

The Role of Short-lived Oxygen Transients and Precursor States in the Mechanisms of Surface Reactions; a Different View of Surface Catalysis

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1 Introduction

The usual strategy adopted by the chemist to unravel the mechanism of a reaction is to identify the composition and structure of the products and to ascertain the temperature and concentration dependences of the reaction rate. Two-dimensional or surface chemistry is, however, an area that did not yield easily to this approach for the very obvious reason that experimental methods which were sufficiently surface sensitive were not readily available until the early 1970s. Prior to the development of surface sensitive spectroscopies, and in particular Auger and photoelectron spectroscopy, progress in understanding surface phenomena had relied very much on indirect methods with kinetics playing a major role and a checker board model of the surface. The only direct method available was that of infrared spectroscopy confined largely to studies of carbon monoxide adsorbed on metals dispersed on high surface area supports such as silica and alumina.

Interest in metal oxidation had led us to explore in 1963 how studies of the energy distribution of photoelectrons might provide definitive information on the transition of chemisorbed oxygen to an oxide overlayer with a discrete band structure.¹ We established that the photoelectron escape depth for the nickel–oxygen system was *ca.* 10 Å but we were limited to a maximum photon energy of 6.2 eV. Evidence was also beginning to emerge² that ESCA, as it was known then, was surface sensitive in that core-level spectra for adsorbed iodostearic acid and chemisorbed oxygen at carbon surfaces were reported. The VG multiphoton, multi chamber spectrometer became available to us³ in late 1970 and we set out to explore what we could learn about chemisorption and reaction mechanisms at metal surfaces. Having established the surface sensitivity of XPS and UPS for studying adsorption one of the early successes was the evidence for the interplay between the molecular and dissociative states of carbon monoxide and the facile nature of

bond cleavage when adsorbed at metals such as molybdenum and iron.^{4,5}

The growth of surface science over the last two decades has provided unprecedented insights into the atomic and electronic structures of metal and oxide surfaces. They have, however, provided little insight as to whether or not transitory complexes might participate in surface reactions – the emphasis has been on static rather than dynamic studies, with EXAFS playing a dominant role. Chemical *reactivity* involving multicomponent reaction systems has, by comparison with structural characterization of the solid surface, been largely neglected.

It was the very distinctive chemistry associated with the reactions of multicomponent gas mixtures at atomically clean metal surfaces that was first reported⁶ in 1986 that led us to explore whether this approach might provide experimental evidence for the transition states that controlled reaction pathways. Experimental evidence suggested that we could control the conversion of reactants to products and therefore offer the opportunity to recognise the transition states involved in the surface reaction. It was an approach that hitherto had not been adopted for studying chemisorption and catalysis at atomically clean metal surfaces. We also had the advantage of an extensive database, generated largely in our laboratory, of X-ray photoelectron spectra for different adsorption states, of the same element. For example C(1s) spectra could distinguish between surface carbide, graphite, carbonate, the anionic form of adsorbed CO₂ and physically adsorbed CO₂ while N(1s) spectra could distinguish between the hydrogenated states of chemisorbed nitrogen; N(a), NH(a), NH₂(a) and NH₃(a). The concentrations of each species present could also be determined from the intensity of the relevant core spectra with, if necessary, appropriate curve fitting, illustrating the unique advantage of XPS.

Although our early photoelectron studies⁵ had of necessity given attention to the chemisorption of inherently simple adsorbate systems (*e.g.* CO, CO₂ and NH₃) our interest in nickel oxidation^{1,7} led us to look in some detail at this and other analogous metal oxide systems. Two points emerged with nickel which emphasised the role of surface defects in chemical reactivity – one was evidence from O(1s) and Ni(2p) spectra for the defect states O⁻ and Ni³⁺ and the relatively unreactive nature of the ‘perfect’ nickel oxide overlayer.^{5,7,8} On the other hand the presence of O⁻-like surface oxygen was associated with activity in H-abstraction reactions. Oxygen activation of adsorbates had been shown to provide a mechanism by which chemisorption replacement reactions could occur at low temperatures^{4b,8,9} and led to extensive studies of this phenomenon. The need to obtain atomically clean metal surfaces for fundamental studies of catalysis and the role of contaminants such as oxygen as surface poisons was an important theme in the 1960s. Electron spectroscopy established, somewhat unexpectedly, that surface oxygen could play a dual role; it could confer on an unreactive atomically clean metal surface very specific chemical reactivity while the thermodynamically stable perfect oxide overlayer was comparatively unreactive. This was intriguing and provided the driving force for much of our work over the last decade.

Do surface oxygen states exist which have not been accommodated thermally, exhibit chemical reactivity which was distinct from that associated with oxygen in its final chemisorbed state and participate in reactions involving dioxygen at metal surfaces was what we set out to investigate?⁶ Furthermore, could an estimate be made of the surface lifetimes of the oxygen transients under the reaction conditions? In general the gas pressures used were in the range 10⁻⁶ to 10⁻⁸ Torr.

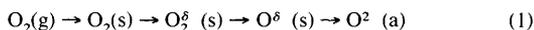
Professor Roberts was born in Carmarthenshire in 1931 and educated at the Amman Valley Grammar School. He graduated from University College Swansea followed by postgraduate research under the supervision of Keeble Sykes. He was a Postdoctoral Fellow at Imperial College with F. C. Tompkins and then joined the Scientific Civil Service as Senior Scientific Officer at the National Chemical Laboratory Teddington. In 1959 he was appointed to a Lectureship in the Department of Chemistry at Queens' University, Belfast, where he collaborated with Charles Kemball. He moved to the Chair of Physical Chemistry at Bradford University in 1966 and in 1979 to his present post at University of Wales, Cardiff. He has

published some 250 papers, is the Founder Chairman of the Surface Reactivity and Catalysis Group of the Royal Society of Chemistry, was awarded both the Tilden Medal and the Royal Society of Chemistry Award in Surface Chemistry and is a Vice-President of the Faraday Division. He is Head of the Chemistry Department at University of Wales, Cardiff, where he has also acted as Pro Vice-Chancellor



2 Atomic Oxygen Transients $O^{\delta-}(s)$

The first question to be addressed was whether the 'oxygen' generated in the act of bond cleavage and dissociative chemisorption of dioxygen had associated with it specific chemical reactivity which distinguished it from the thermally accommodated final chemisorbed state. We designated the two states as $O^{\delta-}(s)$ and $O^{2-}(a)$ respectively and suggested that the dynamics of the dissociative chemisorption of dioxygen chemisorption involved the steps shown in eqn (1)



The proposition we set out to examine was whether short-lived species $O_2^{\delta-}(s)$ and $O^{\delta-}(s)$ had sufficiently long surface lifetimes to determine reaction pathways involving dioxygen at atomically clean metal surfaces.

The Mg(0001) – dioxygen system was chosen^{6,10} as a model system and ammonia as the probe molecule having first established that under the experimental conditions (room temperature or below) both the oxide overlayer and the atomically clean Mg(0001) surface were unreactive to $NH_3(g)$. Fig. 1 shows the N(1s) and O(1s) spectra observed when molecularly adsorbed ammonia characterised by an

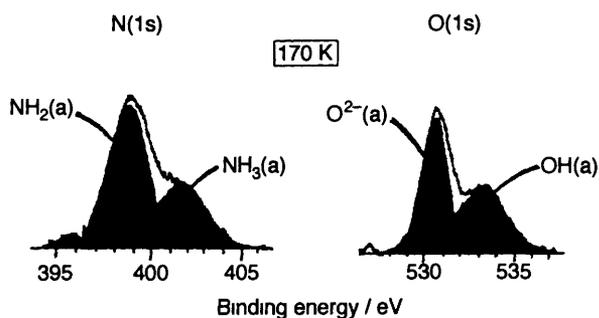
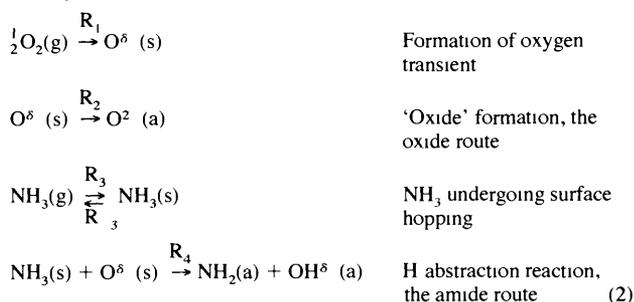


Figure 1 O(1s) and N(1s) spectra after physically adsorbed ammonia present at Mg(0001) and characterised by an N(1s) binding energy of 402 eV is exposed to dioxygen at 170 K. Note the formation of a second N(1s) peak at 399 eV and two O(1s) peaks at 531 and 533 eV. These are assigned to $NH_2(a)$, chemisorbed oxygen $O^{2-}(a)$ and hydroxyl species respectively. This was the first evidence for the possible role of oxygen transients in H abstraction reactions.

N(1s) binding energy of 402 eV was exposed to dioxygen at 170 K, a new N(1s) feature developed at 399 eV assigned to $NH_2(a)$ and two O(1s) features are present with binding energies of 530.5 and 533 eV assigned to chemisorbed oxygen, $O^{2-}(a)$, and hydroxyl species respectively. The binding energies are accurate to ± 0.15 eV. Although both the oxide overlayer and the clean metal are unreactive to NH_3 , surface amide and hydroxyl species have been generated and the following mechanism involving the atomic oxygen transient $O^{\delta-}(s)$ is suggested. Similar chemistry is observed when an NH_3-O_2 mixture (20/1) is exposed to the Mg(0001) surface at 295 K (Fig. 2).



The notation (a) refers to an adsorbed species in its final chemisorbed state while (s) refers to the surface transient $O^{\delta-}$ and in the case of NH_3 a weakly adsorbed molecule undergoing rapid

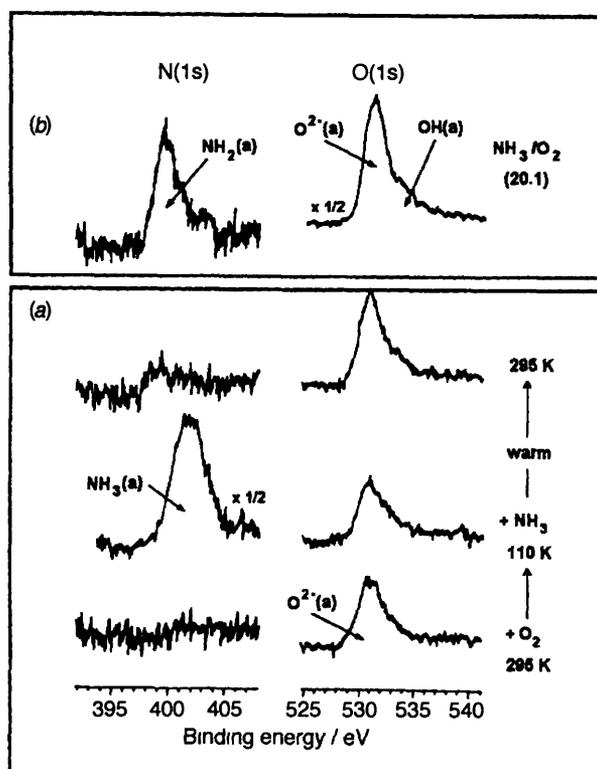


Figure 2 (a) O(1s) and N(1s) spectra for the formation of an oxide overlayer at a Mg(0001) surface at 295 K followed by physical adsorption of ammonia at 110 K and warming the adlayer to 295 K. The ammonia desorbs and the oxide overlayer is unreactive to NH_3 . (b) O(1s) and N(1s) spectra when an ammonia-dioxygen mixture (20/1) is exposed to a Mg(0001) surface at 295 K. Note the formation of amide (NH_2), hydroxyl (OH) and chemisorbed oxygen (O^{2-}).

surface diffusion – the probe molecule. The rate of the reaction R_4 is therefore given by eqn (3)

$$R_4 = (\text{No. of visits of } NH_3 \text{ to surface sites}) \times (\text{fraction of sites occupied by } O^{\delta-}) \quad (3)$$

assuming that the collision mechanism (R_4) occurs with unit efficiency. Central to the model is the concept of an ammonia molecule with a characteristic surface lifetime τ_{surface} that is determined by its heat of adsorption ΔH and the surface site lifetime τ_{site} determined by the kinetics of ammonia surface diffusion ν by expressions of the form eqn (4)

$$\begin{array}{l} \tau_{\text{surface}} \propto 10^{-13} \exp(\Delta H/RT) \\ \text{and} \quad \tau_{\text{site}} \propto 10^{-13} \exp(E_{\text{diff}}/RT) \end{array} \quad (4)$$

If for example we assume $E_{\text{diff}} \approx 0$ (an unrealistically low value) then the ammonia molecule will visit 10^{13} sites s^{-1} . Since for a ΔH value of 40 kJ mol^{-1} – the heat of adsorption of ammonia at a Mg(0001) surface – the value of τ_{surface} at 295 K is $\approx 10^{-6}$ s then each molecule will visit 10^7 surface sites before desorbing. The effective surface concentration σ is related to the pressure or molecular impact rate N and τ_{surface} by the expression $\sigma = N\tau_{\text{surface}}$ which in the present case gives a value for σ_{NH_3} of $\approx 10^{10} \text{ cm}^{-2}$ which is an effective ammonia surface coverage of 10^{-5} at 295 K. However, under these conditions $\approx 10^{17}$ surface sites will be visited, ν each site many times during the surface sojourn time τ_{surface} . We have made a number of assumptions in these calculations in order to illustrate the principle of the probe molecule approach to search for oxygen transients for which the essential prerequisite is that $R_4 \gg R_2$ [see eqn (2)]. If the oxide route is favoured then the amide route is blocked.

That it was the atomic oxygen transient – rather than the molecular species – that was active in the oxygenation reaction was

established further by coadsorbing ammonia with nitrous oxide when the dissociative chemisorption of N_2O generates atomic oxygen unequivocally. Similar conclusions were drawn when nitric oxide was used as coadsorbate.¹⁰ Estimates of $\tau_{O^\delta}(s)$ under the experimental conditions used and using a steady-state model gave values of $ca\ 10^{-8}$ s. The assumption of the steady state model found support from a computer modelling of the reactions by solving the relevant differential equations.¹¹ The model predicted that the $NH_3(s)$ surface concentration was invariant throughout the reaction at a value of $ca\ 6 \times 10^8$ molecules cm^{-2} at 295 K for an assumed activation energy of diffusion E_{diff} of 14 kJ mol^{-1} . Secondly the $O^\delta(s)$ concentration is calculated to be $ca\ 10^9$ cm^{-2} and decreases by about a factor of two as the coverage increases. The value of $\tau_{O^\delta}(s)$ which gave the best fit to the experimental data, and in particular the ratio of $NH_2(a)$ to $O_2(a)$ formed, was $ca\ 10^{-5}$ s. It should be emphasised that the value of $\tau_{O^\delta}(s)$ is with reference to the experimental conditions used in the coadsorption experiments – it is not an intrinsic characteristic of O^δ species. The value will vary with the metal, surface structure, temperature and pressure of reactants.

An important conclusion from these experimental data is that species may have negligible surface coverages but through surface diffusive hopping they can participate in highly efficient reaction pathways to products. In the present systems both reactants $O^\delta(s)$ and $NH_3(s)$ are effectively transients.

This approach was extended to other reactions to explore the generality of the concept that 'hot' oxygen transients were the key participants in oxygenation surface chemistry. The term 'hot' refers to oxygen atoms which are generated in the act of dioxygen bond cleavage leading to either vibrational excitation or atoms with excess translational energy and which have not been thermally accommodated at the metal surface. We chose the aluminium-dioxygen system¹² using carbon monoxide as the probe molecule since it was neither 'adsorbed' at the surface of atomically clean aluminium nor at the oxide overlayer at low temperatures. However, when coadsorbed with dioxygen in a CO-rich mixture, carbonate and carbidic species were formed at 80 K (Fig. 3). These species could be distinguished easily by the chemically shifted C(1s) spectra with C(1s) energies of 282 eV (C^δ) and 290 eV (CO_3) and the following mechanism was proposed, similar chemistry was observed with magnesium [eqn. (5)]

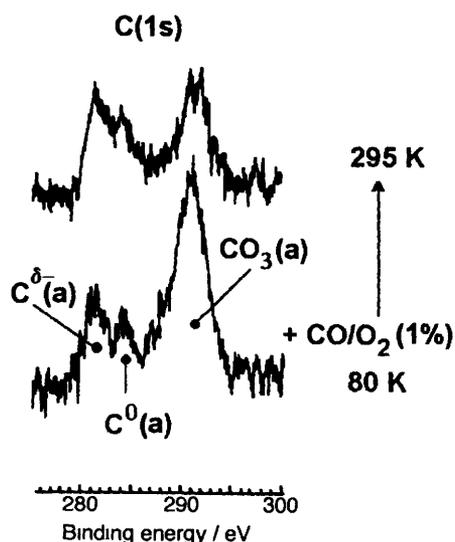
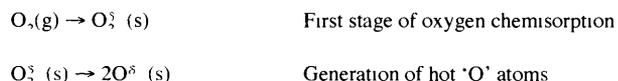
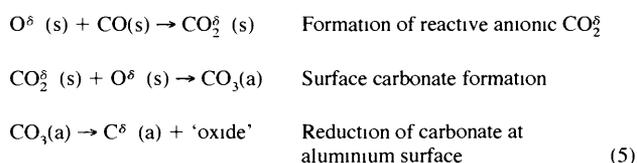


Figure 3 C(1s) spectra of an aluminium surface after exposure to a carbon monoxide-dioxygen mixture (1% CO) at 80 K. Oxidation of CO by the transient $O^\delta(s)$ occurs to give a monolayer of carbonate species which are partially reduced by the aluminium to give carbidic carbon and oxide



We had clearly moved away from a checker board model for surface reactions with neither the Eley-Rideal nor the Langmuir-Hinshelwood mechanism being appropriate models for these reactions. How we viewed the transition state in dioxygen dissociation was not clear. A clue however, was that in both cases, aluminium and magnesium, oxygen chemisorption was a highly exothermic reaction and what was envisaged was that at least one of the oxygen atoms underwent rapid translational motion during bond cleavage. It was the latter that was the chemically reactive species.

3 Dioxygen Transients: $O_2^\delta(s)$

Evidence for the participation of $O^\delta(s)$ as a reactive transient in the surface chemistry of dioxygen at metal surfaces raised the possibility that a molecular oxygen O_2^δ transient could play a role in determining reaction pathways. We chose to investigate the Zn(0001)-dioxygen system¹³ since the dissociative chemisorption of oxygen was unusually slow with a sticking probability of $ca\ 10^{-3}$, suggesting that bond cleavage might be rate-determining. Was this to be associated with a precursor transient state $O_2^\delta(s)$? There was at the time at least one example we were aware of where in metal oxidation the process does not proceed at low temperatures beyond the chemisorbed molecular state¹⁴ – the $O_2^\delta(a)$ state at Ag(111).

The reactivity of ammonia rich dioxygen-ammonia mixtures at Zn(0001) surfaces showed¹³ analogous chemistry to that observed with Mg(0001) but distinctly different kinetic behaviour. Fig. 4 shows the temperature dependence of the formation of surface

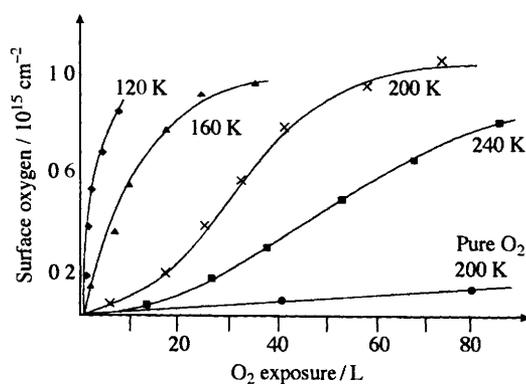


Figure 4 Variation of surface oxygen (chemisorbed oxygen and hydroxy species) at four temperatures, 240, 200, 160 and 120 K as a function of oxygen exposure when a Zn(0001) surface is exposed to an ammonia-dioxygen (2:1) mixture (L = Langmuir). Also shown is the data for pure oxygen. Note the evidence for precursor mediated kinetics and increased efficiency for dioxygen bond cleavage in the presence of ammonia.

'oxygen' species (hydroxyl + chemisorbed oxygen O_2^δ -species) and XP and EEL spectra providing evidence for amide and hydroxyl species (Fig. 5). Also shown for comparison is the chemisorbed oxygen concentration as a function of exposure to pure oxygen at 200 K. There are two points to note: (a) the inverse temperature dependence of the reaction rate and (b) the substantial increase (by a factor of $ca\ 10^2$) in surface oxidation rate observed with the ammonia rich dioxygen-ammonia mixture compared with pure oxygen. Both these point to the participation of an ammonia-dioxygen complex – or transition state – and the reaction scheme [(eqn. (6))] was suggested. This is an example of how the rate of dioxygen bond cleavage is faster for the dioxygen-ammonia

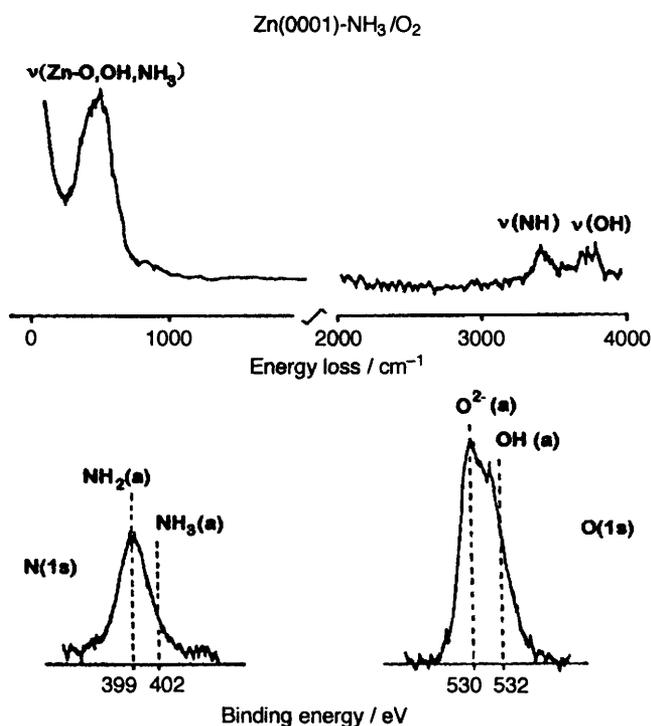


Figure 5 N(1s) and O(1s) spectra for the chemisorbed adlayer at Zn(0001) surface after exposure to the ammonia-dioxygen mixture. Also shown is the corresponding electron energy loss spectra. Note the formation of NH_2 , OH and chemisorbed oxygen.

complex than it is for dioxygen alone. We assume that the enhanced rate be associated with a lowering of the activation energy but

$\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{s})$	Dioxygen accommodation
$\text{O}_2(\text{s}) \rightarrow \text{O}_2^{\delta-}(\text{s})$	Transient formation
$\text{O}_2(\text{g}) \rightarrow \text{O}_2^{\delta-}(\text{s}) \rightarrow 2\text{O}^{2-}(\text{a})$	Inefficient oxide route
$\text{NH}_3(\text{g}) \rightarrow \text{NH}_3(\text{s})$	NH_3 undergoing surface diffusion
$\text{NH}_3(\text{s}) + \text{O}_2^{\delta-}(\text{s}) \rightarrow (\text{NH}_3 \cdots \text{O}_2^{\delta-})(\text{s})$	Complex formation
$(\text{NH}_3 \cdots \text{O}_2^{\delta-})(\text{s}) \rightarrow \text{OH}(\text{a}) + \text{NH}_2(\text{a}) + \text{O}^{2-}(\text{a})$	Complex decomposition; efficient pathway to dioxygen bond cleavage; amide route (6)

driven by a thermodynamically favoured reaction – the amide route. We will return to a theoretical analysis of this concept later. The kinetics of the dioxygen–ammonia system conformed to a precursor-mediated reaction in keeping with the involvement of a charge transfer complex of the kind $(\text{O}_2^{\delta-} \cdots \text{NH}_3)(\text{s})$ suggested in the above reaction scheme. Of particular note is that the rate of the formation of amide and hydroxyl species – the amide reaction pathway in the scheme – was inversely dependent not only on the temperature but also on the $\text{NH}_3(\text{g})\text{:O}_2(\text{g})$ ratio. It is the three centre precursor complex $\text{Zn}^{\delta+} \cdots (\text{O}_2^{\delta-} \cdots \text{NH}_3)$ that is involved in the rate-determining step and clearly its concentration is directly related to the $\text{NH}_3(\text{g})\text{:O}_2$ ratio, being greater the more ammonia rich is the mixture.

The rate of complex formation J_F is given by eqn. (7),¹⁵ where

$$J_F = \theta(\text{NH}_3)\theta(\text{O}_2) \exp\left(-\frac{\Delta H}{kT}\right) \left[\nu(\text{NH}_3) \exp\left(-\frac{E_{\text{NH}_3}}{kT}\right) + \nu(\text{O}_2) \exp\left(-\frac{E_{\text{O}_2}}{kT}\right) \right] \quad (7)$$

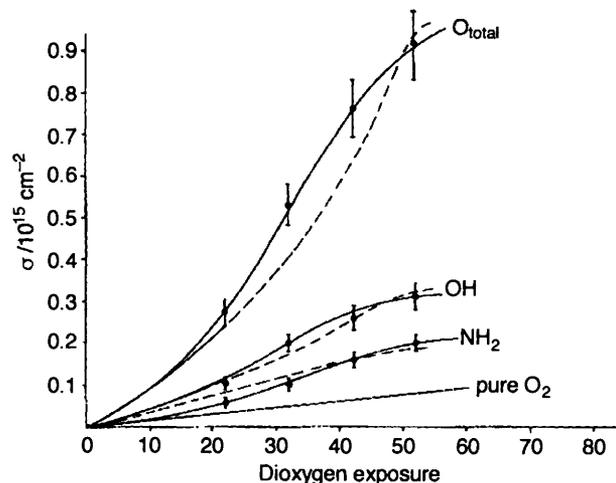


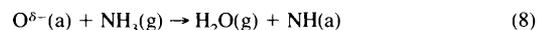
Figure 6 Modelling the kinetics of the dioxygen–ammonia reaction at a Zn(0001) surface; the experimental data (—) are compared with the theoretical model (---); further evidence for the role of a dioxygen–ammonia complex $(\text{O}_2^{\delta-} \cdots \text{NH}_3)$. O_{total} is the sum of OH and chemisorbed oxygen.

the terms in the square bracket are related to the surface diffusion of $\text{NH}_3(\text{s})$ and $\text{O}_2^{\delta-}(\text{s})$ involving a hopping mechanism, θ are surface coverages, ν and E are frequencies and activation energies of diffusion respectively and ΔH is the activation enthalpy of complex formation. The experimental coadsorption kinetics were successfully modelled¹⁵ at both 200 K and 120 K assuming an activation energy of 40 kJ mol⁻¹ and a frequency factor of 10¹³ s⁻¹ for the decomposition of the precursor complex. The surface coverage of the precursor complex is estimated to be *ca.* 10⁻⁵; however, we have no firm grounds for assuming that the frequency factor for complex decomposition is 10¹³ s⁻¹ and the calculations are illustrative only. Nevertheless the theoretical model shows how even though the equilibrium $\text{O}_2(\text{g}) \rightleftharpoons \text{O}_2^{\delta-}(\text{s})$ allows for only a low coverage of $\text{O}_2^{\delta-}(\text{s})$, the rate of complex formation is proportional to the product of $\text{O}_2^{\delta-}(\text{s})$ – a small number, and ν_{diff} the vibrational frequency of surface diffusion of $\text{NH}_3(\text{s})$ which is a large number, 10¹³ s⁻¹. The stability of the dioxygen–ammonia complex is suggested to arise^{13,15} from electrostatic interactions between $\text{O}_2^{\delta-}$ and NH_3 within the $\text{Zn}^{\delta+} \cdots (\text{O}_2^{\delta-} \cdots \text{NH}_3)$ complex, thus providing a route to the more energetically favourable amide pathway.

Further evidence for the participation of the dioxygen $\text{O}_2^{\delta-}(\text{s})$ transient in the chemistry of dioxygen at Zn(0001) surfaces was established by coadsorption with pyridine.¹⁶ Like ammonia it enhanced the rate of dioxygen bond cleavage by a factor of *ca.* 10² which was in keeping with the chemistry of pyridine where dioxygen complex formation is well known.

4 Ammonia Oxidation at Copper Surfaces: which is the Active Species $\text{O}_2^{\delta-}(\text{s})$ or $\text{O}^{\delta-}(\text{s})$?

The activation of ammonia by preadsorbed oxygen at a Cu(111) surface was one of the first examples of a class of reactions^{4b,5,9} we have referred to as ‘chemisorptive replacement reactions’ the chemisorbed oxygen being removed as water with the simultaneous formation of surface imide species $\text{NH}(\text{a})$; the reaction rate was sensitive to oxygen coverage and became unmeasurably slow as the preadsorbed oxygen coverage approach unity [eqn. (8)].



Guided by a scanning tunnelling microscope study of the structure of the Cu(110)–O overlayer we carried out a Monte Carlo simulation of the development of the overlayer as a function of coverage.¹⁷ We then compared the experimentally observed reactivity of Cu(110)–O surfaces for imide formation as a function of oxygen coverage with the presence of structurally distinguishable oxygen states: isolated oxygen adatoms; oxygens at the end of Cu–O–Cu–O

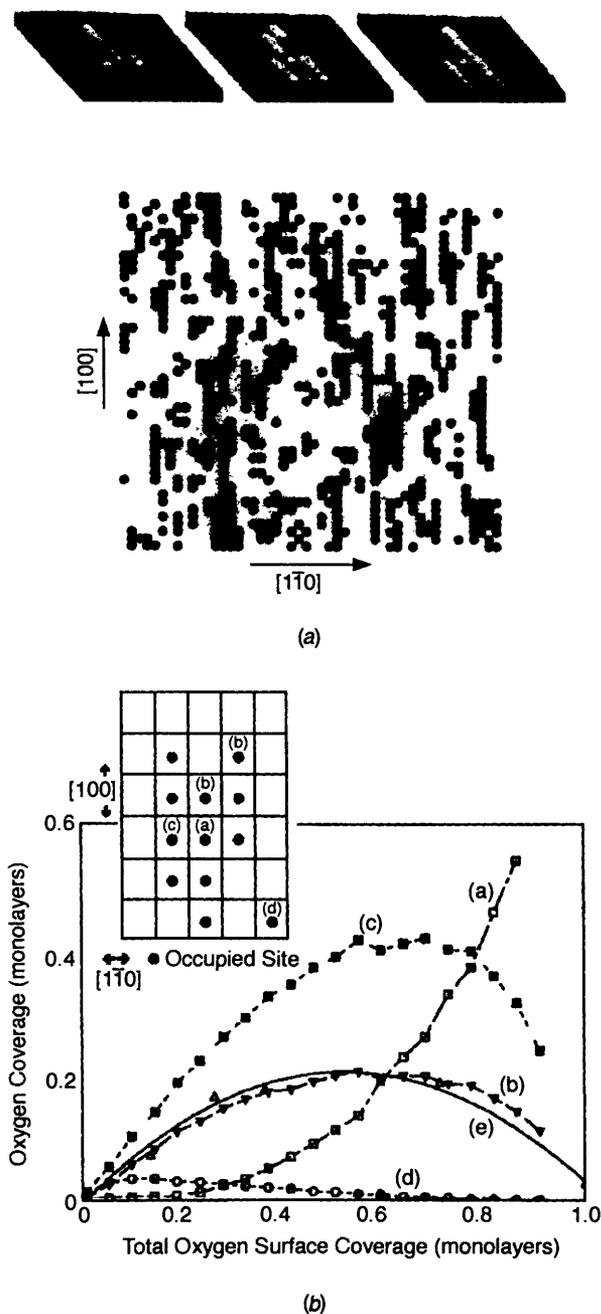


Figure 7 (a) Simulated surface structure at a Cu(110) surface after 300 Monte Carlo equilibrium steps for $\theta_{\text{oxygen}} = 0.3$, $E_{110} = 2$ and $E_{100} = 7$ kJ mol⁻¹. Note the similarity of the surface topography to the Cu-O-Cu-O chains seen by STM. (b) The experimental data for the extent of the chemisorptive replacement of surface oxygen by NH_x species (curve e) as a function of preadsorbed oxygen is compared with the surface oxygen present in four different environments (a), (b), (c) and (d). Good fit is obtained with (d) which corresponds to oxygens at the end of Cu-O-Cu-O chains.

chains and oxygens within oxide islands. The experimental reactivity data for NH formation could only be satisfactorily correlated with those oxygen adatoms that were present at the end of the Cu-O-Cu-O chains [Fig. 7(a) and (b)] and we drew attention^{5,17,18c} to the significant role that the charge associated with the oxygen can play in determining its reactivity; O^{δ-} would best describe the former and O²⁻ the latter. It should be recalled that although O(g) + e → O⁻(g) is highly exothermic, the addition of a further electron is endothermic and O²⁻ can only be formed at metal surfaces when there is a possible contribution from a Madelung term associated with oxide formation. Furthermore the O⁻-like oxygen species would be anticipated to be highly reactive (isoelectronic with F) whereas O²⁻ (isoelectronic with Ne) would be

expected to be relatively unreactive. We therefore associate oxygens situated at the end of Cu-O-Cu chains with O⁻ and analogous to the oxygen atom transients O^{δ-}(s) discussed earlier.

Taking a lead from our studies^{8,10,13} of the activation of water by oxygen at Ni(210) surfaces at low temperatures, the coadsorption of ammonia-dioxygen mixtures at Mg(0001) and Zn(0001) surfaces – all of which provided evidence for O^{δ-}(s) and O₂^{δ-}(s) transients – we studied the reactions of similar mixtures with Cu(111) and Cu(110) surfaces.^{5,18a-c} It was shown that for ammonia rich dioxygen-ammonia mixtures an efficient reaction occurred with Cu(111) at 295 K leading to the formation of chemisorbed imide species (Fig. 8). Even though the reaction is oxygen catalysed virtually a monolayer of NH_x species is formed without any evidence for surface oxygen being present in the O(1s) spectra. The N(1s) binding energy was at 398 eV and the vibrational (HREEL) spectra confirmed this as the bent form of NH(a), characterised by an δ_{NH} loss feature at 1100, ν_{NH} at 3400 and $\nu_{\text{Cu-NH}}$ at 700 cm⁻¹. Recently, Bradshaw *et al.*¹⁹ have shown by photoelectron diffraction that the NH species is present at the short-bridge sites of the Cu(110) surface. What then is the mechanism of this reaction and is it the atomic or dioxygen transient that is the active species? The kinetics did not show any characteristics associated with the participation of a precursor complex and in contrast to Zn(0001) there was no kinetic window available (see Fig. 4) in that the sticking probability of oxygen was already high for Cu(110) at 295 K. At the Cu(110) surface the oxygen dissociation rate was slower than the rate of NH_x formation from an ammonia rich dioxygen-ammonia mixture. This points to a precursor dioxygen state O₂^{δ-} being involved in the reaction;^{18b} if the reactive species was atomic oxygen O^{δ-}(s) then we would expect the rate of NH_x formation to be either less or equal to the rate of dioxygen bond cleavage. This appears to be the case for Cu(111) (Fig. 8). Furthermore the rate of NH_x formation is at least a factor of ten times higher with both Cu(111) and Cu(110) than the chemisorptive replacement reaction when the oxygen surface coverage was about 0.2.

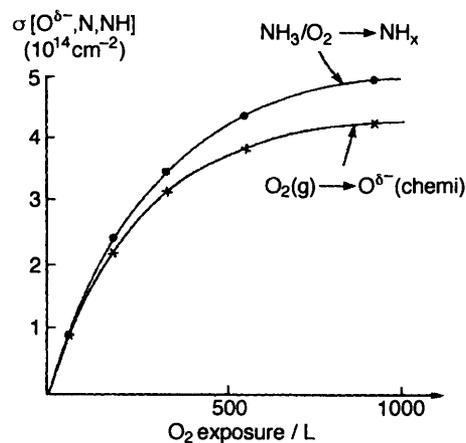
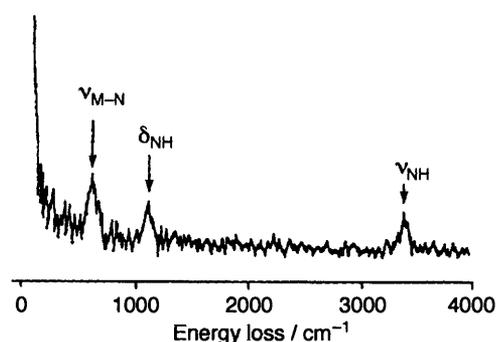


Figure 8 Comparisons of the formation of chemisorbed oxygen when a Cu(111) surface is exposed to dioxygen and the formation of NH_x species when Cu(111) is exposed to an ammonia rich dioxygen-ammonia mixture at 295 K. Also shown is an electron energy loss spectrum of the chemisorbed layer confirming the presence of NH(a).

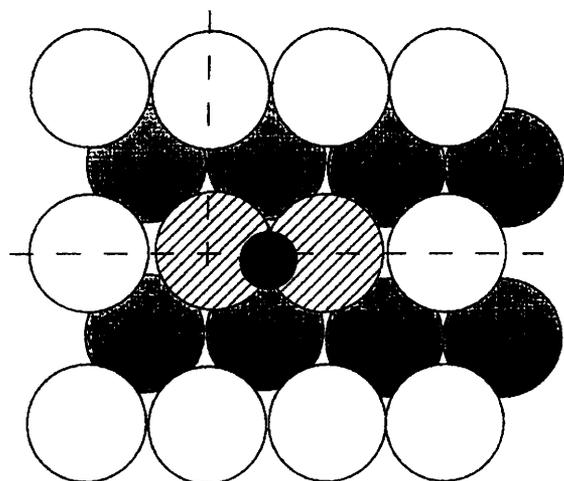
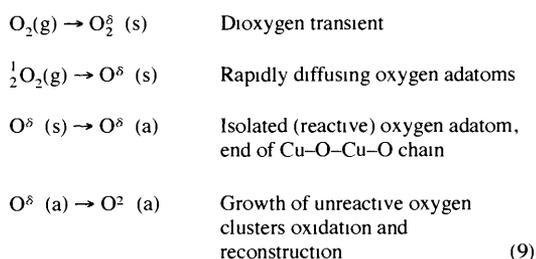


Figure 9 NH species present at the short bridge site of a Cu(110) surface after exposure to an ammonia rich ammonia-dioxygen mixture at 295 K

We therefore have a hierarchy of reactivity for NH_x formation coadsorption of ammonia rich $\text{NH}_3\text{-O}_2$ mixtures is the most efficient, with the chemisorption replacement reaction the rate is always appreciably lower and tends to zero as the oxygen coverage approaches unity. This led to the general proposition^{5,18c} that the activity of oxygen in hydrogen abstraction reactions decreases as oxygen clusters (nuclei) develop and is close to zero for a 'perfect' oxide overlayer [see scheme eqn (9)]



Although comparisons of the rate of dioxygen dissociation and imide formation suggested that the dioxygen transient participated in the dehydrogenation of ammonia at Cu(110) it was also shown^{18c} that *isolated oxygen adatoms* $\text{O}^\delta(\text{a})$ at Cu(110) were also very reactive to $\text{NH}_3(\text{g})$. We therefore were uncertain as to whether during coadsorption of ammonia and dioxygen at Cu(110) surfaces the reaction pathway was *via* the molecular or oxygen atom transients. Provided the oxide pathway $\text{O}^\delta(\text{a}) \rightarrow \text{O}^2(\text{a})$ is not allowed to become a significant route imide formation takes place to complete coverage at 295 K. At low temperature dehydrogenation proceeds only as far as the amide species^{18c} [eqn (10)]

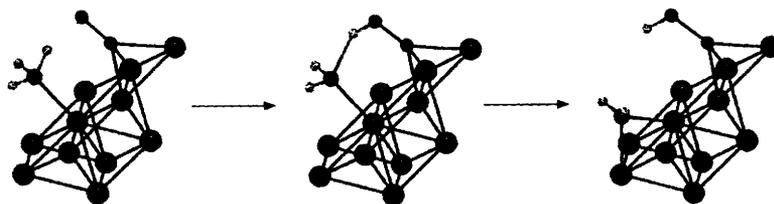
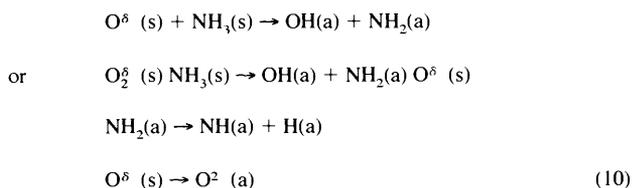


Figure 10 Abstraction of H from NH_3 by molecular oxygen at a Cu(8,3) cluster to form NH_2 and OOH . In the presence of NH_3 , oxygen prefers the perpendicular adsorption geometry whereas at the clean cluster surface oxygen is in a configuration parallel to the surface

Table 1 Density function calculations for ammonia dissociation and oxidation (van Santen *et al.*)²⁰

Reaction	Activation energy /kJ mol ⁻¹	Overall reaction energy /kJ mol ⁻¹
$\text{NH}_3(\text{g}) \rightarrow \text{NH}_2(\text{g}) + \text{H}(\text{g})$	+498	+498
$\text{NH}_3^* \rightarrow \text{NH}_2^* + \text{H}^*$	+344	+176
$\text{NH}_3^* + \text{O}^* \rightarrow \text{NH}_2^* + \text{OH}^*$	+132	+48
$\text{NH}_3^* + \text{O}^* \rightarrow \text{NH}_2^* + \text{H}_2\text{O}(\text{g})$	>200	+92
$\text{NH}_3^* + \text{O}_2^* \rightarrow \text{NH}_2^* + \text{OOH}^*$	+67	-84
$\text{NH}_3^* + \text{O}_2^* \rightarrow \text{NH}_2^* + \text{O}^* + \text{H}_2\text{O}(\text{g})$	+134	-184

As far as we were aware[†] there were no similar experimental studies being pursued elsewhere and certainly no theoretical evidence for or against the role of molecular oxygen transients participating in ammonia oxidation reactions. Phillip Davies, who had completed his PhD thesis at Cardiff, dealing with experimental aspects of ammonia oxidation, joined van Santen's theoretical group in Eindhoven during the summer of 1990 where there was an interest in the role of oxygen in hydrocarbon oxidation and cluster calculations for ammonia adsorption on copper^{20a}. The Eindhoven group using first principle density functional calculations extended this work to make a detailed and elegant analysis of the role of atomic and molecular oxygen precursors in the overall catalytic cycle of ammonia oxidation^{20b}. They used a Cu(8,3) cluster as a model of the Cu(111) surface (Fig. 10) and established that, although atomic oxygen can enhance N-H bond activation by lowering the activation energy for H-abstraction, it may also act as a surface poison inhibiting NH_3 dissociation. This was in keeping with our experimental work. Transient molecular oxygen was shown to adsorb weakly both parallel (17 kJ mol⁻¹) and perpendicular (10 kJ mol⁻¹) to the surface, parallel adsorption appeared to be a precursor for oxygen dissociation whereas the perpendicular form was involved in H abstraction. The theoretical calculations favoured the formation of OOH as an intermediate (with close to zero activation energy) in the H abstraction process rather than the simultaneous transfer of two hydrogens to form water directly. Of the four reaction pathways analysed (Table 1) it was the nonactivated molecular oxygen transient pathway involving sequential H abstraction that was favoured – the next most energetically favoured pathway involved the 'hot' atomic oxygen transient. These calculations provided a theoretical basis for the oxygen transient concept in catalytic oxidation and supported the general conclusions that had emerged from experimental coadsorption studies.

5 Metastable Oxygen States at Metal Surfaces

Although the presence of alkali metals in catalyst formulations is a well established approach to controlling selectivity in heterogeneous catalysis there have been comparatively few studies of the surface chemistry of alkali metals *per se*. The investigation of the caesium-oxygen system^{21a} was stimulated by our earlier studies of the Cu(110)-Cs-oxygen system^{21b} where the oxygen was shown to be highly reactive to carbon monoxide to give $\text{CO}_2^\delta(\text{a})$ species at 80 K and carbonate on warming to 295 K. At caesium surfaces X-ray induced O(1s) spectra have enabled three distinct oxygen states

[†] Since this article was submitted, R. J. Madix has drawn attention to STM data (*Surf. Sci.*, in press) which has confirmed the model proposed [eqn (9) and (10)] for ammonia oxygenation reactions at Cu(110) surfaces.

to be assigned to isolated oxygen adatoms O^δ , peroxy-type species O_2^δ and oxide O^2 . The O^δ state, only observed at low surface coverage, is the precursor to oxide formation in accord with thermodynamic arguments.^{21a} A similar situation exists when oxygen is chemisorbed at Ni(110) and Ni(100) surfaces²² and may indeed be a characteristic of very early stages of oxygen chemisorption and metal oxidation in general. Since carbon monoxide is not adsorbed and unreactive at an atomically clean caesium surface we explored²³ its catalytic oxidation and the relevance of the three oxygen states in the process.

We established that the O^δ (a) state readily gives the anionic CO_2^δ (a) species when exposed to CO(g) at 80 K, this could be oxidized further on exposure to dioxygen to give surface carbonate CO_3 (a). When CO/O₂ mixtures were exposed to caesium,²³ the chemistry observed depended on the ratio of CO to O₂. For CO-rich mixtures the reactive O^δ (s), via the O^δ (a) state, provides a facile route to CO_2^δ (a), however, for oxygen rich mixtures metal oxidation dominates leading to oxidation and carbonate formation. It is the lifetime of the O^δ (s) species, *i.e.* before it is transformed to the O^2 (oxide) species that determines which reaction pathway is followed.

The distinction between the chemical reactivity of O⁻ type and O²⁻ type oxygen species has been one of the cornerstones of our studies of the chemistry of 'oxide' surfaces.⁹ For example the 'oxide' overlayer at a Pb(110) surface is unreactive to water vapour, however the presence of O^δ species provides reactive sites for H-abstraction⁸ while in the case of Ni(100) and Ni(110), when the oxygen coverage is <0.2 the surface is highly reactive to ammonia²² with the formation of NH_x species. This reactivity is also observed in NH_3 -O₂ coadsorption. When oxygen rich dioxygen-ammonia mixtures are exposed to Pt(111) there is rapid development of N(1s) intensity at 397 eV binding energy indicative of N-adatoms – there is no intensity at any stage in the O(1s) spectrum region.²⁴ The LEED pattern indicates that the Pt(111)-N adlayer is well ordered, while the HREEL spectra show features at 500 cm⁻¹ (ν_{Pt-N}) and 1185 cm⁻¹ (δ_{HNH}), the latter due to a small coverage (*ca.* 10¹³ cm⁻²) of NH_3 (a) – sufficient to give some asymmetry on the high binding energy side of the N(1s) peak. Following our conclusions with other metal-oxygen systems we suggested²⁴ that in the Pt(111)-O system the oxygen adatoms were present either as isolated oxygens or as very small clusters. Recently Ertl and his colleagues²⁵ have reported an STM study of the Pt(111)-O system and established that subsequent to dissociation the oxygen atoms appear in pairs on the surface but separated by an average distance of two lattice constants. This is entirely in keeping with the general conclusions suggested by the ammonia-dioxygen studies.²⁴

6 Direct Experimental Evidence for 'Hot' Oxygen Transients: Scanning Tunnelling Microscopy and Mass Spectrometry

Experimental evidence for oxygen transients at metal surfaces relied initially on the unique chemistry observed, which could not be associated with the thermally accommodated oxygen in its final chemisorbed state and also kinetic behaviour which was indicative of the participation of precursor states. There were also strong analogies with homogeneous gas phase radical chemistry (*e.g.* the $NH_3 + O \rightarrow NH_2 + OH$ reaction) and also the chemistry of O species present at bulk oxide surfaces, in that low energy reaction pathways were available only under conditions where oxygen transients or metastable oxygen adatoms were present. We designated the oxygen transients as O^δ (s), *i.e.* O⁻ like, and most likely to be associated with metal-oxygen systems where oxygen chemisorption is highly exothermic and characterised by high oxygen sticking probabilities. For metal-oxygen systems where dioxygen bond cleavage is slow, then the O_2^δ (s) transient is likely to determine the chemistry, in such systems oxidation is also less exothermic. This is the case for the Zn(0001)-dioxygen-ammonia system.¹³ Earlier optical simulation studies²⁶ of LEED patterns observed for oxygen chemisorption at Cu(210) surfaces had suggested that subsequent to dissociation a correlated or semi-correlated diffusion of oxygen adatoms by a hopping mechanism, occurring over large distances

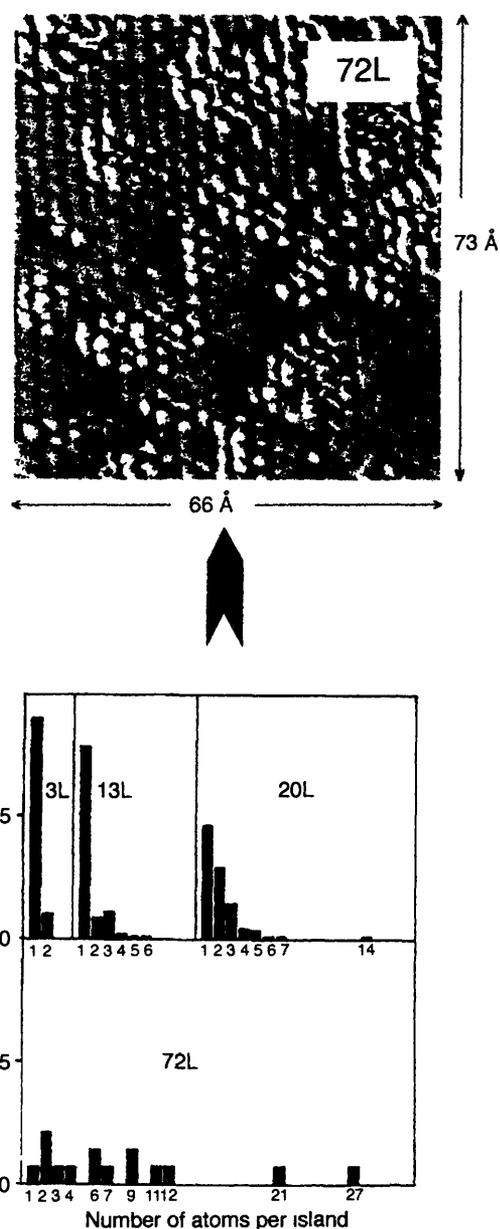


Figure 11 STM evidence for 'hot' oxygen transients at an Al(111) surface, note also that for an exposure of 72 L very few isolated oxygen adatoms are present. At low oxygen exposures isolated oxygen adatoms predominate.²⁷

(*ca.* 10 nm), is necessary to generate the defective structures that would give rise to the observed LEED patterns. However, we did not consider that this might have any influence on chemical reactivity. In spite of these compelling observations more direct experimental evidence for oxygen transients being associated with oxygen chemisorption at metal surfaces was needed.

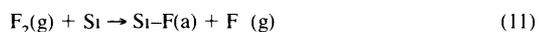
This became available first for the Al(111)-dioxygen system through STM studies by Ertl's group,²⁷ Fig. 11 shows an STM image of an Al(111) surface after exposure to dioxygen at 300 K. Although the oxygen adatoms in the final chemisorbed state are completely immobile at this temperature, ordered patches of 'oxygen islands' are observed as a consequence of the generation of 'hot' oxygen transients. The STM experiments also revealed that at low exposures (coverages) dissociative oxygen chemisorption led to the two oxygen atoms being separated from each other by at least 80 Å before they became thermally accommodated with the surface through relaxation of the excess energy of several eV to phonon or electronic excitations of the substrate. At low oxygen exposures (3 L[†]) isolated oxygen adatoms are mainly present but with increasing

[†] 1 L (Langmuir) = 10⁻⁶ Torr s

exposure (72 L) the oxygens cluster together to give the island-type structures shown in Fig 11, with very few isolated oxygen adatoms. Also shown is a histogram showing the size distribution of the oxygen islands for four oxygen exposures, 3 L, 13 L, 20 L and 72 L. That 'hot' oxygen atoms are generated during dissociative chemisorption of dioxygen at aluminium surfaces was established first through the adsorption of carbon monoxide-dioxygen mixtures when even at 80 K surface carbonate is formed¹² (Fig 3). The STM observations add definitive evidence to support the mechanism involving rapidly diffusing oxygen atoms.

More recently Wintterlin *et al.*²⁵ have studied the dissociation of O₂ at a Pt(111) surface by STM. The two oxygen atoms generated by the process of dissociation appear in pairs at 150 K with an average distance of two lattice constants. This is an appreciably smaller distance than that observed at the Al(111) surface (*ca.* 80 Å) which is compatible with the much smaller heat of oxygen chemisorption at platinum than at aluminium. The authors conclude that the separation of the oxygen atoms results from transient ballistic motion where the short range travelled is in agreement with molecular dynamics calculations. The reactivity of oxygen adatoms at Pt(111) to ammonia is high undergoing chemisorptive replacement to give NH species²⁴ and cannot be distinguished from the similar chemistry and reactivity observed when ammonia-rich dioxygen mixtures are exposed to Pt(111) at the same temperature. This is in accord with the STM observations of Ertl – isolated oxygen adatoms being the reactive species in both cases.

The mode by which the oxygen atoms fly apart particularly in the Al(111)-O system is uncertain. Do they translate parallel to the surface or do they follow a parabolic, through-space type of trajectory? In some cases adsorbate atoms have indeed been detected in the gas phase, O⁻ ions from caesium surfaces²⁸ (Fig 12) and F⁻ ions from silicon surfaces,²⁹ suggesting that a 'cannon ball' trajectory involving surface hopping is the likely mechanism for such reactions [eqn (11)].



The cleavage of the F₂ bond by the formation of a single F-Si bond is argued to be thermodynamically feasible on the grounds that the energy released upon adsorption at a single Si dangling bond, which does not require cleavage of a Si lattice bond, is 5–6 eV compared with 1.5 eV for the F₂ bond energy. Some of the exothermicity is thus converted into translational energy of the scattered F atom. How then do we view the transition state involved in the dissociative chemisorption of dioxygen at say aluminium and magnesium

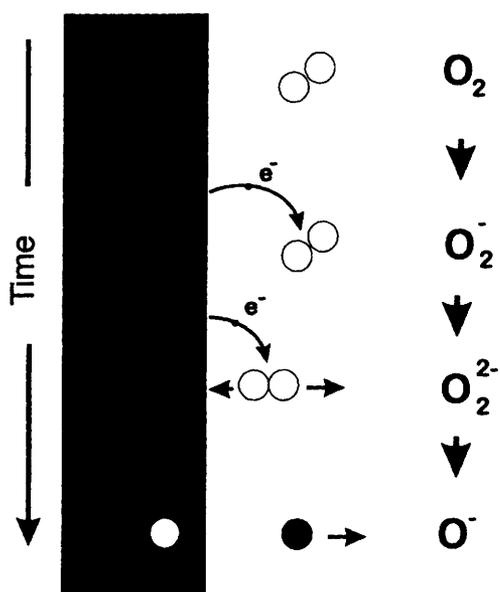


Figure 12 Exposure of Cs surfaces to O₂ causes ejection of O⁻ ions during the first stage of dissociative chemisorption – followed by exoelectron emission at higher exposures²⁸

surfaces and what is the relationship between the heat of chemisorption and the strengths of the metal-oxygen bonds formed?

7 Excited States generated by O-atoms

A question relevant to 'hot' oxygen surface chemistry is the temperature of the vibrational modes of the reaction products – particularly if the latter might open up reaction channels not available to the 'cold' molecules. Haller³⁰ has recently addressed this in studies of the oxidation of carbon monoxide by 'nascent oxygen' – the latter being generated by a discharge. It was shown that the apparent temperature of CO₂ generated by nascent oxygen atoms in the presence of a palladium catalyst is much higher than that from thermally accommodated O-adatoms, *i.e.* it is vibrationally excited. A two-dimensional gas model, analogous to that put forward for oxygen transient reactions at Mg(0001) and Cu(110)^{10, 11, 18} surfaces, is suggested to account for the higher temperature. It is significant that Coulston and Haller³¹ had estimated that the CO coverage when the oxidation rate is maximum is only of the order of 10⁻³. The mechanism proposed³⁰ is suggested to involve a 'weakly physically adsorbed oxygen atom with a finite lifetime' which is similar to the arguments developed here and discussed at the Faraday Symposium,^{10a} where the classical Eley-Rideal mechanism was seen to be an inappropriate model³² for the oxygenation of ammonia at Mg(0001). The physical reason for CO₂ excitation arises from the less demanding energetics for the CO-nascent oxygen reaction, in that fewer surface-adsorbate bonds are broken. Breaking fewer bonds will result in more energy from the oxidation reaction CO + ½O₂ → CO₂, about 280 kJ mol⁻¹, being channelled into the product CO₂.

In the systems studied where hot O-atoms have been generated by dissociative chemisorption – magnesium-dioxygen, magnesium-nitrous and nitric oxides and aluminium-dioxygen – the reactions are all highly exothermic. The CO-O₂ catalytic reaction at aluminium,¹² where surface carbonate is formed at 80 K, is a particularly good example of hot oxygen atom chemistry involving CO present at 'negligible' surface coverage. The exothermicity of the reaction – oxygen chemisorption and CO oxidation being possible contributors to generating 'hot' CO₂ molecules which undergo further surface reactions *via* the reactive CO₂⁻ species to chemisorbed carbonate (Fig 3). Haber³³ has also recently drawn attention to the role of oxygen transients in heterogeneous catalysis.

8 Conclusions

The significance of oxygen transients in providing low energy pathways in surface oxygenation reactions was first established through using surface sensitive photoelectron and vibrational spectroscopies in conjunction with the probe-molecule approach. Both atomic O^{δ-}(s) and dioxygen O₂^{δ-}(s) transients have been shown to participate in a wide range of reactions at single crystal metal surfaces including the oxidation of ammonia, carbon monoxide and hydrocarbons. Which of the two transients participate in the surface chemistry depends on the metal, O₂^{δ-} at the Zn(0001) surface, O^{δ-} at Mg(0001). The mechanisms are non-classical in that they are analogous to two-dimensional gas phase reactions where neither of the reactants are strongly adsorbed – are present at immeasurably small coverages but undergoing rapid surface diffusion to generate surface complexes (transition states) which decompose to chemisorbed products. There is a clear need to consider the chemistry of the total system rather than making deductions based on the chemistry of the individual reactants – the latter could be misleading. For example dioxygen bond cleavage is much faster *via* the transient ammonia-dioxygen complex than it is from dioxygen alone whether viewed theoretically or on the basis of experimental data.

Support for the transient concept has been provided by other experimental approaches, in particular the STM results from Ertl's group, and the quantum mechanical calculations of van Santen for ammonia oxidation at copper surfaces. Not only have coadsorption studies provided a different view of catalytic chemistry at single

metal surfaces but also to unexpected structural assignments of surface species through the photoelectron diffraction studies of Bradshaw

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