Commentary on Electron Spectroscopy and Kinetics

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Commentary on electron spectroscopy and kinetics

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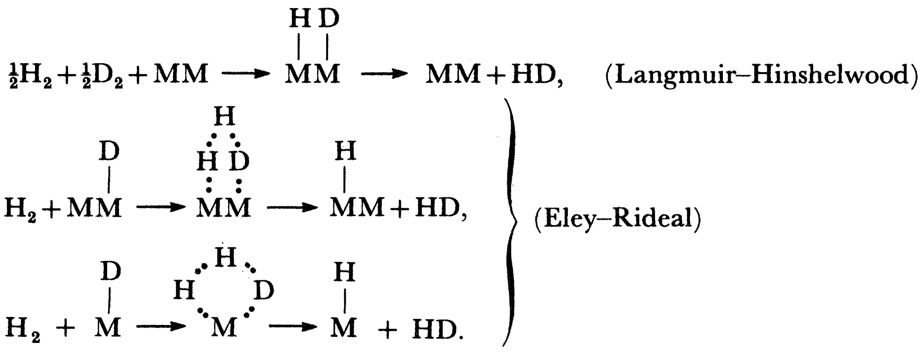
The following topics, taken from the three preceding surface science papers, are discussed in the light of conventional kinetics: subsurface adsorbed O^{2-}, molecular beam results for H_2+D_2 on Cu, Pt and Pd, ethylene hydrogenation, S-adsorbate interactions, and the evolution of 'catalytic entities'.

Work with single-crystal planes eliminates multiple-plane and grain-boundary effects found in wires and evaporated films, but still leaves, in many cases, complications due to lateral interactions in adsorbates. Also, in our experience, single-crystal planes yield more accurate and reproducible data than polycrystalline specimens.

In their work on O_2 and Zn(0001), Au & Roberts (1984) were able to distinguish surface adsorbed O^-(a) from subsurface O^{2-}(b), and to identify a small activation energy for $O^-(a) \rightarrow O^{2-}(b)$. It would be interesting to apply the method to Al, where the idea that Madelung forces lead to an increase in ionicity of a growing oxide film, was held responsible for the observed Elovich kinetics (Eley & Wilkinson 1960). Again, in our study of N_2O decomposition on Pd, and PdAu alloy wires, we found that adsorbed oxygen inhibited the rate according to $p^{1}_{O_2}$ rather than $p^{\frac{1}{2}}_{O_2}$, i.e. adsorbed oxygen molecules rather than atoms (Eley & Knights 1966). In analysing recent single-crystal Pd studies, we have found that on certain assumptions, the Knights kinetic equations can also result from a recombination desorption of adsorbed, with subsurface, O (Eley *et al.* 1985). There is definite evidence here for a stable subsurface O layer on Pd(111) from both t.d.s. and l.e.e.d. (Conrad *et al.* 1977), and u.p.s. (Weissman *et al.* 1980). It would be of great interest to repeat the N_2O work with the use of these techniques.

I should like to include with Professor Somorjai's molecular beam studies the similar work on Cu and Pd, all recently reviewed by Engel & Ertl (1982). In all three cases, made at equivalent pressures of *ca.* 10^{-7} Torr (1 Torr ≈ 133.3 Pa), the Langmuir–Hinshelwood (L.H.) mechanism (1) was shown to be operative. I shall try to examine how far Eley–Rideal (E.R.) mechanisms (2*a*, *b*) take over at higher pressures, such as 1 Torr, with conventional reactors. The mechanisms are



$$\tfrac{1}{2}\mathrm{H_2}+\tfrac{1}{2}\mathrm{D_2}+\mathrm{MM} \longrightarrow \overset{\mathrm{H\,D}}{\overset{|\;|}{\mathrm{MM}}} \longrightarrow \mathrm{MM}+\mathrm{HD}, \quad \text{(Langmuir–Hinshelwood)} \qquad (1)$$

$$\mathrm{H_2}+\overset{\mathrm{D}}{\overset{|}{\mathrm{M}}}\mathrm{M} \longrightarrow \overset{\mathrm{H}}{\overset{\vdots\;\vdots}{\overset{\mathrm{H\,D}}{\overset{\vdots\;\vdots}{\mathrm{MM}}}}} \longrightarrow \overset{\mathrm{H}}{\overset{|}{\mathrm{M}}}\mathrm{M}+\mathrm{HD}, \qquad (2a)$$

$$\mathrm{H_2} + \overset{\mathrm{D}}{\overset{|}{\mathrm{M}}} \longrightarrow \overset{\mathrm{H}}{\mathrm{H}\;\mathrm{M}\;\mathrm{D}} \longrightarrow \overset{\mathrm{H}}{\overset{|}{\mathrm{M}}} + \mathrm{HD}. \qquad (2b)$$

(Eley–Rideal)

Here, M denotes a surface metal atom, and there is a *prima facie* case for supposing that as the surface coverage θ_H of H or D atoms increases towards unity, as a result of going to lower temperatures, higher pressures, or to metals of higher heat of adsorption, q, there will be a tendency for mechanisms to change in the direction $(1) \rightarrow (2a) \rightarrow (2b)$. To summarize for Cu, it seems that over 10^{-7}–1 Torr at *ca.* 400 K the L.H. mechanisms holds, which can be described by the one-dimensional potential energy curves of Lennard-Jones (1932). An analysis of the para-H_2 conversion on a Cu film at 1.2 Torr was interpreted in terms of the recombination of 2H atoms with activation energy $E_d = 54$ kJ mol^{-1}, in a Langmuir film of heat of adsorption $q = 33$ kJ mol^{-1}, independent of coverage (Eley & Rossington 1957), confirmed in essence by uptake measurements (Alexander & Pritchard 1972), and leading to an activation energy for dissociative chemisorption of H_2 molecules of $E_a = E_d - q = 21$ kJ mol^{-1}. Balooch *et al.* (1974*a*, *b*) have interpreted permeation, and molecular beam scattering from single-crystal Cu surfaces, monitored for purity by Auger electron spectroscopy, in terms of this model, and have derived E_a values of 21 kJ mol^{-1} for Cu(100), 21 for Cu(310), 25 for Cu(111), and 8.4 and 12.6 for Cu(110).

Salmeron *et al.* (1977, 1979) in their latest molecular beam $H_2 + D_2$ studies on Pt, have concluded that the L.H. mechanism (1) is operative, and that the high-coordination Pt atom at the bottom of a step offers a site seven times more active than a terrace Pt(111) site. From beam-temperature dependence it appeared that E_a values were less than 1.7 kJ mol^{-1} for both stepped and terrace planes, while from crystal temperature variation $E_a = 0$, $E_d = 54$ kJ mol^{-1} for the stepped Pt(332), and $E_a = 2.1$ or 6.3, $E_d = 59$ kJ mol^{-1} for Pt(111). The latest heat of adsorption for Pt(111) is $q = 68$ kJ mol^{-1} (Norton *et al.* 1982), which fits in quite well. The flow-reactor study at 1.8×10^{-7} Torr by Lu & Rye (1974) gave a fivefold decrease in rate over Pt(110) > Pt(211) > Pt(111) > Pt(100), which is approximately their order of sticking coefficients, and which supports an L.H. mechanism, but not a special activity for steps. Norton & Richards (1974) found that for a Pt wire at 1.3×10^{-5} Torr and 244 K, $\theta_H = 0.5$. They deduced that an L.H. mechanism was operative, but their observation that exchange of D_2 with adsorbed H was only five times slower than $H_2 + D_2$ equilibration at 244 K, and equal rates at 210 K, suggests that an E.R. mechanism was also becoming operative at lower temperatures. We may infer from the experiments above that at 1 Torr and 183–233 K, $\theta_H \approx 1.0$, and for a Pt wire at five temperatures over this range we found an external order of 0.7 ± 0.1, which points strongly to an E.R. mechanism, the order being determined by H_2 molecules in a Van der Waals layer (Breakspere *et al.* 1972). At higher pressures still (400 Torr), Pradier *et al.* (1983) found orders of 0.5 on Pt(110) and Pt(111), corresponding to mechanism (2*a*), since the rate in this case is proportional to $p/p^{\frac{1}{2}}$, where the denominator gives the probability of a bare single site in the nearly complete film of H atoms. On S-poisoned surfaces orders over 1.0 were found. The molecular beam results of Engel & Kuipers (1979) for $H_2 + D_2$ on Pd(111) yielded an L.H. mechanism, which we would also think most probable for a Pd wire at 6 Torr, since McElhiney (1974) found an order of 0.05 for the comparable temperature, corresponding to recombination of H atoms in an almost complete layer. Why Pd and Cu should give L.H. mechanisms at higher pressures, and Pt an E.R. mechanism, is not clear at present.

A further example of E.R. mechanisms at higher pressures is illustrated by

$$^{28}N_2 + {}^{30}N_2 \rightleftharpoons 2\ {}^{14}N^{15}N,$$

the rate of which follows $p^{\frac{1}{2}}$ (i.e. mechanism (2*a*)) on W and Mo wires, and p^1 with low nitrogen atom coverages on Re wires, where mechanism (1) operates. The difference in mechanisms was supported by calculations of the frequency factors (Eley & Russell 1974). As a last example, if we consider the catalyst GdH_2, for $T < T_c = 454$ K, there is a population of interstitial H, H_i, in octahedral holes in bulk and in the surface, $\square_S$, which has completely evaporated above T_c. Nevertheless, in both régimes the $H_2 + D_2$ reaction has an order near unity, so we have assigned mechanisms (Eley & Needham 1984)

$$T < T_c,\ D_2 + H_i\square_s \rightarrow (D_2H_i)\square_s \rightarrow \square_s D_i + HD \quad \text{(E.R.)},$$

$$T > T_c,\ \tfrac{1}{2}D_2 + \tfrac{1}{2}H_2 + 2\square_s \rightarrow (D_i\,\square_s)\ (H_i\,\square_s) \rightarrow 2\,\square_2 + HD \quad \text{(L.H.)}.$$

Considering the kinetics of hydrogenation of ethylene at *ca* 293 K, metals like Ni (Eley 1955) and Pd (Podmore 1974) typically have rates proportional to $p^1_{H_2} p^0_{Et}$, while Pt is untypical, with $p^1_{H_2} p^{-0.4}_{Et}$ on average (Bond 1962). We expect the composition of the chemisorbed film to depend on the order of admission of the reactants, the concentration ratio of reactants, nature of the metal, temperature, etc. It is, therefore, dangerous to generalize on mechanism. Originally the formation of an ethylidene film on Ni, $Ni{=}CH{-}CH_3$, was predicted by simple bond-energy calculations (Eley 1955). Application of the same method to ethylidyne, $Ni{\equiv}C{-}CH_3$, would suggest this is even more stable, and similarly for Pt. However, we should expect at first sight that H atom transfer through an ethylidyne film to weakly adsorbed ethylene would result in $p^0_{H_2} p^1_{Et}$ kinetics, different from those observed for Pt. Incidentally, such kinetics has been observed for Ag, or Au, promoted by alkali metals (Hayashi *et al.* 1977), where H atom diffusion to weakly adsorbed ethylene may well be involved.

Professor Yates's dramatic demonstration of the electron population of the $2\pi^*$ orbital of chemisorbed CO brings important confirmation of the Blyholder model. His discussion of the way an adsorbed S neighbour may influence chemisorbed CO must be of importance in explaining effects on catalytic action. For example, I would cite the recent demonstration (Pradier *et al.* 1983) that adsorption of S up to $\theta_S = 0.1$ on Pt(111) actually promotes the rate of $H_2 + D_2$ by a factor three, before poisoning the reaction at higher coverages.

In summary, demonstrations of subsurface O, the important effects of steps in activating diatomic molecules, especially N_2 in ammonia synthesis, and lateral interactions, both electrostatic and electron-transfer, have all been brought to reality by electron spectroscopy.

In so far as a catalytic process requires a low activation energy, we are concerned with the valencies binding the activated complex to the catalyst. In Taylor's active-site model, he had in mind metal atoms in low-coordination positions on edges and corners, exposing two or more 'dangling bonds', in place of the conventional single dangling bond of the Langmuir terrace site (Taylor 1925). Professor Somorjai's concept of high-coordination atoms with a high density of electron–hole states clearly differs from the Taylor picture. It does, however, seem to be on an evolutionary ladder from the 'd-band holes' theory considered at the memorable Faraday Discussion on heterogeneous catalysis in 1950. Originally, the d-vacancies were considered delocalized over, for example, a PdAu alloy, but the modern tendency has been to follow the considerations advanced by Dowden (1972) and localize the d-vacancies on Pd_9 ensembles (Eley & Moore 1981). There is also an obvious link between the language of electron–hole states, and that of the 'local density of states' used by Professor Yates.

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