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Preliminary communication

Catalytic O_2-fixation with new Co^{II} complexes

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SUMMARY

Solutions of Co^{II} salts of organic acids in primary amines absorb molecular oxygen rapidly and irreversibly forming μ-dioxygen–cobalt complexes. Thermolysis leads to a homopolar cleavage of the O–O bond with subsequent radical reactions involving ligand amine. After thermolysis the capacity of oxygen uptake is reestablished (catalysis).

Cobalt–oxygen complexes have found considerable interest as models for natural oxygen carriers[1]. We wish to report on particular properties of some new Co^{II}–O_2 complexes.

Co^{II} salts of organic acids (acetate, benzoate, etc.) are soluble in primary, aliphatic amines (propylamine, methylamine, etc.), giving isolable, non crystallizable, paramagnetic complexes of approximate composition $X_2N_4Co^{II}$ (X = anion, N = amine). The complexes, dissolved in amine, rapidly absorb molecular oxygen, up to a ratio of O_2/Co 0.5, the rate of oxygen uptake depending on the amine ligand. Removal of the excess of amine *in vacuo* leaves a red, hygroscopic powder, analyzing as $X_4N_6O_2Co_2$. The product is stable in a dry atmosphere at room temperature, is soluble in alcohols, dimethylformamide (DMF) and chlorinated solvents and is diamagnetic, indicating a O_2 bridged μ-peroxo structure[1]: $X_2N_3Co–O–O–CoN_3X_2$. On heating a DMF solution of the oxygenated complex for several hours at 70–90°, paramagnetism is reestablished ($\mu \simeq 4.4$ BM, characteristic for Co^{II}, high spin[2]), although no gaseous O_2 is evolved, as checked by mass spectroscopy.

The kinetics of conversion of the diamagnetic into the paramagnetic species can be investigated by measuring the magnetic susceptibility (χ_{mol}) of the complex in solution as a function of time. It is found that the μ-peroxo complex disappears according to a first order rate law, the rate constant, depending upon the amine ligand in the complex (allylamine > hexylamine ≃ propylamine > methylamine).

Free radicals are formed in the course of the decomposition; this is unequivocally shown by adding styrene and methylmethacrylate in a 1/1 molar ratio, and obtaining a

1/1 copolymer[3]. The rate of radical formation, as evaluated from the kinetics of styrene polymerization, is identical with the rate of conversion of the diamagnetic to the paramagnetic species.

Homopolar cleavage of the O–O bond is assumed to be the radical-generating step. This view is supported by an Arrhenius activation energy of 26–30 kcal/mol (k_d from polymerization data, with various amines, in the temperature range 70–110°).

The electron density in the antibonding π^* molecular orbital of the oxygen (destabilization of the O–O bond) is expected to depend on the donor ability of the amine ligands. In fact it has been shown by Brauman *et al.*[4] that the basicity of aliphatic saturated amines increases as the size of the alkyl group increases. The difference appears to be more pronounced for the first members, and from a certain size (located in the C_4–C_5 range[4]) all primary alkylamines have about the same basicity.

We also investigated the products of thermolysis of the peroxo complex, in order to obtain information about the fate of the radicals in the absence of the scavenger styrene. The dry complex (with N = propylamine) was heated for 5 h in a vacuum sealed tube. The amine functions were not greatly affected during the heating period, since >90% of the ligand amine could be titrated with HCl. A fraction, containing 50% of the original amine functions could be distilled off after the heating period. No oxygenated nitrogen derivatives, such as oximes, nitroso compounds or amine oxides, were detected in the distillation or in the residue (IR and NMR). The distillate showed evidence for ether linkages and OH groups (IR). Furthermore, a GC/MS analysis* of the volatile fraction revealed, apart from propylamine, some 5–10% of allylpropylamine, with some dipropylamine and a $C_9H_{15}N$ species with an *N*-propyl group, probably $\underline{\mathrm{CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}N}}(\mathrm{C_3H_7})$.

The total picture indicates that the thermal decomposition of the μ-peroxo–cobalt complex is not a simple, clear-cut reaction. Presumably the primary radical formation by cleavage of the O–O bond is followed by the dehydrogenation of propyl to allyl groups, leading to weak allylic C–N (75.2 kcal/mol) and C–H (82.5 kcal/mol)[5] bonds. Radical cleavage of these bonds may lead to the observed alkylation of the primary amine, and ether formation. Most of the oxygen appears to end up with hydrogen or carbon as partner.

The residue, containing cobalt, dissolves in fresh amine and the resulting solution takes up oxygen at essentially the same rate as during the first oxygenation; thermolysis leads to the same products.

REFERENCES

1 E. Bayer and P. Schretzmann, *Struct. Bonding (Berlin)*, 2 (1967) 181; V.J. Choy and C.J. O'Connor, *Coord. Chem. Rev.* 9 (1972) 145.

2 See *e.g.*: H.L. Schläfer and G. Gliemann, *Einführung in die Ligandenfeldtheorie*, Akadem. Verlagsgesellschaft, Frankfurt, 1967.

3 See *e.g.*: G. Henrici-Olivé and S. Olivé, *Polymerisation; Katalyse, Kinetik, Mechanismen*, Verlag Chemie, Weinheim, 1969.

4 J.I. Brauman, J.M. Riveros and L.K. Blair, *J. Amer. Chem. Soc.*, 93 (1971) 3914.

5 K.W. Egger and A.T. Cocks, *Helv. Chim. Acta*, in press.

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