

Effect of some transition metals on interactions of simple ammonium carboxylates with hydrogen peroxide

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Abstract. Reactions of equimolar mixtures of copper (Cu), zinc (Zn) metal powders with either ammonium formate or acetate or tetrabutyl ammonium acetate (1:1:2) in excess hydrogen peroxide (H_2O_2) at ambient conditions results in decarboxylation yielding mixed metal oxide $[Cu, ZnO_2 \cdot H_2O]$, while the corresponding reaction with ammonium succinate results in formation of mixed metal peroxo carbonate $[Cu, Zn(O_2^{2-})(CO_3)(H_2O)_2]$. Interestingly, in all the above mentioned carboxylates, the corresponding reactions in the presence of H_2O_2 and imidazole (HIm) results in formation of HIm adducts of mixed metal peroxo carbonates $[Cu, Zn(O_2^{2-})(CO_3)(HIm)_x(H_2O)_2]$. It is noteworthy to mention that all the above mentioned reactions in presence of either Cu or Zn powder alone, did not give any homogeneous reaction product, and instead the metal powder remained undissolved. Similarly, it is very significant to observe that the reaction of sodium salts of the above mentioned carboxylic acids with H_2O_2 in presence of either Cu–Zn mixture or Cu–Zn–HIm mixture did not give any decomposed products and instead the metal powders remained undissolved. Hence this work is of significance as it reports for the first time, the profound effect of the presence of both ammonium ion and carboxylic group in simple carboxylates and its reaction with H_2O_2 in the presence of Cu–Zn mixture. The new mixed metal peroxo carbonates and the imidazole adducts isolated from the above mentioned reaction systems were characterised by chemical, elemental and thermogravimetric analyses, ESR, electronic and IR spectral studies.

Keywords. Transition metals; thermogravimetric analyses; ammonium acetate; hydrogen peroxide.

1. Introduction

Recently the present authors have reported for the first time, that some simple aliphatic amino acids on interaction with hydrogen peroxide (H_2O_2) in presence of copper (Cu) and zinc (Zn) metal mixture decompose yielding a mixed metal peroxo carbonate or oxide^{1–3}. However, the mechanism or the factors responsible for the said decarboxylation of amino acids is not yet known. It is considered to be of interest to extend these studies, primarily to address some of the factors considered to play an important role in the above mentioned interactions. Hence, with a view to finding out whether the simultaneous presence of amino group and carboxylic moiety in the aliphatic chain of amino acids or Cu and Zn mixture or both are the main causative factors responsible for the decarboxylation on interaction with H_2O_2 , the present work was undertaken,

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because the ammonium carboxylates rudimently resembles the basic skeleton of aliphatic amino acids containing amine nitrogen and carboxylic group and with an added advantage of facile substitution of amine nitrogen moiety or completely replacing the amine nitrogen group. This paper discusses the interactions of ammonium acetate, tetrabutyl ammonium acetate, ammonium formate, ammonium succinate and sodium acetate with H_2O_2 , in presence of Cu and Zn mixture by isolating and characterising the reaction products by various physico chemical methods.

2. Experimental

All chemicals and reagents used were of AR grade. Aqueous 30% H_2O_2 solution was used for reactions which were carried out at ambient conditions.

Copper and zinc were determined by the atomic absorption method. C, H, N were determined by microanalysis. Peroxo oxygen atoms (O_2^{2-}) were determined by ceric sulphate method¹. IR spectra were recorded with an FTIR cygnus 100 spectrometer using CsI discs with both nujol and fluorolube mulls. Diffuse reflectance spectra of solid complexes were taken on a Shimadzu model 210-A spectrophotometer using $BaSO_4$ as reference in the region 200–800 nm. ESR spectra of polycrystalline compounds were recorded at room temperature (300 K) and liquid nitrogen temperature (77 K) at X-band frequencies on a Bruker ESP-300 spectrophotometer using DPPH as an internal field marker. Thermogravimetric analysis (TGA) were carried out in air and argon on a Shimadzu DT-300 micro TG instrument, with the sample weight in the 10 mg range and the end products were identified by X-ray diffraction data.

2.1 Reactions of ammonium formate/acetate/succinate and tetrabutyl ammonium acetate with H_2O_2 in presence of Cu and Zn metal powder mixture

In general, the above four reactions were carried by stirring continuously an equimolar mixture of Cu and Zn powders with an aqueous solution of ammonium or tetrabutyl ammonium carboxylates (2mMol) in excess H_2O_2 for about 2–3 days at room temperature (or occasionally slightly warming on water bath) whereby the metal powders dissolved slowly giving a green precipitate in case of succinate and light greenish-brown precipitate in case of formate and acetate, along with copious amounts of ammonia gas (tested by qualitative methods¹). Within 2–3 days, the reaction was completed in all cases (no trace of undissolved Cu or Zn powder could be seen and no ammonia gas evolution was observed). The precipitates were filtered, washed thoroughly with water and acetone and dried *in vacuo*.

A known compound $Cu, ZnO_2(H_2O)_2$ **1** was obtained with ammonium formate, acetate and tetrabutyl ammonium acetate and was characterised by elemental and thermogravimetric analyses. The IR, electronic and ESR spectral data obtained for these reaction products were compared with data recorded for the corresponding synthetic mixture of $CuZnO_2$ prepared in the laboratory, and were found to be identical.

A new compound $Cu, Zn(O_2^{2-})(CO_3)(H_2O)_2$ **2** was formed in the case of ammonium succinate reaction.

Analysis. Found: Cu, 24.65, Zn, 25.15, C, 4.60, H, 1.50, O_2^{2-} , 11.85% Calc. for $Cu, Zn(O_2^{2-})(CO_3)(H_2O)_2$; Cu, 24.73, Zn, 25.44, C, 4.67, H, 1.55, O_2^{2-} , 12.45%

TGA. Found: 37% loss in air, residue Cu, ZnO_2 Calc. loss, 37.36%

IR absorption bands (ν , cm^{-1}): 3480 (s, br), 1670(sh), 1600(m), 1360(sh), 1160(w), 1050(m), 970(vs), 920(m), 830(s), 850(s), 820(m), 480(s).

2.2 Reactions of ammonium formate/acetate/succinate and tetrabutyl ammonium acetate with H_2O_2 in presence of Cu, Zn metal powder and imidazole mixture

The above four reactions were carried out in an analogous manner described above except that an aqueous solution of imidazole (HIm) (4 mM) was added in each case. A new compound $\text{Cu, Zn}(\text{O}_2^{2-})(\text{CO}_3)(\text{HIm})_2(\text{H}_2\text{O})_2$ **3** (green) was obtained in all except in the case of ammonium acetate reaction system.

Analysis. Found: Cu, 15.95, Zn, 16.10, C, 21.10, N, 14.15, H, 2.80, O_2^{2-} 7.5%. Calc. for $\text{Cu, Zn}(\text{O}_2^{2-})(\text{CO}_3)(\text{HIm})_2(\text{H}_2\text{O})_3$; Cu, 16.17, Zn, 16.63, C, 21.37, N, 14.25, H, 3.05, O_2^{2-} , 8.14%.

IR absorption bands (ν , cm^{-1}): 3360(s, br), 3260(vs, br), 2200(br), 1660(sh), 1630(vs, br), 1580(s), 1550(s), 1490(s), 1410(m), 1340(m, br), 1320(w), 1310(m), 1290(w), 1250(m), 1200(m), 1180(m), 1100(vs), 1080(vw), 980(w, br), 960(s), 910(s), 870(vw, br), 850(m), 750(s), 670(vs), 600(m), 550(m), 500(w, br), 390(m), 340(s), 300(w), 270(m).

Thermogravimetric analysis. Found: 85% loss in air, residue (Cu, ZnO_2) Calc. loss 59.05%.

$\text{Cu, Zn}(\text{O}_2^{2-})(\text{CO}_3)(\text{HIm})(\text{H}_2\text{O})_2$ **4** (light green), was formed in the case of ammonium acetate reaction.

Analysis. Found: Cu, 18.90, Zn, 19.80, C, 14.20, N, 8.20, H, 2.00, O_2^{2-} , 9.15%. Calc. for $\text{Cu Zn}(\text{O}_2^{2-})(\text{CO}_3)(\text{HIm})(\text{H}_2\text{O})_2$; Cu, 19.55, Zn, 20.11, C, 14.77, N, 8.65, H, 2.46, O_2^{2-} , 9.84%.

IR absorption bands (ν , cm^{-1}): 3400(vs, br), 3260(vs, br), 2200(w, br), 1670(vs, br), 1630(vs, br), 1490(sh), 1345(vw), 1330(w), 1270(m, br), 1150(w, br), 880(sh), 860(w), 830(m, br), 750(w, br), 620(w, br), 570(sh), 550(s), 390(s), 300(m), 270(m).

TGA. Found: 52.5% loss in air, residue (Cu, ZnO_2). Calc. loss 50.47%.

2.3 Reactions involving sodium salts of above mentioned carboxylic acids along with Cu and Zn powder mixture, H_2O_2 and with imidazole did not give any homogeneous reaction product, leaving behind the unreacted metal powders

Reactions involving either Cu or Zn powder, ammonium or sodium salts or pure carboxylic acids of above mentioned acids with or without imidazole in presence of excess H_2O_2 , did not give any reaction product leaving behind the unreacted metal powder.

3. Results and discussion

All compounds (**1** to **4**) are stable at room temperature, amorphous in nature (no X-ray diffraction pattern could be observed) and are insoluble in water and common organic solvents. Compounds **2**–**4** dissolve readily in dilute mineral acids with effervescences

due to CO_2 liberation, giving clear blue solution, suggesting the presence of carbonate group. The stoichiometric formulae of 1–4 were arrived at from chemical, micro and thermal analyses and from the determination of peroxo oxygen atoms by volumetric method¹.

Compounds 2–4 exhibit an isotropic broad ESR spectrum both at 300 K and 77 K with g_{iso} value of 2.09 for 2, 3 and 2.10 for 4. Compound 1 is ESR inactive and the diamagnetic nature of 1 is in accordance with the reported CuO compound for which an ESR spectrum was taken along with 1. The paramagnetic behaviour and the identical nature of ESR spectrum and g value for the Cu–Zn peroxo carbonate 2 and its imidazole adduct 3 suggests the coordination geometry around Cu(II) centre may be the same in 2 and 3. It is likely that the slight variation of g value for 4 may be due its slight change in composition.

The diffuse reflectance electronic spectra of 1–4 are similar with a broad low intensity peak due to d – d electronic transition of Cu(II) ion at 700, 720, 640 and 650 nms respectively, along with an intense absorption band at 350 nm. The position of d – d absorption bands in 1–2 is similar to the bands observed for freshly prepared, synthetic mixture of Cu(II) and Zn(II) oxides and carbonates. The considerable increase in d – d transition energy of Cu(II) in 3 and 4 compared to 1–2, supports the coordination of imidazole nitrogen atom at Cu(II) centre. The intense band observed at 350 nm in 1–4 is in the region reported for charge transfer transitions¹.

The IR absorption bands for 1–4 are listed in the experimental section and they are compared with spectra of freshly prepared synthetic mixtures of Cu–Zn oxides/carbonates along with the reported assignments for coordinated carbonate⁴ and imidazole complexes⁵. The IR spectra of 2–4 clearly indicate the coordination of peroxo ion as $\nu(\text{O}_2^-)$ bands are observed at 880, 870 and 875 cm^{-1} respectively which are conspicuously absent in corresponding nonperoxo compound 1 and corresponding nonperoxo imidazole complexes⁵ and are in the region reported for many peroxo complexes^{1–3}. However no unambiguous assignment could be made due to overlap of carbonate, imidazole absorption peaks in the region of interest for structural characterisation of 3–4. The two strong bands, one at 3300–3400 cm^{-1} and the another at 3200–3300 cm^{-1} , have been tentatively assigned to $\nu(\text{OH})$ of H_2O and $\nu(\text{NH})$ of neutral imidazole molecule⁵. However the absence of $\nu(\text{NH})$ absorption band in 1 and 2 and the presence of this absorption peak in 3 and 4 in addition to the $\nu(\text{OH})$ of H_2O peak, clearly supports the coordination of neutral imidazole molecule because if imidazole coordinates as a deprotonated imidazolate ion, only one band due to $\nu(\text{OH})$ is expected. Since no mass loss was observed on heating in air/argon up to 130°C from TGA experiment (loco cit.), it is likely that only coordinated water molecules are present in 1–4. Accordingly the two bands observed in 1600–1700 cm^{-1} region for 2 and 4 (loco cit.) are tentatively attributed due to deformation mode of NH and HO of imidazole and water molecules. The other bands observed in 3 and 4 (loco cit.) are in accordance with the reported data for coordinated imidazole complexes⁵. The IR spectrum of 2 exhibits a broad strong band at 1600 cm^{-1} with a shoulder at 1670 cm^{-1} and a weak band at 1330 cm^{-1} (loco cit.). The presence of carbonate in 2 is ascertained qualitatively (loco cit.). The absence of any bands in the 1400–1500 cm^{-1} due to ν_3 mode of carbonate group^{6,7}, and the presence of strong band at 1600 cm^{-1} and 1330 cm^{-1} suggests that carbonate ion may be functioning as a bridging bidentate ligand.

The TGA data is given in experimental section, the close agreement of expected and observed weight loss both for number of water molecules in the 100–200°C range and

total weight loss clearly supports the molecular formulae thus corroborating the stoichiometric formulae arrived at from elemental analysis and estimation of peroxy oxygen. The thermal decomposition patterns are almost identical both in air and argon for all compounds 1–4. The main features of TG curves are the beginning of weight loss at $\approx 130^\circ\text{C}$, suggesting the presence of coordinated water molecule in 1–4.

Thus, the combined evidence of elemental and thermogravimetric analyses, ESR, electronic and IR data clearly indicated that compounds 1–4 are clearly homogeneous (not a mixture of individual components) containing coordinated neutral imidazole, carbonate, water, oxo and peroxy groups. Hence, these compounds are structurally formulated as $[\text{Cu}, \text{ZnO}_2(\text{H}_2\text{O})_2]$, $[\text{Cu}, \text{Zn}(\text{O}_2^{2-})(\text{CO}_3)(\text{H}_2\text{O})]$, $[\text{Cu}, \text{Zn}(\text{O}_2^{2-})(\text{CO}_3)(\text{HIm})_2(\text{H}_2\text{O})_2]$, $[\text{Cu}, \text{Zn}(\text{O}_2^{2-})(\text{CO}_3)(\text{HIm})(\text{H}_2\text{O})_2]$. It is pertinent here to point that except compound 1, all other compounds 2–4 are reported for the first time.

The earlier work reported by us¹ indicated that only amino acids are decomposed to carbonate/oxide but not the corresponding carboxylic acids, and the present work clearly shows that only ammonium/substituted ammonium salts of carboxylic acids are decomposed but not the sodium salts of carboxylic acids. These novel findings therefore suggest that the presence of both amino/amine-nitrogen group and carboxylic acid moiety in the molecule is the main causative factor for the decarboxylation of amino acids on interaction with hydrogen peroxide in the presence of Cu–Zn mixture. The effect of Cu–Zn mixture and not either Cu or Zn metal on the decomposition of amino acids on interaction with H_2O_2 was earlier reported by the present authors¹. Also, it is of interest to note that while addition of imidazole to Cu–Zn amino acid H_2O_2 reaction system inhibits the decomposition of amino acid³, in the case of corresponding reaction systems involving ammonium carboxylates, the decomposition is not inhibited, and perhaps suggests the unique behaviour of amino acids in these systems.

Thus, as stated at the outset; this study was taken up to find primarily the causative factors responsible for the decomposition of amino acids at ambient conditions in the titled reaction systems. It is therefore significant to note that this study has clearly indicated the effect of presence of ammonium group along with carboxylic moiety in the decomposition process because the corresponding sodium carboxylates have not decomposed or reacted with reactants in the corresponding reaction systems. These findings also corroborate our reported behaviour of amino acids compared to their corresponding carboxylic acids¹. To conclude, this study has also reported for the first time, a facile decomposition of some ammonium carboxylates at ambient conditions yielding new mixed metal peroxy carbonates.

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