Rhodium-catalysed, Carbon Dioxide-mediated Aerobic Oxidation of Ethers

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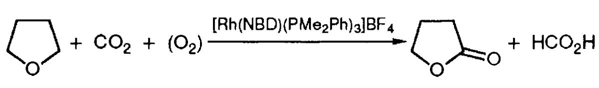
In the presence of carbon dioxide [Rh(NBD)($PMe_2Ph)_3$][BF_4] (NBD = 2,5-norbornadiene) **1** catalyses the aerobic oxidation of ethers to esters with coproduction of formic acid.

The search for new, selective oxidation methods for organic compounds[1] and the development of metal-mediated transformations of carbon dioxide[2] constitute two seemingly divergent objectives in catalytic research that are receiving immense attention worldwide. In connection with a recent study of the rhodium-catalysed hydrogenation of carbon dioxide to formic acid,[3] we made the surprising observation that THF (tetrahydrofuran) solutions of [Rh(NBD)-($PMe_2Ph)_3$]BF_4 (**1**; NBD = 2,5-norbornadiene) when pressurized with CO_2 (50 atm, 20–60 °C) alone (*i.e.* in the absence of hydrogen) still produce significant quantities of HCO_2H [turnover no. (tn) *ca.* 5 in 5 days] along with γ-butyrolactone as the major product (tn = 50 in 5 days) [eqn. (1)]. The novelty and facility of this transformation, combined with our continuing interest in CO_2 activation by transition metal complexes[4] and a recent related report,[5] prompt us to communicate our initial findings on the features and scope of these redox processes.

Although eqn. (1) proceeds in the absence of added O_2, use of 1:2 O_2–CO_2 at lower pressures (1–5 atm) significantly accelerates the reaction (tn lactone = 200 in 8 days). A series of control experiments showed that: (*i*) formation of lactone and HCO_2H requires the presence of the Rh-complex and (*ii*) in the absence of CO_2 2-hydroperoxytetrahydrofuran is the major product along with a small amount of butyrolactone but no formic acid is detected (Table 1). Subsequent introduction of a CO_2–O_2 atmosphere to the latter reaction mixture resulted in formation of HCO_2H and accelerated production of lactone. Thus, CO_2 has a striking promotional effect on the oxidation of THF to lactone and the production of HCO_2H.

Isotopic labelling experiments have revealed important features of the THF–CO_2 redox process. Oxidation of THF using $^{18}O_2$–$^{16}O_2$–$C^{16}O_2$ (*ca.* 1:1:1) indicates that the lactone carbonyl oxygen is derived largely from molecular oxygen (*ca.* 40% ^{18}O incorporation by GC–MS and IR). Oxidation of [$^2H_8$]THF (95%) produced DCO_2D (analysed by ^2H NMR spectroscopy) showing that THF served as the source of hydrogen for the formic acid. Finally, it was found from reactions utilizing $^{13}CO_2$–$^{16}O_2$ that the formic acid is only partially derived from reduction of $^{13}CO_2$ (*ca.* 15% by ^1H NMR integration of formate ^{13}C satellites); we presume that the remainder is derived from oxidative degradation of THF.

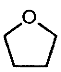
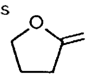
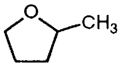
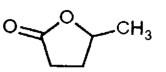
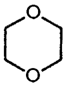
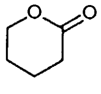
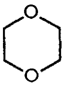
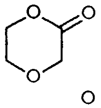
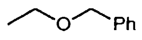
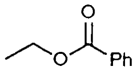
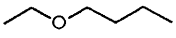
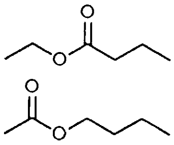
A survey of the oxidation of several other ethers was conducted to define the scope of this method. Product analysis and quantification were carried out using a combination of IR, ^1H NMR and GC–MS for the esters and ^1H NMR spectroscopy, titration, and Na_2CO_3 neutralization (with NMR spectroscopic determination of $NaHCO_2$) for HCO_2H. The results (Table 1) show that the CO_2-mediated, Rh-catalysed reaction has considerable generality as a method for the aerobic oxidation of ethers to esters although the rates are relatively slow. Both cyclic and acyclic ethers are seen to participate. Furthermore, the detection of succinic anhydride in the oxidation of THF suggests that esters may serve as precursors to anhydrides. A potential application of the Rh-catalysed, CO_2-mediated system for the oxidation of amines to amides is suggested by the finding that *N*-methylpyrrole was converted into *N*-methylpyrrolidone (tn = 130 in 3 days) when treated with O_2–CO_2 (1–2 atm, 20 °C) in the presence of **1**. The ether → ester transformation is traditionally accomplished stoichiometrically with RuO_4[6] or catalytically with Ru compounds using HClO or IO_4^- as oxidants,[7] but selective oxidations of ethers to esters with dioxygen have little precedent.[8]



(1)

At present, mechanistic details of these novel transformations are few and postulates are, therefore, speculative. However, ^1H and ^{31}P NMR monitoring of the THF reaction solutions indicate the presence of a number of Rh–H species (several multiplets from δ −8 to −24), free $OPMe_2Ph$ (*ca.* 75% of P present), and coordinated PMe_2Ph species (δ 3.5 and 4.5). The well-known autoxidation of THF to 2-hydroperoxy-THF,[9] the observed production of 2-hydroperoxy-THF (and little lactone or formic acid) using O_2–**1** in the absence of CO_2, and the greatly accelerated lactone and formic acid production observed when CO_2 is introduced into a solution of THF-hydroperoxide + **1**, suggest that lactone and HCO_2H (in part) are derived from initial formation of the hydroperoxide followed by Rh-catalysed decomposition of the latter with H-transfer (*via* Rh) to CO_2. We note that formic acid has not been previously detected in metal-catalysed oxidations of THF.[6–8, 10] The origin of the interesting CO_2-mediating effect is presently unclear but could be the result of involvement of a CO_2-derived transitory auxiliary ligand, *e.g.* formate or peroxocarbonate.[5] Additional studies directed towards probing the details of these novel H-transfer reactions are underway.

Table 1 Catalytic oxidation of ethers by O_2/CO_2

Substrate	Conditions[a]	Ester	Turn-over of ester[b]	Turn-over of HCO_2H[c]
	O_2(50 psi), 25 °C, 8 days CO_2–O_2(50–500 psi), 25 °C, 8 days 60 °C, 8 days		25 200[d] 1000	<1 10 80
	CO_2–O_2 (65 psi), 70 °C, 7 days		150	10
	CO_2–O_2 (65 psi), 65 °C, 8 days		100	12
	CO_2–O_2 (65 psi), 50 °C, 8 days		—	15
	CO_2–O_2 (45 psi), 60°C, 5 days		250	19
	CO_2–O_2 (65 psi), 65°C, 5 days		—	23

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[a] [**1**] = 0.65 mol dm^{-3}. [b] Determined by IR using C=O absorption. [c] Determined by titration. [d] Succinic anhydride and 2-hydroxytetrahydrofuran also detected.

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References

1 R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.

2 Reviews: *Carbon Dioxide Activation by Metal Complexes* by A. Behr, VCH, W. Germany, 1988; T. Ito, and A. Yamamoto, in *Organic and Bioorganic Chemistry of Carbon Dioxide*, ed. S. Inoue ad N. Yamazaki, ch. 3, pp. 79–151, Halstead Press, New York, 1982; D. Darensbourg, and R. A. Kudaroski, *Adv. Organomet. Chem.*, 1983, **22**, 129.

3 J. Tsai and K. M. Nicholas, *J. Am. Chem. Soc.*, 1992, **114**, 5117.

4 K. A. Belmore, R. Vanderpool, J. C. Tsai, M. A. Khan and K. M. Nicholas, *J. Am. Chem. Soc.*, 1988, **110**, 2004. M. Farmer, M. Khan, K. M. Nicholas, *J. Chem. Soc., Chem. Commun.*, 1988, 1384. J. C. Tsai, M. Khan and K. M. Nicholas, *Organometallics*, 1989, **8**, 2967; 1991, **10**, 29. P. F. Fu, M. Khan and K. M. Nicholas, *Organometallics*, 1991, **10**, 382. J. C. Tsai, R. A. Wheeler, M. A. Khan and K. M. Nicholas, *Organometallics*, 1991, **10**, 1344. W. Ziegler and K. M. Nicholas, *J. Organomet. Chem.*, 1992, **423**, C35.

5 M. Aresta, C. Fragale, E. Quaranta and I. Tommasi, *J. Chem. Soc., Chem. Commun.*, 1992, 315.

6 A. B. Smith and R. M. Scarborough, Jr., *Synth. Commun.*, 1980, **10**, 205; L. M. Berkowitz and P. N. Rylander, *J. Am. Chem. Soc.*, 1958, **80**, 6682; Review: D. G. Lee and M. van den Engh, *The Oxidation of Organic Compounds by Ruthenium Tetroxide*, ch. 4 in *Oxidations in Organic Chemistry*, part B, ed. W. S. Trahanovsky, Adacemic Press, New York, NY, 1973.

7 P. H. J. Carlsen, K. Katsuki, V. S. Martin and K. B. Sharpless, *J. Org. Chem.*, 1981, **46**, 3936; M. Bressan, A. Morrillo and G. Romanello, *Inorg. Chem.*, 1990, **29**, 2976.

8 K. Heyns and H. Buchholz, *Chem. Ber.*, 1976, **109**, 3707; K. Hirai, A. Nutton and P. M. Maitlis, *J. Mol. Catal.*, 1981, **10**, 203; P. Li and H. Alper, *J. Mol. Catal.* 1992, **72**, 143.

9 J. A. Howard and K. U. Ingold, *Can. J. Chem.*, 1969, **47**, 3809; P. Grosborne and I. Seree de Roch, *Bull. Soc. Chim. Fr.*, 1967, 2260; G. I. Nikishin, V. G. Glukhovtsev, M. A. Peikova and A. V. Ignatenko, *Izv. Akad. Nauk SSSR Ser. Khim.*, 1991, 2323.

10 S. Murai, N. Sonoda and S. Tsutsumi, *Bull Chem. Soc. Jpn.*, 1963, **36**, 527; H. Arzoumanian, A. A. Blanc, J. Metger and J. E. Vincent, *J. Organomet. Chem.*, 1974, **82**, 261.