

Gold-catalyzed aerobic co-oxidation of *trans*-stilbene and methylcyclohexane: identification of a key reaction intermediate

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Introduction

The liquid phase transformation of alkane and alkene into useful oxygenated intermediates, such as alcohols and epoxides, is a key-step in the synthesis of fine chemicals. Supported gold nanoparticles have been shown to catalyze the epoxidation of larger alkenes using air as the oxidant [1], as well as the oxidation of alkanes, such as cyclohexane [2]. Recently, we achieved the gold-catalyzed aerobic co-oxidation of stilbene and methylcyclohexane (MCH), which was suggested to rely on the in-situ formation of a peroxide species from the alkane [3]. Apparent reaction rates could be improved by using a hydrophobic Au/SiO₂ catalyst which exhibited enhanced wettability in the poorly polar reaction medium [4] or by using unsupported, soluble gold colloids [5]. We here prepare a new Au/SiO₂ catalyst exhibiting high affinity with the apolar solvent and give direct evidence for the formation of methylcyclohexyl hydroperoxide (MCOOH). Following its evolution throughout the reaction with different types of initiator, reaction temperatures and catalyst amounts gives further insight into the reaction mechanism.

Experimental

AuPPh₃Cl was synthesized from reduction of HAuCl₄ by dimethylsulfide, followed by ligand exchange with triphenylphosphine [6]. 5 g of Aerosil R972 hydrophobic fumed silica (Evonik Industries, 110 m²g⁻¹) was added to a solution of AuPPh₃Cl in ethanol (220 mL / 2.3 10⁻³ mol L⁻¹), stirred for 1 h at 22°C and for 16 more hours after addition of NaBH₄ (20 mL of a freshly prepared 0.3 mol L⁻¹ solution in ethanol). The dark brown powder was then isolated by centrifugation, washed twice with 200 mL water/ethanol (60/40), then with 150 mL hexane, and dried at 90°C for 16 h. It was heated at 200°C for 2 h under vacuum, yielding 0.75wt.% Au/SiO₂ (ICP) with 3.0±1.2 nm Au particles (TEM). Catalytic evaluation is carried out in round-bottom flasks, in the presence of *trans*-stilbene (1 mmol), the Au/SiO₂ catalyst (Au: 1, 2 or 10 μmol), methylcyclohexane (20 mL / 155 mmol) and an initiator (TBHP, DTBP, AIBN, BP / 0.05 mmol), stirred together at 500 rpm, 25-95°C for 72-100 h in air at atmospheric pressure. Products are quantified by HPLC and GC analysis, using external calibration.

Results/Discussion

Tert-butyl hydroperoxide and benzoyl peroxide initiators (initiator/alkene = 5mol.%) give very similar reaction profiles (Fig. 1a), with full stilbene conversion achieved in 50 h. On the other hand, di-*tert*-butylperoxide initiator yields reaction profile close to that obtained without any initiator (Fig. 1b), epoxidation rate markedly slowing down after 10 h and never reaching completion under our conditions. Similar profiles are observed in the presence of large amount of catalyst or at higher reaction temperature (95°C). In all these cases, the production of MCOOH reaches a maximum at 10 h and decreases to zero in the following hours.

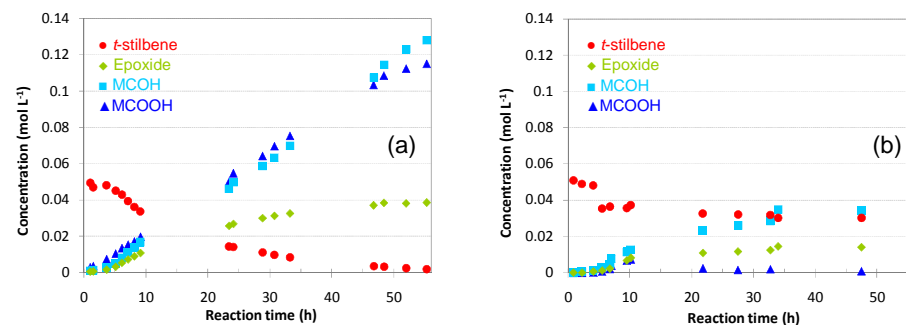


Figure 1. Aerobic co-oxidation of methylcyclohexane and *trans*-stilbene at 80°C, 2 μmol Au, with TBHP as initiator (a) or no initiator (b).

These observations are consistent with the formation of a gold-hydroperoxide complex, as described in [7] for homogeneous autoxidations, which will be explained in detail.

References.

1. M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin and C. J. Kiely, *Nature*, **437**, 1132 (2005); M. Turner, V. B. Golovko, O. P. H. Vaughan, P. Abdulkin, A. Berenguer-Murcia, M. S. Tikhov, B. F. G. Johnson and R. M. Lambert, *Nature*, **454**, 981 (2008)
2. B. P. C. Hereijgers and B. M. Weckhuysen, *J. Catal.*, **270**, 16 (2010)
3. V. Mendez, K. Guillois, S. Daniele, A. Tuel and V. Caps, *Dalton Trans.*, **39**, 8457 (2010)
4. D. Gajan, K. Guillois, P. Delichère, J.-M. Basset, J.-P. Candy, V. Caps, C. Copéret, A. Lesage and L. Emsley, *J. Am. Chem. Soc.*, **131**, 14667 (2009)
5. M. Boualleg, K. Guillois, B. Istria, L. Burel, L. Veyre, J.-M. Basset, C. Thieuleux, V. Caps, *Chem. Commun.*, **46**, 5361 (2010)
6. G. Jia, R. J. Puddepath, J.D. Scott, J. J. Vittal, *Organometallics*, **12**, 3565 (1993)
7. J. F. Black, *J. Am. Chem. Soc.*, **100**, 527 (1978)