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MOLECULAR MECHANISM OF ALKENE EPOXIDATION: A MODEL STUDY WITH 3,3-DIMETHYL-1-BUTENE ON Ag(111)

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On chlorine-promoted Ag(111) oxygen adatoms selectively oxidise 3,3-dimethyl-1-butene (DMB) to the corresponding epoxide with very high selectivity providing direct verification of the mechanism advanced earlier for alkene epoxidation over single crystal silver and silver catalysts.

1. Introduction

The molecular mechanism of ethene epoxidation over silver catalysts has been vigorously researched, reviewed and debated over many years (for a recent review, see for example ref. [1]). A principal issue concerns the nature of the oxygen surface species responsible for the competing reactions of deep oxidation and epoxide formation. In common with some other authors [2] we have argued that chemisorbed atomic oxygen is responsible for all the observed chemical activity [3]; although adsorbed dioxygen species can be formed on single crystal surfaces of silver, they appear to play no more than a spectator role in the oxidation chemistry of ethene [4]. However, in earlier work, single crystal observations have also led us to the conclusion that it is chemisorbed ethene rather than gaseous ethene which reacts with the atomic oxygen to produce epoxide; this stands in contradistinction to the conclusions of Force and Bell [2] who proposed epoxidation by an Eley-Rideal mechanism between adsorbed atomic oxygen and gaseous ethene.

The difficulties encountered in working with ethene itself under low pressure conditions may be circumvented by using higher alkenes which are significantly more strongly adsorbed, and indeed Roberts and Madix have recently made elegant use of this approach to demonstrate the epoxidation by chemisorbed atomic oxygen of norbornene to norbornene epoxide on single crystal silver [5].

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Using a similar approach, we have investigated the epoxidation of styrene (phenylethylene) to styrene epoxide on Ag(111), including the effect of potassium and chlorine promoter species [6]. Once again, it was shown that atomic oxygen is responsible for deep oxidation and epoxide formation; in addition, the opposite effects of K and Cl promoters on the reaction selectivity were shown to be in good accord with the mechanistic arguments advanced by us in ref. [6]. In the present paper we report on the epoxidation of another higher alkene by chemisorbed atomic oxygen. In this case (DMB), the reacted species does not contain a carbon cycle of any kind suggesting that Ag-catalysed heterogeneous epoxidation by atomic oxygen is the general rule for alkenes of all types, including ethene itself. DMB is an analogue of propylene but with the important difference that it does not contain γ-hydrogens. The use of DMB as a probe molecule for epoxidation studies has also been suggested by Carter and Goddard in a theoretical paper which appeared after the present work was undertaken [7].

2. Experimental

All measurements were carried out in a stainless steel ultra high vacuum system which has been described elsewhere [8]. Clean, well ordered Ag(111) surfaces were generated as required by Ar^+ etching (330 eV/7 $\times 10^{-2}$ A m^{-2}/650 K) of an oriented high purity Ag single crystal, characterisation being carried out by LEED and Auger spectroscopy. Trace amounts of carbon were removed by repeated oxygen adsorption/desorption cycles, oxygen dosing being carried out by means of a calibrated quartz capillary array directed at the specimen. DMB exposures were performed by backfilling the chamber via a leak valve while potassium and chlorine dosing were carried out using a thermal evaporation source and a solid state electrochemical source respectively [9]. Temperature programmed desorption and reaction spectra were obtained by means of a multiplexed quadrupole mass spectrometer which could be programmed to monitor simultaneously up to sixteen mass signals.

3. Results and discussion

DMB chemisorbs on clean Ag(111) at 110 K with a high sticking probability; TPD spectra obtained with a heating rate of 4 Ks^{-1} show that desorption occurs as a single peak centred at ~ 212 K (E_d ~ 53 kJ mol^{-1}) as shown in fig. 1. Figure 1 also illustrates the effect of preadsorbed potassium or chlorine on the binding of DMB to Ag(111). It can be seen that these important promoter species cause either a very substantial decrease or a very substantial increase in the adsorption

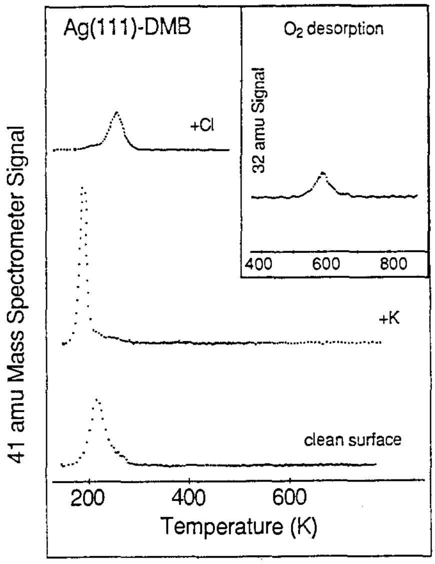

Fig. 1. Desorption of DMB from clean and K or Cl-promoted Ag(111). DMB dose = 1 L at 120 K; heating rate 4 K/s. (Inset shows oxygen desorption from clean surface).

enthalpy of DMB as follows:

K dosed/DMB peak temperature ~ 187 K/$E_\mathrm{d} \sim 47$ kJ mol^{-1}
Cl dosed/DMB peak temperature ~ 254 K/$E_\mathrm{d} \sim 64$ kJ mol^{-1}.

Neither promoter brings about any detectable decomposition of the alkene. Also shown in fig. 1 is the characteristic oxygen TPD fingerprint associated with the recombinative desorption of oxygen adatoms from Ag (peak temperature ~ 590 K, $E_\mathrm{d} \sim 150$ kJ mol^{-1}). This spectrum was taken from a surface dosed with ~ 4800 L of O_2 and establishes the exclusive presence of chemisorbed atomic oxygen to be used in the experiments which follow: control experiments also showed that neither promoter induces the adsorption of dioxygen surface species under the conditions of these experiments, nor any detectable change in the desorption energy of atomic oxygen.

No reaction was observed between adsorbed DMB and preadsorbed oxygen atoms on unpromoted Ag(111): the alkene desorbed before any detectable reaction occurred. Although the presence of oxygen results in strengthening of the bonding between the alkene and silver (peak temperature ~ 228 K, $E_\mathrm{d} \sim 58$ kJ mol^{-1}) the effect is significantly less pronounced than in the case of chlorine. Again, no reaction between DMB and oxygen was observed in the case of potassium promoted silver. Here, DMB desorbs at an even lower temperature so that the result is not unexpected. However, the substantial increase in alkene binding energy which is induced by chlorine promotion resulted in extensive and efficient selective reaction between chemisorbed DMB and preadsorbed atomic

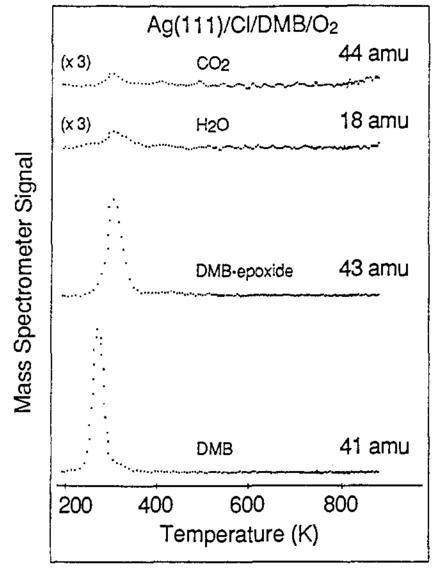

Fig. 2. Reaction products from DMB + atomic oxygen overlayers in the presence of preadsorbed Cl. DMB dose = 1 L at 195 K followed by oxygen dose = 4800 L at 225 K; heating rate 5 K/s.

oxygen. In this case, the activation energy to alkene desorption is evidently comparable with that of the epoxidation reaction, indicating a possible previously undiscussed role for chlorine promoter in epoxidation over silver–namely that of increasing *activity* (as opposed to selectivity) by increasing the residence time of the alkene on the metal surface.

Figure 2 illustrates the results of a typical TPR experiment carried out at a heating rate of 5 K s^{-1}. In this experiment the Ag(111) surface was precovered with chlorine at 300 K ($\theta_{Cl} \sim 0.14$ ML) followed by 1 L of DMB at 195 K and ~ 4800 L of O_2 at 225 K. It can be seen that under these conditions all the surface oxygen is consumed, and selective oxidation of DMB to its oxide occurs with extremely high efficiency. Some unreacted alkene is also observed along with negligible amounts of combustion products (CO_2, H_2O). In fact, use of mass spectrometric sensitivity factors reveals that under these conditions the overall reaction selectivity towards epoxide formation is 99%. Unequivocal identification of DMB epoxide (as opposed to the isomeric aldehyde or ketone) is provided by the intensity and appearance of a fragment ion spectrum at 58 amu [10] which exactly mirrors the 43 amu spectrum shown in fig. 2. As in the case of styrene [6] we may ascribe the very high selectivity observed here to the absence of γ-hydrogens in the parent alkene. This precludes the possibility of energetically favoured H-abstraction leading to the formation of stable adsorbed allylic species, and ultimately to deep oxidation products.

Acknowledgements

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