LEAD(IV) COORDINATION CHEMISTRY: ALCOHOL OXIDATION

R. Partch and J. Monthony

Department of Chemistry
Clarkson College of Technology
Potsdam, New York 13676
(Received in U.S.A. 17 July 1967)

We wish to report the isolation and characterization of lead tetraacetate pyridinate (LTA-PYR) and its influence on alcohol oxidation(1,2).

The monopyridinate is easily isolated as a yellow-white solid (40-60%) yield from a benzene solution 0.05 M in lead tetraacetate (LTA) and 0.25 M in pyridine. Elemental analysis (3) and conductance measurements (see Table I) indicate the structure is $(Pb(OAc)_4(C_5H_5N))$ and not $(Pb(OAc)_3(C_5H_5N))(OAc)$.

TABLE I(4,5)

Molar Conductivities (Λ_m)

Solvent	Substrate	Conductance (measured)	Λ m
Pyridine	--	1.210	--
"	$(Ph)_4AsCl$	412.5	36.40
"	LTA	2.575	0.1550
"	$(Ph)_3As$	4.150	0.2070
DMSO	--	22.90	--
"	$(Ph)_4AsCl$	332.5	30.65
"	LTA	30.30	2.746
"	$(Ph)_3As$	25.60	1.882

Infrared analysis of solutions of LTA in various solvents (Figure I) shows that the carbonyl character of the acetate groups attached to the lead atom increases as the apparent coordinating power of the solvent molecule increases. This indicates that one or more of the acetate groups is becoming non-chelated(6). Temporarily(7) we would like to suggest that one pyridine nitrogen donates its electron pair to the lead atom, thereby displacing one of the chelated acetoxyl oxygen atoms away from lead and generating a full "ester type" carbonyl moiety.
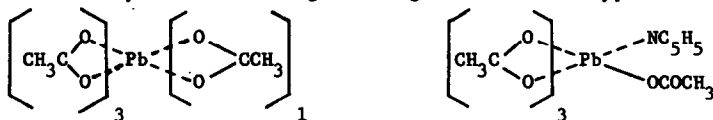
The carbonyl band of LTA dissolved in dimethylsulfoxide (DMSO) is even more pronounced; however, a solid coordination complex with DMSO has not yet been isolated.

FIGURE I

Infrared Spectra of LTA
in Benzene — • —
in Pyridine ——
in DMSO — — — —
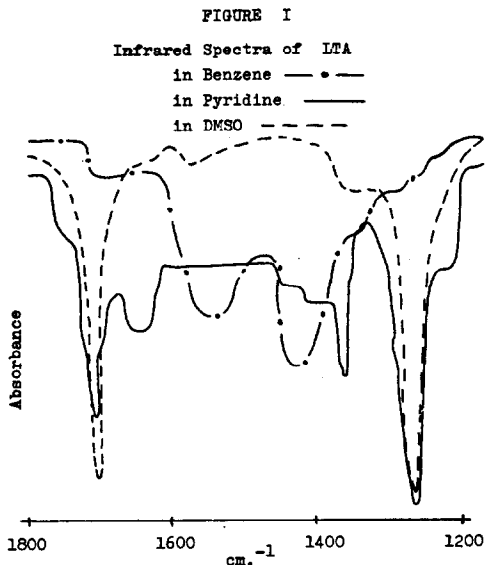
Attempts have been made to prepare a series of heterocyclic base coordination complexes with LTA(8). Little success can be reported except for the less bulky ligands. For instance, quinoline, 2,2'- and 4,4'-bipyridyl, collidine and picoline demonstrate solution characteristics of complex formation but workable solids have not been isolated(9).

In earlier work it was demonstrated that pyridine had a product influencing effect on alcohol oxidation by LTA(10). Indeed, under these oxidation conditions most primary and secondary alcohols are converted in high yield to the carbonyl product. This method is of value due to the lack of danger when mixing LTA with pyridine, thus competing with the CrO_3- pyridine oxidant which continually presents serious hazard(11). Recently, others(12) have noted the influence of pyridine on substrate reaction with LTA, yet no positive evidence of coordination has here-to-for been provided.
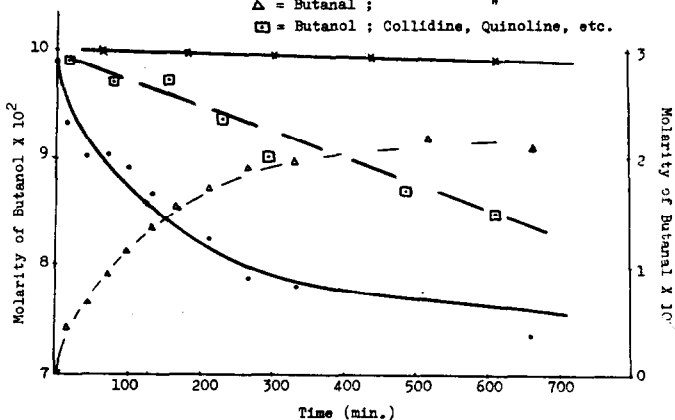
Rates of butanol oxidation have been measured and are shown in Figure II. Unlike the results of Kochi(13) on lead(IV) decarboxylation reactions, butanol oxidation is not inhibited by oxygen. From Figure II it will be noted that there is about a 1:1 conversion of alcohol to aldehyde (one by-product is known to be butyl acetate) and that oxidation in benzene and in DMSO is almost non-existent at $30°(14)$. Heterocyclic complexing agents other than pyridine have been considered for catalysis and demonstrate rate effects intermediate between pyridine and benzene. As expected, both steric and electronic factors seem capable of influencing coordination with lead(IV), and thereby oxidation rate.

Figure II also reveals information regarding ligand coordination to LTA. The rate of butanol oxidation is negligible at $30°$ in DMSO even though 1) Infrared data indicate strong coordination of LTA with solvent, and 2) Conductance of LTA in DMSO is similar to that of a non-electrolyte. These facts suggest that in DMSO, the solvent ligands coordinate more strongly with the lead atom and prevent the alcohol moiety from exchanging with an acetate

FIGURE II

RATES OF BUTANOL OXIDATION

X = Butanol ; Benzene or DMSO solvent

• = Butanol ; Pyridine or Pyridine-N-oxide
                            solvent

△ = Butanal ;   "

☐ = Butanol ; Collidine, Quinoline, etc.

Molarity of Butanol X 10^2

Molarity of Butanal X $10^?$

Time (min.)

group. Some support for this theory comes from the fact that butanol is readily oxidized, and only to butanal, when the DMSO solution is heated to 80°.

Suggestion that the oxidation of butanol by LTA is not base catalyzed comes from the following: 1) pyridine-N-oxide is quite as efficient a catalyst as pyridine and, 2) variable pyridine concentrations (benzene solvent) do not alter the rates of oxidation. We suspect pyridine-N-oxide is functional as a catalyst, as opposed to the non-catalyst DMSO, because its oxygen atom has much less coordinating power than the oxygen in DMSO.

To test for dielectric constant effects the oxidation of butanol was carried out in acetonitrile. The rate of conversion to butanal was greater than the rate in benzene but less than that in the heterocyclic bases. In addition, sodium acetate had no effect, even though this salt has been shown to accelerate the rate of hydroperoxide decomposition by lead(IV) species(15).

In addition to the above kinetic data, Figure III shows the first kinetic isotope effect measured in LTA oxidations. Its relation to alcohol oxidation by CrO_3 is very strict and implies that the oxidation rate is dependent on cleavage of the C-H bond alpha to the hydroxyl group. Regarding intermediate, $(Pb(OAc)_{4-n}(OR)_n(C_5H_5N))$, decomposition, it is most probable that the C-H bond cleaves to expel a proton(16). Contrary to the above isotope effect, no oxidation rate difference is observed when hydroxyl protons are replaced by deuterium.

FIGURE III

Rate of Aldehyde Formation in Pyridine
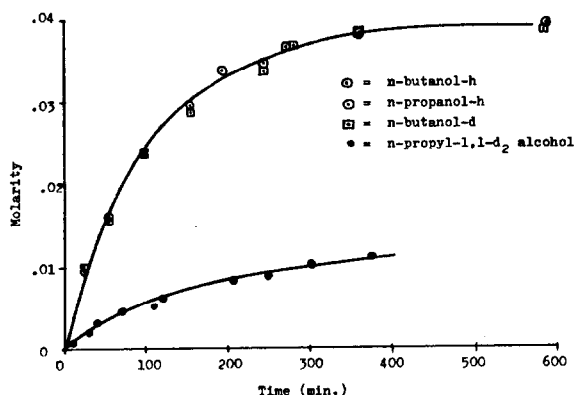
It is not possible to fully describe a mechanism at this time; however, some conclusions can be drawn. They are: 1) exchange of the alcohol ligand for an acetate ligand is not rate determining, 2) the lability of LTA towards decomposition by alcohol, when in coordinating solvents, is defined by the strength of coordination of solvent to lead(IV), 3) at 30° the conversion of butanol to butanal is not base catalyzed, and 4) a major rate determining step is cleavage of a C-H bond <u>alpha</u> to the hydroxyl group.

FOOTNOTES

1. Part of this paper is taken from the senior thesis of J.M.; the authors are grateful for support from NSF-USE grant 876.
2. a) After conclusion of this work, incomplete data on this compound was found hidden in: R. Barter and J. Littler, <u>J. Chem Soc.</u> No. 3B, 205 (1967).
   b) LTA-PYR is the first example of intermolecular coordination to a lead tetracarboxylate. Examples of chelated lead(IV) are: 1) LTA itself; 2) lead tetratropolonate (E. Muetterties and C. Wright, <u>J. Am. Chem. Soc.</u> 86, 5132 (1964)); and 3) see F. Fink, <u>ibid</u> 88, 1571 (1966).
3. a) From Galbraith Laboratories, Tennessee: Found; C, 30.09; H, 3.38; N, 2.65; Calc'd: C, 29.8; H, 3.25; N, 2.68. Lead analysis was carried out at Clarkson College: Found (four trials): 40.07 $\pm$ .04; Calc'd.: 39.66.
   b) To authenticate the lead analyses, uncomplexed LTA gave 46.77% Pb; Calc'd: 46.73.
4. Industrial Instruments Inc. conductivity bridge, Model RC-16B2 (accuracy $\pm$ 1%).
5. There is the possibility that LTA-PYR is an intimate ion pair and non-dissociated in these solvents.
6. LTA is eight coordinate with distorted dodecahedral geometry; B. Kamenar, <u>Acta Cryst</u>. 16A, 34 (1963).
7. a) The crystal appearance of LTA-PYR is considerably altered from that of LTA. X-ray crystallographic measurements are contemplated.
   b) Littler (footnote 2a) states that he has NMR and IR data supporting the structure LTA-PYR; however, no details are given. We report the following for the methyl NMR signals: a fresh solution of LTA in benzene shows a singlet at 1.58 (ppm); solution in pyridine gives a singlet at 2.06; solution in DMSO gives a singlet at 1.92.
8. Compare H. Sisler, <u>J. Am. Chem. Soc.</u> 75, 446 (1953); <u>J. Inorg. Nucl. Chem.</u> 16, 257 (1961).
9. Low temperature work should net lead(IV) complexes of the more sterically hindered pyridines. Molecules which effectively catalyze the butanol to butanol conversion form colored solutions with LTA. Since the complexation of pyridine with LTA is directly related to the butanol oxidation rate, and, LTA is colored in excess pyridine, we assume that coloration is a <u>solution</u> complexation characteristic. The molecular weight of LTA

in pyridine solution is yet to be determined.

10. R. Partch, Tetrahedron Letters No. 41, 3071 (1964).

11. L. Sarett, J. Am. Chem. Soc. 75, 427 (1953).

12. a) Reference 23 in J. Kochi, ibid 87, 3609 (1965); J. Org. Chem. 30, 3265 (1965).
    b) K. Heusler, Tetrahedron Letters No. 52, 3975 (1964).
    c) M. Mihailovic, Tetrahedron 23, 721 (1967).

13. see footnote 5a.

14. a) Vapor phase chromatography was carried out using an Aerograph A-90-P2 instrument with a 300 x 10 mm column packed with Carbowax 1540 on Chromosorb. Standards of alcohol and aldehyde were injected intermittantly with unknown aliquots.
    b) Kinetic experiments were carried out as follows: freshly prepared LTA was dried over KOH pellets under vacuum and was added to purified (in N_2) pyridine. This 0.05 M LTA solution was stirred under N_2 for 15 minutes. Butanol was added quickly to make its concentration 0.1 M and then the flask was sealed. Aliquots were removed through a septum.
    c) Substitution of dimethylsulfone for pyridine caused the rate to decrease to that in benzene.

15. D. Benson and L. Sutcliffe, Trans. Faraday Soc. 55, 2107 (1959).

16. a) The isotope effect is operative with heterobases other than pyridine as solvent.
    b) Compare footnote 2a and J. Littler, J. Chem. Soc., 2190 (1962).
    c) Chapter II, K. Wiberg, Oxidation in Organic Chemistry, Part I. Academic Press (1965).