

THE PHOTO-DECOMPOSITION OF LEAD (IV) CARBOXYLATES

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In connection with the decomposition of alkoxides of tetra-valent lead (1,2,3) we became interested in the structure and decomposition of lead (IV) acylates in general. A recent communication (4) on the mechanism of thermal oxidative decarboxylation with lead (IV) acetate prompts us to report some of our results.

Apparently no detailed information was available about the nature of the Pb-O bond in lead (IV) acylates. Since this bond character should be reflected in the carbonyl vibration we investigated the infrared spectra of a number of lead (IV) acylates in methylene chloride solution. In all cases where stable solutions of the lead salts free from any carboxylic acid (e.g. lead (IV) pivalate and benzoate) could be obtained the spectra were characterized by the complete absence of any carbonyl bands shorter than  $6.3 \mu$ . Instead a prominent band around  $6.55 \mu$  was always observed which must be ascribed to an asymmetric carboxylate vibration<sup>a)</sup>. We therefore conclude

a) The symmetric  $\text{COO}^-$  vibration is sometimes obscured by additional bands of the acyl residues. The reported spectrum of lead tetraacetate in Nujol (5) supports the above assignment. We believe that the band at  $5.8 \mu$  observed in the spectra of lead (IV) diisobutyrate and lead (IV) diazolate (6) are due to vibrations of free carboxylic acid groups.

that the Pb-O bond in lead (IV) acylates is essentially ionic. The solubility in organic solvents such as acetonitrile, methylene chloride or benzene is probably due to complex formation of the lead salt with solvent <sup>b)</sup>. Radical forming decompositions of lead (IV) carboxylates (such as methylation or phenylation (7) ) should therefore be considered as one electron transfers rather than homolytic reactions.

In view of the high redox potential of lead (IV) and the ionic nature of the lead (IV) acylates the occurrence of relative long wave length charge transfer bands in the UV could be expected. Some UV maxima of lead (IV) acylates are summarized in Table 1. It is assumed that these absorptions are associated with the transfer of an electron from the acylate to the lead (IV) ion. The shift of the maximum to shorter wave length in the lead tetra-trichloroacetate is in accord with this interpretation <sup>c)</sup>.

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- b) Lead (IV) has a strong tendency to accommodate 6 ligands and the acetic acid stabilized lead (IV) acetate is probably more correctly formulated as  $H_2[Pb(OAc)_6]$ ; cf. also the stable lead (IV) chloride complexes such as  $Cs_2PbCl_6$ .
- c) In a similar way the absorption maxima of lead (IV) hexachloroplumbates have been interpreted by Heal and May (8).

TABLE 1

Maxima in  $m\mu$  and molar extinction coefficients in cyclohexane (0.025% of the corresponding free carboxylic acid <sup>d</sup>) added to the solution and to the reference cell)

Pb <sup>IV</sup> salt	Maximum	Extinction
Valerianate	230	26700
Oenanthate	230	25300
Palmitate	230	21300
Isobutyrate	232	15000
Hexahydrobenzoate	243	24200
Pivalate	236	21300
Trichloroacetate	223	7400

The excited state of the lead (IV) acylate formed by light absorption corresponds therefore to a lower oxidation state of lead (namely lead (III) ) and can either revert to the electronic ground state (lead IV) or lose one of the acyloxy groups as a radical and form a lead (III) acylate<sup>e</sup>). In fact lead tetraacylates can easily be decomposed at low temperatures by UV light<sup>f</sup>).

- d) The spectra are thus, at least in the cases of the moisture sensitive primary secondary carboxylates, due to the hexacoordinated lead (IV)  $H_2Pb(OCOR)_6$ .
- e) Although, in contrast to the dimeric lead (III) alkyls such as hexaphenyldilead and hexacyclohexyl dilead, lead (III) acylates have never been isolated. Their existence and fair stability is suggested by a number of reactions of lead tetraacylates, notably by the experiments of Bachmann and Wittmann (9). The colorless solution produced by reaction of 2 moles of lead (IV) palmitate and 1 mole of iodine at low temperature seems to contain 2 moles of palmitoyl hypoiodite and 1 mole of dilead hexapalmitate, which decomposes at higher temperature to  $CO_2$  and pentadecyl palmitate.
- f) This reaction has first been observed at room temperature by Franzen (10). Details and examples of the photolytic decarboxylation of lead (IV) acylates, which is of considerable practical importance will be published elsewhere.

The fast decarboxylation of the acyloxy radicals formed leads to alkyl radicals which could be identified by ESR measurements.

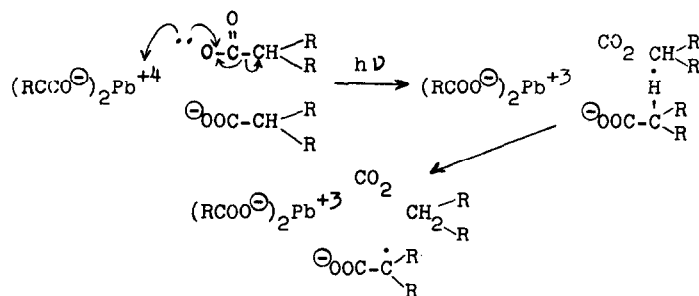
Irradiations of frozen benzene solutions (0.01 - 0.1 molar) or crystals of lead (IV) acylates in Vycor quartz tubes at 77° K with a Philips high pressure mercury burner HPK (125 Watt) produced typical ESR signals. In spite of the line broadening caused by the anisotropic behaviour of the radicals in the solid matrix these signals could easily be identified. Some of our results are summarized in Table 2. The hyperfine splitting constants found are in good accord with published data on alkyl radicals prepared by different methods <sup>g)</sup> (11, 12). The type of spectrum obtained is illustrated in Fig. 1a and 1b for the lead tetraisobutyrate irradiation products. In all cases where the carboxylate anion has at least one  $\alpha$ -hydrogen the formation of secondary radicals was observed. The rate of their formation seemed to be influenced by the bulk of the groups attached to the primary radical and was temperature dependent (thus diffusion controlled). For example with lead tetraacetate the secondary radical is formed almost simultaneously with the primary radical whereas with the lead (IV) palmitate formation of the secondary radical is very slow at -180°, but becomes fast when the temperature is raised to -100°. It is assumed that the secondary radicals are formed by hydrogen abstraction from an acyloxy anion by the primary radical:

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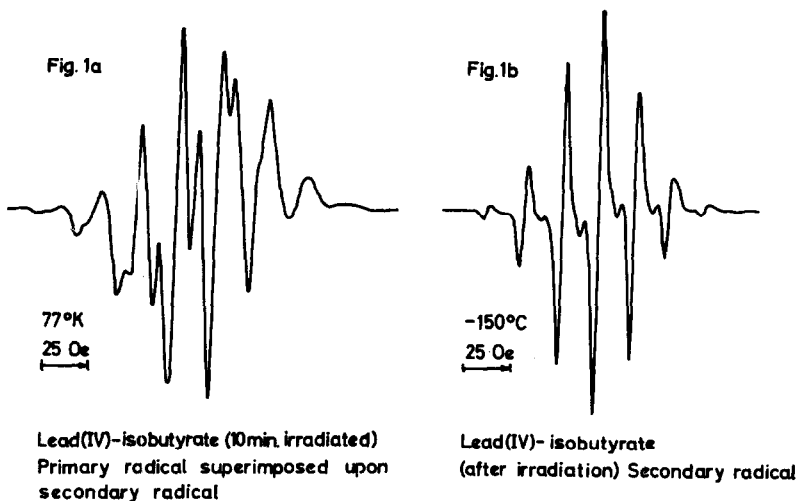
g) A full discussion will be given in a future communication.

TABLE 2  
ESR-Spectra of irradiated lead (IV) salts.

lead (IV) salt	radicals	number of lines	mean line with (Oe)	relative intensities (approx.)	$a_H$ (Oe)	hyperfine splitting $a_{H\beta}$ (Oe)
Pb(OOCOCH <sub>3</sub> ) <sub>4</sub>	prim. $\dot{C}H_3$	4	3.0 - 3.5	1:3:3:1	22.7 ± 0.5	-
	sec. $\dot{O}COCH_2$	3	~ 10	1:2:1	20.5 - 22.0	-
Pb(OOCOCH <sub>2</sub> CH <sub>3</sub> ) <sub>4</sub>	prim. $\dot{C}H_2CH_3$	(3 x 4)	3.7 - 4.3	1:2:3:1:6:3:3:6:1: 3:2:1	19.5 - 21.0	26.0 ± 0.7
	sec. $\dot{O}COCH-CH_3$	5	7.0 - 9.0	1:4:6:4:1	24.3 ± 0.5	-
Pb(OCOCH(CH <sub>3</sub> ) <sub>2</sub> ) <sub>2</sub> /4	prim. $\dot{C}H(CH_3)_2$	8	8.0 - 10.0	1:7:21:35:35:21:7:1	23.7 ± 0.8	-
	sec. $\dot{O}CO\dot{C}(CH_3)_2$ (cf. Fig. 1a & b)	7	5.0 ± 0.5	1:6:15:20:15:6:1	-	21.6 ± 0.5
Pb(OCOOC(CH <sub>3</sub> ) <sub>3</sub> ) <sub>4</sub>	prim. $\dot{C}(CH_3)_3$	10	4.1 - 5.5	1:9:36:84:126:126: 84:36:9:1	-	22.6 ± 0.5
	sec. -	-	-	-	-	-
Pb(OCC(CH <sub>2</sub> ) <sub>14</sub> (CH <sub>3</sub> ) <sub>3</sub> ) <sub>4</sub>	prim. $\dot{C}H_2(CH_2)_{13}CH_3$	6	10 - 14	1:3:4:4:3:1	21 - 22	$\left\{ \begin{array}{l} a_H \sim a_H \alpha \\ \beta_1 \sim 2a_H \beta_1 \\ a_H \beta_2 \end{array} \right.$
	sec. $\dot{O}COCH(CH_2)_{13}CH_3$	5	~ 20	1:2:2:2:1	20 - 21	$\left\{ \begin{array}{l} a_H \sim a_H \alpha \\ \beta_1 \sim 2a_H \beta_1 \\ a_H \beta_2 \end{array} \right.$



In support of this assumption the ESR signal of primary radical  $\ominus\text{OOC}-\dot{\text{C}}\text{H}-\text{CH}_3$  formed by irradiation of lead (IV) C - methyl malonate is identical with the secondary radical from lead tetra propionate.



From our results so far obtained it appears that the irradiation of lead (IV) carboxylates in the solid state is an extremely simple and efficient method for the production of alkyl radicals. Obviously this opens a way to the investigation of alkyl radicals of more complicated structure. The required lead (IV) carboxylates can easily be prepared by the exchange reaction of the particular carboxylic acid with lead tetraacetate in benzene solution by azeotropic removal of acetic acid which in case of thermolabile lead(IV) salts can be effected by lyophilisation.

It should be emphasized that even thermostable lead (IV) salts (such as lead tetra (1)-adamantyl carboxylate which is stable up to 280°C) can easily be decomposed by UV irradiation.

If such irradiations are done in a liquid phase the primary radicals produced are oxidized by the lead (III) (and IV) species to carbonium ions at a rate which is dependent on the ionisation potential of the primary radical. With increasing stability of the carbonium ion formed the products from radical reactions decrease. In all cases so far investigated the results from thermal and photolytic decomposition of lead (IV) carboxylates closely parallel each other. Our own results in photo-decomposition and Kochi's results (4) in thermal decompositions seem to indicate that both reactions occur by two consecutive one electron transfers rather than a direct two electron change (14).

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