Carbon Dioxide as Modulator of the Oxidative Properties of Dioxygen in the Presence of Transition Metal Systems

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In the presence of transition metal (Fe, Rh) catalysts, CO_2 can modulate the oxidative properties of O_2 towards tetrahydrofuran (THF) and styrene; the intermediate formation of metal–peroxocarbonate species, [L$_n$MOC(O)O–O], seems to play a key role in these processes.

In the context of organic substrate oxidation, the oxidation of ethers is of relevance to biotic systems and of great synthetic interest. The search for selective catalysts has received considerable attention. Metalloporphyrins[1a] and, more recently, Ru catalysts have been tested with success,[1b] in the latter case hypochlorite was used as oxidant.

The oxidation of alkenes has also received considerable attention for its synthetic implications and the mechanism of biomimetic catalytic systems has been investigated in detail.[2]

In the course of our studies aimed at obtaining organic carbonates *vid* oxidative carboxylation of alkenes using CO_2 and O_2,[3] we have tried several transition metals as catalysts in

various solvents. We have observed that, depending on the catalyst used and on the operative conditions, CO_2-O_2 mixtures can convert alkenes into cyclic carbonates as the major products or else into oxygenated products. In the latter case, the utilization of CO_2-O_2 mixtures produces a different product distribution with respect to pure O_2. Moreover, when tetrahydrofuran (THF) was used as solvent, oxidation products derived from THF were formed.

We decided to investigate further the chemistry of these systems and have found that both O_2 alone and CO_2-O_2 mixtures oxidize THF in the presence of transition metal complexes (under the reaction conditions used for the oxidative carboxylation of alkenes†) and that CO_2 plays an important role in the oxidation reaction, as it improves the conversion rate and induces higher selectivity.

When a THF solution of $FeCl_2 \cdot (1.5 \, THF)$[4] was exposed to 0.103 MPa of O_2 at room temperature, continuous gas chromatographic (GC) monitoring of the solution showed the appearance, after 30 min, of several new species that accumulated in solution at different rates. The GC–MS (mass spectrometric) analysis demonstrated that they are distributed over a wide range of m/z (84–300). Fractional distillation of the reaction mixture allowed us to isolate as pure major products 2-hydroxytetrahydrofuran, butyrolactone, succinic anhydride, succinaldehyde; 2-hydroperoxotetrahydrofuran was detected in the mother solution but pure material could not be isolated. Species with molecular mass ranging from 120 to 300 are unlikely to be considered as oxidation products. Most probably their formation can be explained on the basis of a ring opening reaction of THF and coupling of the oxobutyl species thus obtained. THF ring opening is known to be promoted by nucleophiles[5] and electrophiles.[6] In particular, as we have already demonstrated,[4] $FeCl_2$ in the presence of HCl is able to convert selectively THF into 1-chloro-4-hydroxybutane.
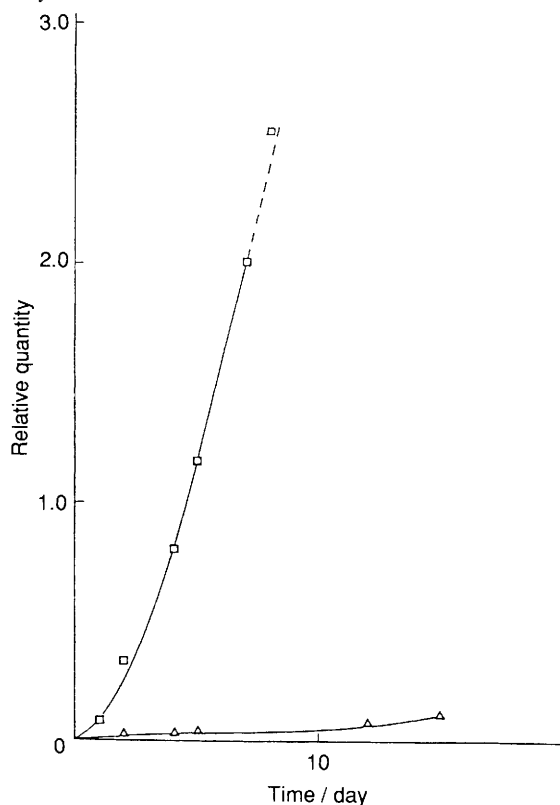

Fig. 1 Relative rate of formation of butyrolactone in the presence of O_2 (△) and O_2-CO_2 (□) mixtures

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When a CO_2-O_2 (1:1 volume, 0.103 MPa total pressure) mixture was used with the same iron compound, 2-hydroxy-THF and butyrolactone were formed as major products accompanied by very small amounts (0.1%) of succinic anhydride, succinaldehyde and 2-hydroperoxo-THF and polymerization products were not detected. The role of CO_2 was not only to enhance the selectivity, but also to increase the rate of reaction. Fig. 1 represents the relative rate of formation of butyrrolactone in systems in which only O_2 (△) or O_2-CO_2 (□), 1:1 volume, were used.

We have also investigated the catalytic behaviour of some Rh catalysts used as carbonating agents.
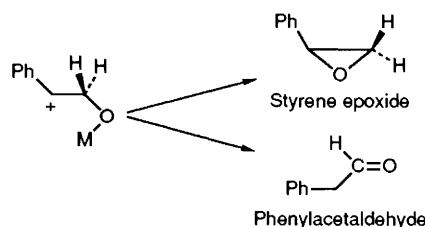
$Rh(bipy)(C_2H_4)Cl$[7] (bipy is 2,2'-bipyridyl) alone in THF also afforded 2-hydroxy-THF and butyrolactone (turnover 30 and 50 per hour, respectively) as the only oxidation products in the presence of CO_2-O_2 (1:1 volume, 0.103 MPa total pressure) with an induction time of roughly 2 h. The addition of traces of $FeCl_2$ to the Rh-system reduced to zero the induction time and speeded up the reaction tenfold without changing the selectivity.

These results are quite unique and suggest that CO_2 can modulate the oxidation of organic substrates by O_2 in the presence of metal systems.

The effect of the presence of CO_2 on the distribution of the products is also evident in the oxidation of styrene. When pure O_2 is used, $[Rh(diphos)Cl] \cdot C_6H_6$[8] [diphos = 1,2-bis(diphenylphosphino)ethane] converts styrene into benzaldehyde, acetophenone and styrene epoxide in a molar ratio 5:1:3, while when CO_2-O_2 mixtures are used benzaldehyde, acetophenone, styrene epoxide and phenylacetaldehyde were formed in a 1:3:5:5 molar ratio. It is worth emphasizing that the presence of CO_2 reduces the formation of benzaldehyde (derived from O_2 addition to the alkene double bond) and enhances the formation of products obtained by 'one oxygen' transfer to the alkene. Styrene epoxide and phenylacetaldehyde may be formed through the formation of a carbocation[9] (Scheme 1).

However, both the oxidation of THF and of styrene show that the CO_2-O_2 mixtures show oxidation properties different to those of pure O_2. Most probably different catalysts are active: indeed, peroxocarbonate species can originate from CO_2-O_2 mixtures in the presence of metal complexes. We have reported that $RhCl(O_2)(PEt_2Ph)_3$[10] reacts with CO_2 to afford the peroxocarbonate species mer-$[RhCl(CO_4)(PEt_2Ph)_3]$, that readily transfers one oxygen atom to the phosphine at temperatures above 250 K in solution,‡ as does $Ni(CO_4)(PCy_3)_2$, obtained from $Ni(CO_2)(PCy_3)_2$ (PCy_3 is tricyclohexylphosphine) and O_2.[11]

It seems obvious to assume that in the presence of alkenes or other species an oxygen transfer from peroxocarbonate metal complex to the oxophile substrate can take place. In

Scheme 1 Mechanistic pathway for the oxidation of styrene

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order to verify this assumption, peroxocarbonate, {*mer*-[RhCl(CO₄)(PEt₂Ph)₃]} was treated with styrene at low temperature and the formation of acetophenone, styrene epoxide and phenylacetaldehyde was ascertained, besides phosphine oxide. When *mer*-[RhCl(CO₄)(PEt₂Ph)₃] was dissolved in THF at 273 K the formation of traces of butyrolactone was evident, this also was true if the main oxygen transfer process was the one involving the phosphine. When diphos or bipy were used as ligands the oxygen transfer to the ligand was avoided, and only the organic substrate was implied in the oxidation process. Nevertheless, peroxocarbonate species of formula RhCl(CO₄)(bipy) or RhCl(CO₄)(diphos) were never isolated. Their presence in solution was inferred on the basis of IR spectroscopic evidence.

These results support the idea that peroxocarbonates can act as oxidants towards ethers and alkenes. The kinetics of the reaction depends strongly on the nature of the metal used and of the ancillary ligands coordinated to the metal centre.

Alternatively, one can suppose that a radical reaction is taking place and that the role of the metal is just that of generating superoxo-radicals of the type [M–O–C(O)O–O]·. This hypothesis is ruled out by the fact that the typical ESR signal is never observed in the present metal systems. Superoxocarbonates that are formed by reaction of CO_2 with Group I metal superoxo-species have also been demonstrated to be active in the selective oxidation of alkenes and other organic species.[12]

However, it turns out that CO_2–O_2 mixtures in the presence of metal centres (Group I or transition metals) are selective oxidation systems in a variety of cases. Either radical or metal assisted§ reactions are, therefore, possible.

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§ In the present instance the role of the metal is unequivocal as the observed reactions do not take place under radical conditions and are not inhibited by radical scavengers.

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