Lead Tetra-acetate Oxidation of Metallic Copper to Cu^{2+}: An Unusual Oxidation

Abhijit Debroy, Mahinder P. Mahajan,* Manabendra N. Bhattacharjee, and Mihir K. Chaudhuri *
Department of Chemistry, North-Eastern Hill University, Shillong 793 003, India

Copper powder is directly oxidised to Cu^{2+} by lead tetra-acetate in a non-aqueous medium (CH_2Cl_2) under mild conditions (20—30 °C). In the presence of pyridine or a substituted pyridine, compounds of the type $[\{Cu(O_2CMe)_2L\}_2]$ (L = pyridine, 2-, 3-, or 4-methylpyridine) are obtained in very high yields. The mononuclear complex $[Cu(O_2CMe)_2(bipy)]$ is readily obtained by the oxidation of copper powder by $Pb(O_2CMe)_4$ in the presence of 2,2′-bipyridyl (bipy) by this simple procedure.

Lead tetra-acetate is a very efficient oxidant for organic substrates. It has been also used for the oxidation of inorganic species from their lower oxidation states to relatively higher oxidation states,[1] *e.g.* Co^{II} to Co^{III}, Mn^{II} to Mn^{III}, and Ce^{III} to Ce^{IV}. However, there is no report of the oxidation of a metal by $Pb(O_2CMe)_4$. We report here, for the first time, the oxidation of metallic copper by $Pb(O_2CMe)_4$ to Cu^{2+}, achieved by the reaction of copper powder and the oxidant in a non-aqueous medium (CH_2Cl_2). The Cu^{2+} was isolated in the solid state as $[\{Cu(O_2CMe)_2L\}_2]$ (L = pyridine, 2-, 3-, or 4-methylpyridine) or as $[Cu(O_2CMe)_2(bipy)]$ (bipy = 2,2′-bipyridyl) by performing the oxidation reactions in the presence of the corresponding amines.

Experimental

The chemicals used were all reagent grade products. Spectroscopic grade copper powder was used. The solvents were purified and dried by standard procedures.[2] Lead tetra-acetate was prepared by the literature method.[3]

The oxidation state of copper in each of the compounds was estimated by the reduction of a known amount of the compound with acidified potassium iodide solution followed by estimation of the liberated iodine in the solution.

Reactions of Copper Powder with Lead Tetra-acetate in the Presence of Pyridine, 2-, 3-, *or* 4-*Methylpyridine or* 2,2′-*Bipyridyl.*—Since the conditions for the reactions of copper with lead tetra-acetate in the presence of various amines were similar only a representative procedure is described.

A suspension of copper powder in dichloromethane (*ca.* 50 cm^3 per 0.5 g Cu) was placed in a dry round-bottomed flask fitted with a reflux condenser. The amine and lead tetra-acetate were added, maintaining the molar ratio of Cu : L : $Pb(O_2CMe)_4$ at 1 : 6 : 1.1 (L = pyridine or methylpyridine) and Cu : bipy : $Pb(O_2CMe)_4$ at 1 : 1 : 1.1. The mixture was refluxed over a steam-bath for about 20—30 min whereupon the solution became deep green or blue. It was filtered and solvent removed in a rotary vacuum evaporator to obtain a solid mass. The latter was then treated with hot benzene, and the deep green or blue benzene extract was separated by filtration and concentrated to obtain highly crystalline deep green $[\{Cu(O_2CMe)_2L\}_2]$ or blue $[Cu(O_2CMe)_2(bipy)]$ (bipy = 2,2′-bipyridyl).

The specific amounts (g) of the reactants used, reaction times, and percentage conversion of metallic copper into Cu^{2+} are set out in Table 1, while the analytical data, estimated oxidation state of copper, and magnetic moment are given in Table 2.

Table 1. Amounts of reactants used, yields of products, percentages of copper oxidised, and reaction times

Amount of copper powder/g (mmol)	Amount of $Pb(O_2CMe)_4$/g (mmol)	Amount of amine/g (mmol)	Amount of product/g	Percentage of copper oxidised	Reaction time/min
0.5 (7.87)	2.05 (8.68)	Pyridine 3.74 (47.27)	$[Cu_2(O_2CMe)_4(py)_2]$ 2.9	94	20
0.5 (7.87)	2.05 (8.68)	2-Methylpyridine 4.4 (47.24)	$[Cu_2(O_2CMe)_4(2Me\text{-}py)_2]$ 4.1	95	20
0.5 (7.87)	2.05 (8.68)	3-Methylpyridine 4.4 (47.24)	$[Cu_2(O_2CMe)_4(3Me\text{-}py)_2]$ 4.0	93	20
0.5 (7.87)	2.05 (8.68)	4-Methylpyridine 4.4 (47.24)	$[Cu_2(O_2CMe)_4(4Me\text{-}py)_2]$ 4.1	95	25
0.5 (7.87)	2.05 (8.68)	2,2′-Bipyridyl 7.38 (47.25)	$[Cu(O_2CMe)_2(bipy)]$ 1.4	52	30

Table 2. Analytical data, estimated oxidation states of copper, and magnetic moments of the oxidation products

Oxidation product	Estimated oxidation state of copper	$\mu_{eff.}$ [a]/B.M.	Analysis [b]/%			
			Cu	C	H	N
$[Cu_2(O_2CMe)_4(py)_2]$	1.9	1.41	24.2	41.3	4.10	5.25
			(24.35)	(41.45)	(4.20)	(5.35)
$[Cu_2(O_2CMe)_4(2Me\text{-}py)_2]$	2.0	1.42	23.35	43.8	4.80	5.15
			(23.1)	(43.7)	(4.80)	(5.10)
$[Cu_2(O_2CMe)_4(3Me\text{-}py)_2]$	2.0	1.40	23.35	43.8	4.85	5.15
			(23.1)	(43.7)	(4.80)	(5.10)
$[Cu_2(O_2CMe)_4(4Me\text{-}py)_2]$	2.1	1.41	23.3	43.5	4.80	5.15
			(23.1)	(43.7)	(4.80)	(5.10)
$[Cu(O_2CMe)_2(bipy)]$	2.0	1.83	18.75	50.1	4.25	8.35
			(18.8)	(49.75)	(4.20)	(8.25)

[a] $T = 295$ K; 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2. [b] Calculated values in parentheses.

Results and Discussion

Finely divided copper powder is readily oxidised to Cu^{2+} by lead tetra-acetate, $Pb(O_2CMe)_4$, in dry dichloromethane. The method, based on electron transfer between Pb^{4+} and Cu^0, is very effective and gives high yields (Table 1) of $[\{Cu(O_2CMe)_2L\}_2]$ (L = pyridine or methylpyridine) or $[Cu(O_2CMe)_2(bipy)]$ in the presence of the appropriate amine, sufficient to leave little doubt that this oxidation of metallic copper could be developed for the synthesis of various other types of copper(II) compounds, particularly those which are soluble in organic solvents. The conversion of metallic copper into Cu^{2+} is very facile and gram quantities of the products can be synthesised in 20—30 min by this simple procedure.

The oxidation products of the reactions were obtained as deep green or blue highly crystalline compounds. The chemically estimated oxidation state of copper in the compounds was found to lie between 1.9 and 2.1 (Table 2), lending strong support to the contention that the metallic copper has been oxidised to Cu^{2+}. The analytical and magnetic moment data show that the compounds are the same as those which have been prepared by other methods and characterised structurally.[4–6] The i.r. and electronic absorption spectra of the compounds also support this view.

References

1 D. Benson and L. H. Sutcliffe, *Trans. Faraday Soc.*, 1960, **56**, 246.
2 A. I. Vogel, ‘A Text Book of Practical Organic Chemistry,’ Longmans, London, 1978, p. 277.
3 Ref. 2, p. 300.
4 R. L. Martin and H. Waterman, *J. Chem. Soc.*, 1957, 2545; 1959, 1359.
5 G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, 1961, 5244.
6 M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

Received 22*nd March* 1983; *Paper* 3/450