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REACTION OF NITROGEN TETROXIDE WITH TETRAALKYLLEAD AND NEW METHOD OF PREPARATION OF LEADDIALKYL SALTS

B. HETNARSKI and T. URBAŃSKI
Institute of Organic Chemistry, Polish Academy of Science,
Warsaw, Poland

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Abstract—Tetraalkyllead reacts with dinitrogen tetroxide forming tetraalkyldinitrosyllead nitrates, for which the following structure has been proposed:

$$[PbAlk_4(NO)_2]^{2+}(NO_3)_2^-.$$

Tetraalkyldinitrosyllead nitrates can react as diazotizing agents. A new method for the preparation of dialkyllead salts consists in the acting of mineral acids on tetraalkyldinitrosyllead dinitrates.

Reaction of tetraalkyllead with dinitrogen tetroxide

IT HAS been found that dinitrogen tetroxide reacts with tetraalkyllead (e.g. tetraethyllead and tetra-n-propyllead) at 0° producing tetraalkyldinitrosyllead nitrates as white crystalline compounds in good yield. The compounds are relatively stable; they can be crystallized from a number of polar organic solvents, provided the solution is not boiled for a prolonged period; they contain a nitrate ion and show a high electric conductivity.

They decompose above their melting points and above 100° yield alkyl nitrates (ethyl and n-propyl respectively) as gaseous products leaving a residue of lead nitrate.

The presence of C—Pb bonds in the compounds was proved by treatment with mercuric acetate in neutral medium which on acidifying with hydrochloric acid yielded ethylmercuric and n-propylmercuric chlorides respectively. This reaction is known for the preparation of ethylmercuric salts from tetraethyllead in acid medium.[1]

The presence of nitrosyl groups in the compounds is indicated by the action of mineral acids, nitrosonium cations apparently being formed. Concentrated sulphuric acid decomposes the compounds with evolution of NO_2 ($NO^+ + NO_3^- \rightarrow N_2O_4 \rightleftharpoons 2NO_2$). Application of the Griess test,[2] showed that the compounds possess diazotizing properties.

Infra-red spectrum of tetraethyldinitrosyllead nitrate

NO_3^-*frequencies*. The two bands at 1378 (very strong) and 832 cm^{-1} are assigned to the $(ONO_2)^-$ frequency although the former is somewhat shielded by deformation vibrations of C—H bonds in the alkyl groups.

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[1] U.S. Pat. 1,987,685 (1935).

[2] P. Griess, *Ber. Dtsch. Chem. Ges.* **12**, 427 (1879).

NO *frequencies*. Two weak bands at 2375 and 1762 cm^{-1} and one strong band at 1134 cm^{-1} are characteristic of nitrosyl groups. The two former bands are assigned to the nitrosyl[3] cation and nitrosyl group bonded by coordination and ionic bonds ($NO^+ \rightarrow M^-$) respectively.[4] The band 1134 cm^{-1} has the frequency near this of the coordinate nitrosyl anion.[5]

Tetra-n-propyldinitrolyllead dinitrate gives an identical spectrum.

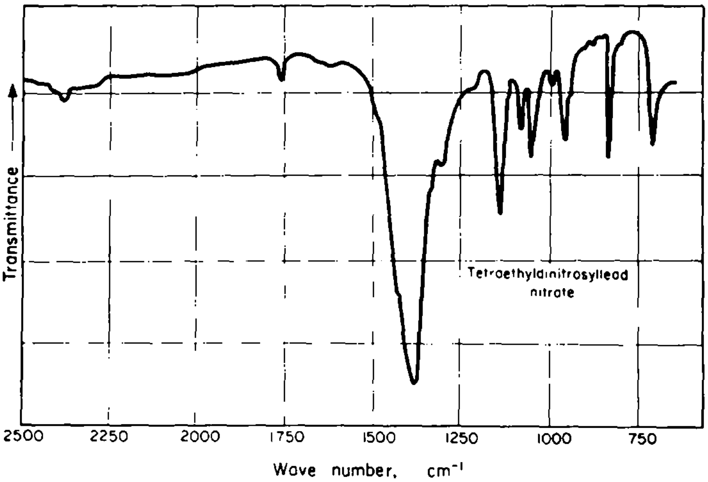
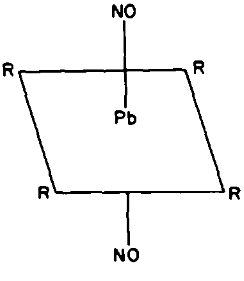


FIG. 1

On the basis of chemical properties, analysis and I.R. spectra, the compounds are probably tetraalkyldinitrosyllead dinitrate (I)

$$\underset{\text{I}}{[R_4Pb(NO)_2]^{2+}(NO_3)_2^-} \qquad R = C_2H_5,\ n\text{-}C_3H_7\,.$$

The stereostructure of the cation of I is probably as follows:



The formation of I indicates that N_2O_4 dissociates:[6] $N_2O_4 \rightarrow NO^+ + NO_3^-$

[3] A. D. Cross, *Introduction to Practice Infra-Red Spectroscopy*. Butterworths, London (1960).

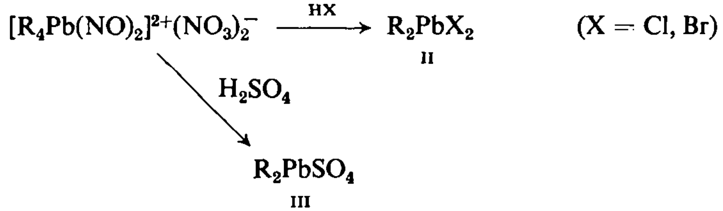
[4] J. Lewis, R. J. Irving and G. Wilkinson, *J. Inorg. Nuclear Chem.* **7**, 32 (1958).

[5] W. P. Griffith, J. Lewis and G. Wilkinson, *J. Inorg. Nuclear Chem.* **7**, 38 (1958).

[6] K. Clusius and M. Vecchi, *Helv. Chim. Acta* **36**, 930 (1953).

Formation of dialkyllead salts

It has been stated that the nitrate anions stabilize the system, and if replaced by other anions the molecule decomposed yielding salts of dialkyllead as follows:



$$[R_4Pb(NO)_2]^{2+}(NO_3)_2^- \xrightarrow{HX} \underset{II}{R_2PbX_2} \qquad (X = Cl, Br)$$

$$[R_4Pb(NO)_2]^{2+}(NO_3)_2^- \xrightarrow{H_2SO_4} \underset{III}{R_2PbSO_4}$$

This reaction is carried out by dissolving I in water or acetone and acidifying with an acid, the dialkyllead salt being formed as a crystalline precipitate. This method is superior to the hitherto known methods for the preparation of dialkyllead salts.[7–9]

EXPERIMENTAL

Tetraethyllead was prepared from lead-sodium alloy and ethyl bromide.[8] Tetra-n-propyllead was prepared from n-propylmagnesium chloride and lead chloride.[10]

Tetraethyldinitrosyllead dinitrate (I, R = C_2H_5). Tetraethyllead (32·2 g; 0·1 mole) was dissolved in dry ether (100 ml) and cooled (solid CO_2). Dinitrogen tetroxide (22·2 g; 14·2 mole) in dry ether (60 ml) was added dropwise with vigorous stirring at 0° precipitating a white crystalline product. The resulting mixture was stirred. Stirring was continued for 1 hr and then without cooling until the mixture reached room temp.

The product (38 g) was purified by being dissolved in cold acetone and the solution concentrated at room temp under red. press., yielding after a few crystallizations, crystals m.p. 104–105° (dec) readily soluble in water, alcohol, acetone, acetic acid but insoluble in ether and non-polar solvents. (Found: C, 19·1; H, 3·9; N, 11·4; Pb, 40·8; NO_3, 24·3 (nitron method); $C_8H_{20}O_2N_2Pb[NO_3]_2$ requires: C, 18·9; H, 3·9; N, 11·1; Pb, 41·2; NO_3, 24·5%).

The I.R. spectrum of the nitron complex with nitric acid was identical with that of an authentic sample.

The electroconductivity of an aqueous solution at a concentration of 0·002 gram equivalents in 1 l. solution at 30° was 162·69 $cm^2\ ohm^{-1}$. Lead dinitrate at the same concentration has a conductivity of 176·59 cm^2 $ohm.^{-1}$

Reaction of I (R = C_2H_5) *with mercuric acetate.* Tetraethyldinitrosyllead dinitrate (3 g) was added to a solution of mercuric acetate (7·6 g) in water (25 ml) and boiled for 15 min yielding a copious crystalline precipitate of lead salts (acetate and nitrate). The filtrate was acidified first with hydrochloric and then with sulphuric acid. The precipitated product in anhydrous ethanol (25 ml), was heated to boiling and filtered. Ethylmercuric chloride (0·4 g) crystallized. M.p. 190–191°, unchanged when mixed with an authentic sample.

Pyrolysis of I (R = C_2H_5). Tetraethyldinitrosyllead dinitrate (5 g) was heated to 110° on a calcium chloride bath. A decomposition occurred and the liquid distillate (0·5 g) collected in a receiver cooled with solid CO_2 was dried ($CaCl_2$) and examined by gas chromatography (AerographA-110-C, Wilkens Instrument Research Inc., Walnut Creek, Cal.). The column was filled with Silicone Dow II on fire brick 50/80 mesh and a stream of nitrogen was drawn through the column. The product was found to be pure ethyl nitrate. The residue formed during decomposition was washed with acetone and identified as lead nitrate (2·3 g).

Tetra-n-propyldinitrosyllead dinitrate (I: R = n-C_3H_7). Tetra-n-propyllead (11·3 g, 0·03 mole) was

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[7] H. Gilman and J. D. Robinson, *J. Amer. Chem. Soc.* **52,** 1975 (1930).

[8] R. C. Saunders and G. J. Stacey, *J. Chem. Soc.* 919 (1949).

[9] R. Heap, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.* 658 (1951).

[10] G. Grüttner and E. Krause, *Ber. Dtsch. Chem. Ges.* **49,** 1415 (1916).

dissolved in dry ether (30 ml), the solution cooled (solid CO_2) and dinitrogen tetroxide (4·5 g) in dry ether (17 ml) added dropwise.

The product (10·5 g) was crystallized from acetone, m.p. 110–111° (dec). It is readily soluble in water, alcohol, acetone, acetic acid but insoluble in ether and non-polar solvents. (Found: Pb, 37·7; $C_{12}H_{28}O_2N_2Pb(NO_3)_2$ requires: Pb, 37·6%).

Griess diazotization test of compound I ($R = C_2H_5$). Sulphanilic acid dihydrate (50 mg) and 50 mg of I ($R = C_2H_5$) was treated with 1 ml water, the resulting suspension mixed thoroughly and treated with 5 drops conc sulphuric acid followed by 6 drops of a 5% solution of α-naphthylamine in acetic acid (the latter solution was previously decolourized with active carbon). An intense carmine colour developed.

Diethyllead halogenides (II, $R = C_2H_5$, X = Cl and Br). Tetraethyldinitrosyllead dinitrate (2 g) was dissolved in a small vol. water (2–4 ml) and conc hydrochloric acid (2 ml) and 46·8% hydrobromic acid (2 ml) added. A copious precipitate of diethyllead dichloride (1 g) and diethyllead dibromide (1·7 g) respectively resulted. The products were crystallized from ethanol and acetone respectively. (Found (II, $R = C_2H_5$, X = Cl): Pb, 52·8; Calc. for $C_4H_{10}PbCl_2$: Pb, 52·8%); Found (II, $R = C_2H_5$, X = Br): Pb, 48·7; Calc. for $C_4H_{10}PbBr_2$: Pb, 48·6%).

Diethyllead sulphate (III, $R = C_2H_5$). Tetraethyldinitrosyllead dinitrate (2 g) was dissolved in water (10 ml) and acidified with 5% sulphuric acid (Congo red). A small amount of precipitate was formed, filtered off and acetone was added to the clear filtrate.

A copious precipitate of III (0·8 g) was formed, insoluble in most organic solvents. The product was purified by washing with acetone. (Found: Pb, 57·0; $C_4H_{10}PbSO_4$ requires: Pb, 57·3%).

Di-n-propyllead dichloride (II, $R = n\text{-}C_3H_7$, X = Cl). Tetra-n-propyldinitrosyllead dinitrate (1·5 g) was dissolved in water (3 ml), conc hydrochloric acid (3 ml) was added to yield a copious precipitate of the product (1·1 g) which was crystallized from ethanol. (Found: Pb, 56·8; Calc. for $C_6H_{14}PbCl_2$: Pb, 56·8%).

Di-n-propyllead dibromide (II, $R = n\text{-}C_3H_7$, X = Br). Tetra-n-propyldinitrosyllead dinitrate (4 g) was dissolved in cold acetone (15 ml) and 46·8% hydrobromic acid (5 ml) added. The product was precipitated (4 g) and carefully crystallized from ethyl acetate. (Found: Pb, 46·8; $C_6H_{14}PbBr_2$ requires: Pb, 45·9%).

Di-n-propyllead sulphate (III, $R = n\text{-}C_3H_7$). Tetra-n-propyldinitrosyllead dinitrate (3 g) was dissolved in cold acetone (15 ml) and 10% sulphuric acid (10 ml) added. The precipitated product (1·5 g) was insoluble in organic solvents, and was purified by washing with acetone and then with water. (Found: Pb, 53·2; $C_6H_{14}PbSO_4$ requires: Pb, 53·2%).

Infra-red spectra. Spectroscopic measurements were made with a Hilger H-800 double-beam spectrophotometer with a 60° sodium chloride prism. The substances were examined in potassium bromide pellets.

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