cyanide. The precipitated silver chloride was removed by filtration and the solvent was removed under vacuum. The product was purified by extraction with chloroform.

Anal. Calcd. for Et_3PbNO_3 : C, 20.2; NO_3^- , 17.4. Found: C, 20.6; NO_3^- , 17.2.

All solvents were dried and purified by standard methods and organo-lead halides used were reagent grade chemicals.

Ultraviolet spectra were recorded using a Cary No. 14 spectrophotometer using fused silica cells and dried spectroscopic solvents.

Infrared spectra were recorded using a Beckman IR 12 spectrophotometer, with Nujol and halocarbon mulls between both KRS-5 and high density polyethylene windows

Molecular weights were determined using a Hewlett-Packard vapor pressure osmometer model 302.

Conductivities were recorded using a Beckman model RC-18 bridge system, and a cell following the design of Greiner (8).

Thermogravimetric analysis was done using an R. L. Stone furnace and a Cahn electrobalance.

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