Role of Dioxygen as an Activator in Olefin Metathesis

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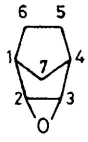
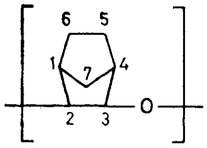
Summary Evidence is presented that the beneficial or essential influences often noted when small amounts of dioxygen are added to catalytic systems for olefin metathesis and ring-opening polymerization are due to the formation of epoxides and the corresponding metallaoxacyclobutanes, $\overline{[\mathrm{Mt}]\text{–O–CHR–CHR}^1}$; fission of the latter affords initiating metallacarbenes but isomerization and dimerization of the epoxide *via* this metallacycle are the major reaction pathways.

There are numerous examples where additions of small amounts of O_2 to catalytic systems, both homogeneous[1,2] and heterogeneous,[3] are either beneficial or essential in generating activity for olefin metathesis and ring-opening polymerization,[4] but practically nothing is known about the chemistry involved. Furthermore there are many systems where the mechanism(s) of formation of the initiating metallacarbene intermediate is (are) not obvious;[1] in such cases dioxygen, perhaps present as a trace impurity, is a possible key ingredient. In this context we were particularly intrigued by a set of well-defined Ru compounds, *e.g.*, $RuCl_2(PPh_3)_4$, (**1**), which are slow but effective long-lived unicomponent catalysts for the ring-opening polymerization of norbornene (NBE) in dry chlorobenzene under nitrogen, giving a polymer containing mainly *trans* double bonds. It is very difficult to see how NBE and (**1**) alone can generate carbene ligands, so the previous observation by Wilkinson *et al.*[5] that these electron-rich compounds



(**4**)



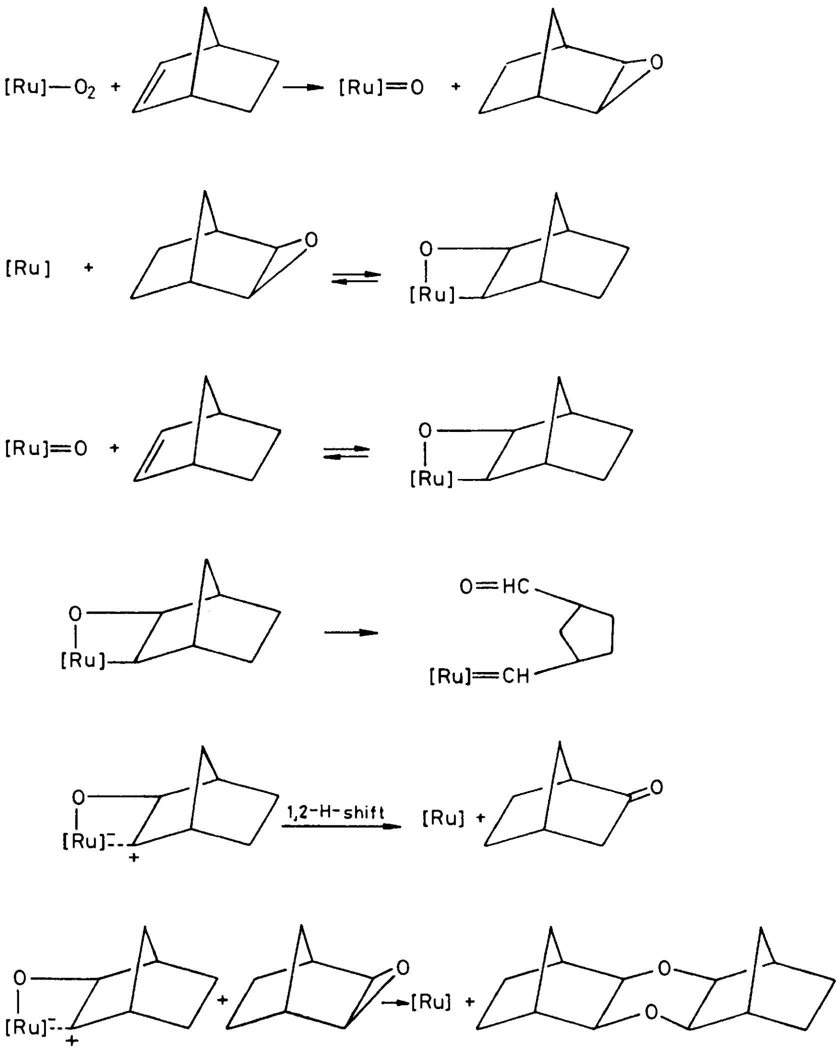
(**5**)

are readily oxidized by O_2 seemed to us to be very pertinent to the question of the source of metathesis activity. We now report novel results which show that O_2 does play a significant role in these systems and which, at the same time, shed light on the mechanisms involved.

When O_2 is bubbled at room temperature through solutions of NBE in chlorobenzene containing (**1**), or $RuCl_2(py)_2(PPh_3)_2$ (**2**) (py = pyridine), the rate of ring-opening polymerization is increased by as much as 100-fold. Oxidation of NBE to the corresponding epoxide was also noted, especially with (**2**) (10% conversion into epoxide after 5 h at 20 °C; NBE/Ru = *ca.* 300). The same type of beneficial effects on polymerization rates could also be achieved if the Ru compounds were first separately oxidized by O_2 at 100 °C in chlorobenzene solution, and the products isolated then used as catalysts. Oxidation was evident from i.r. spectra and from the colour change, usually to dark green. This treatment was also very beneficial for $RuCl_2(PPh_3)_3$, $RuHCl(PPh_3)_3$, (**3**), and a $RuCl_3$–cyclo-octa-1,5-diene complex, and essential for activity for $RuCl_2$[bis(diphenylphosphino)butane]$_2$,[6] Compound (**3**) is of interest since a hydride mechanism was previously advocated[7] for initiation of ring-opening polymerization of NBE by $RuCl_3.3H_2O$. However O_2 treatment completely removes the hydride ligand in (**3**), while the polymerization activity is greatly increased (the hydride ligand gives a strong i.r. band at 2035 cm^{-1} which is absent for the oxidized compound).

Since *exo*-2,3-epoxybicyclo[2.2.1]heptane (**4**) is a product in the above reactions, we tested the effect of the epoxide alone in the absence of O_2 for the above six catalysts (epoxide/Ru = 1/1). Again the rates of polymerization increased by 30–100 fold at temperatures from 20 to 100 °C. Also *endo*-5-methylcarboxynorbornene does not polymerize at all at 60 °C with (**1**) (20 days under N_2) but in the presence of O_2 or epoxide gives 20—30% polymer in 48 h. Similar experiments on the effect of epoxide additive on NBE polymerizations were then carried out using the family of catalysts, (mesitylene)$Mt(CO)_3/EtAlCl_2$ (Mt = Cr, Mo, W) which are known[2] to be activated by O_2 for the metathesis of pent-2-ene. Rate increases of up to two orders of magnitude were observed at 20 °C and

$$[\mathrm{Ru}] + \mathrm{O_2} \longrightarrow [\mathrm{Ru}]\text{—}\mathrm{O_2} \qquad (1)$$



(2)

(3)

(4)

(5)

(6)

(7)

indeed the W-based system with the epoxide additive becomes, in our experience, one of the most active for polymerization of cyclopentene.

In all of these experiments some isomerization of the epoxide to norbornanone was observed. An excess of epoxide alone (epoxide/Ru = *ca.* 300) was therefore treated with several of these catalysts at 20—100 °C. Isomerization to ketone [45% after 12 h at 100 °C with (**1**) and (**2**)] occurred, together with extensive dimerization and oligomerization to polyethers (**5**) (as indicated by g.l.c. and ^{13}C n.m.r. spectroscopy†).

Epoxides have previously been used[8] as benficial additives to tungsten-based metathesis systems, and the role of dioxygen in activating WCl_6 for the ring-opening polymerization of cyclopentene has recently been discussed.[9] However this is the first example where epoxide and ketone are formed from monomer during ring-opening polymerization when several Ru complexes are deliberately activated by dioxygen. Reactions (1)—(4) represent the sequence of possible basic steps which may be involved in the catalytic formation of epoxide, but the actual mechanisms are probably more complex including deco-ordination and oxidation of some of the phosphine ligands. The key point in all the work is that an oxometallacyclobutane is the obvious intermediate in isomerization of epoxide to ketone [reaction (6)] and oligomerization to polyethers [reaction (7)]. The simultaneous beneficial or essential effect of dioxygen or epoxide on these Ru complexes for ring-opening polymerization activity can then be explained if the oxometallacyclobutane also ruptures to give the initiating metallacarbene [reaction (5)]. The role of oxygen as a permanent ligand in active Group 6 metathesis catalysts has recently been theoretically discussed.[10]

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† ^{13}C Shifts in p.p.m. Epoxide (**4**): C^1C^4 36·78; C^5C^6 25·23; C^7 26·27; C^2C^3 **51·24**. Polyether (**5**): C^1C^4 37·70; C^5C^6 25·30; C^7 25·87; C^2C^3 53·21.

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