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Ethylene Oxide Isomerisation on Single-Crystal Ag(111) in Atomically Clean and Cs-Moderated Conditions

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The isomerisation of ethylene oxide to acetaldehyde has been investigated over a single crystal Ag(111) surface between 300 and 500 K and at pressures of up to 2 Torr. It is found that the nature of the rate-determining step changes at ~410 K; at lower temperatures the rate of isomerisation of the adsorbed reactant is rate limiting, at higher temperatures the rate of adsorption becomes rate controlling. There is qualitative and quantitative agreement between the high-pressure reaction rate data and the measured adsorption/desorption properties of the reactant and product molecules. The rate parameters and reaction order are in satisfactory agreement with data obtained for conventional supported Ag catalysts indicating that it is indeed a metal-catalysed reaction which determines the isomerisation behaviour of such materials. The promoter and moderator actions of dissolved oxygen and preadsorbed Cs are characterised and a model for the observed behaviour is presented.

INTRODUCTION

In the selective oxidation of ethylene over silver catalysts, the further oxidation of the product, ethylene oxide, is a process which may act to decrease the overall selectivity of the reaction. Ethylene oxide can be oxidised to CO_2 + H_2O over supported Ag catalysts (*1*, *2*) at a rate which is lower than that observed for CO_2 formation during ethylene oxidation (*3*), and Ide *et al.* have suggested that the isomerisation of ethylene oxide to acetaldehyde is rate determining in the oxidation of ethylene oxide (*4*). However, this is disputed by Kenson and Lapkin (*5*) who concluded that it is the rate of adsorption of ethylene oxide which is rate determining in the oxidation reaction. Other workers have shown (*6*, *7*) that ethylene oxide isomerisation can occur on the catalyst support.

We have already reported on the results of a single-crystal investigation of ethylene epoxidation over pure Ag (*8*). Among other things, this work showed that *metal*-catalysed oxidation of ethylene oxide does occur. The present paper deals with ethylene oxide isomerisation over single-crystal Ag(111), the reaction which is thought to be the first step in the further oxidation of ethylene oxide (*4*, *5*). It is shown that adsorption of the reactant is not always rate determining and we have also investigated the effect on the isomerisation reaction of Cs (a known selectivity promoter for ethylene epoxidation) and of dissolved oxygen.

METHODS

The apparatus consisted of an ultrahigh vacuum (UHV) chamber coupled directly to a high-pressure reactor cell. The UHV chamber was equipped with the usual facilities for LEED/Auger analysis and Ar^+ etching. It also contained a computer-controlled quadrupole mass spectrometer which could *simultaneously* record TPR spectra from up to eight different ion signals. These multimass TPR spectra greatly increased the reliability of the experimental data. The specimen could be rapidly transferred between the UHV chamber and a 75-ml reactor via a special gate valve; reactant

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and product partial pressures and their time dependence were monitored by a second quadrupole mass spectrometer sampling through a variable leak valve. Transfer time in the reverse direction from ~10 to 10^{-9} Torr was typically 1 min. The orientation, cutting, and polishing of the Ag(111) specimen followed standard methods. Cs dosing was carried out with a thermal evaporation source (SAES Getters). An absolute calibration for Cs coverage was obtained by measuring the total charge leaving the specimen as Cs^+ under desorption conditions which led to positive surface ionisation (*10*). The quoted fractional coverages of Cs and ethylene oxide are referred to the number density of silver atoms in the Ag(111) surface.

RESULTS

Ethylene oxide adsorption and isomerisation experiments were carried out on a silver surface which was active for the selective oxidation of ethylene (*8*); the active surface was generated by conditioning the specimen for ≈1 h at 425 K in a 6 : 1 mixture of oxygen and ethylene at 10 Torr. Residual adsorbed oxygen was removed by heating the crystal to ≈650 K after evacuation and prior to Auger examination. In this condition the specimen contained a significant amount of subsurface or dissolved oxygen (O(d)) which gave rise to a large O(KLL) Auger signal. The intensity ratio O(KLL)/Ag(351 eV MNN) was typically 0.03–0.05 (cf. ≈0.02 for an oxygen-saturated surface in the *absence* of dissolved oxygen).

Temperature-Programmed Desorption Studies

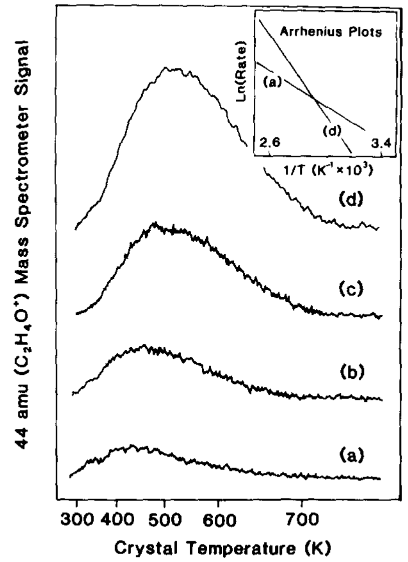


FIG. 1. C_2H_4O thermal desorption spectra from the active Ag(111) surface. (a)–(d) Exposures of 0.6, 2.4, 4.8, and 10 × 10^7 L, respectively. Inset shows Arrhenius plots taken from low- and high-coverage data. Heating rate 13 K s^{-1}.

At 298 K ethylene oxide chemisorbed on this active surface with a very low sticking probability, an exposure of ~10^9 L (1 L = 10^{-6} Torr sec) being required to saturate the surface. Subsequent 44-a.m.u. ($C_2H_4O^+$) temperature-programmed desorption spectra exhibited a single peak whose behaviour indicated the occurrence of a desorption reaction with complex kinetics. The peak temperature increased from ~426 K at low coverage to ~500 K at saturation (Fig. 1). Arrhenius plots taken from the leading edges of these traces (effectively constant coverage) yield values of 20 ± 5 and 37 ± 5 kJ/mol for the activation energies to desorption at low coverage and at saturation coverage, respectively. The larger value is in agreement with the value of 37.8 kJ/mol which has been reported for the saturated Ag(110) surface (*9*). In our experiments, no signals were detected at 28 a.m.u. (CO^+, $C_2H_4^+$) or 27 a.m.u. ($C_2H_3^+$), indicating the absence of catalytic decomposition to C_2H_4 and CO or CO_2. However, fragment ion signals at 43, 42, and 29 a.m.u. were observed whose desorption spectra mirrored the 44-a.m.u. spectra. These ions are characteristic of both ethylene oxide and acetaldehyde, so that control experiments were performed in order to establish whether significant isomerisation of ethylene oxide occurred during chemisorption and the subsequent temperature sweep. Multimass desorption spectra for adsorbed ethylene

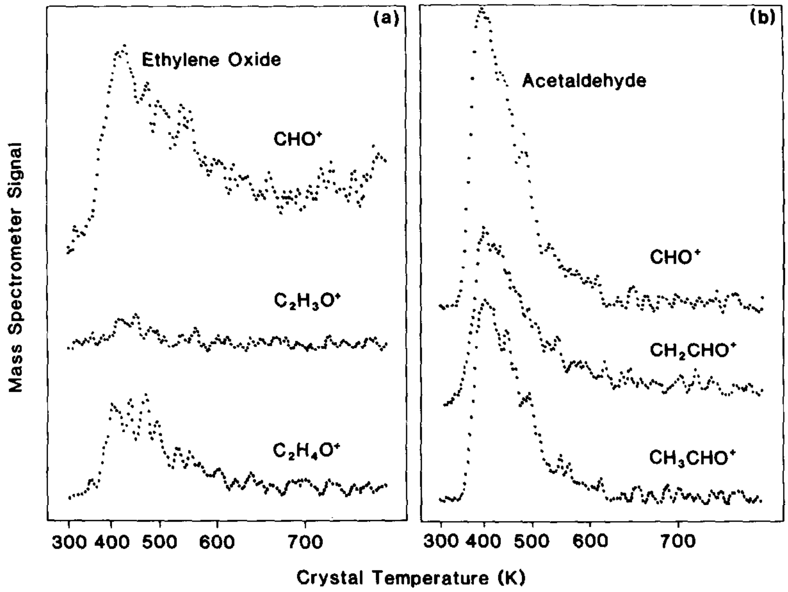


FIG. 2. Multimass thermal desorption spectra from the active surface. (a) Following exposure to 3.6 × 10^7 L *ethylene oxide*, (b) following exposure to 0.9 × 10^7 L *acetaldehyde*. Heating rate 13 K s^{-1}.

oxide and acetaldehyde were recorded (Figs. 2a,b) and the derived fragmentation patterns were compared with the mass spectra of gaseous C_2H_4O and CH_3CHO measured in the same apparatus under the same conditions. The results (Table 1) show that under our conditions both ethylene oxide and acetaldehyde adsorb and desorb without decomposition. Ethylene oxide uptake curves derived from the 44-a.m.u. desorption spectra are shown in Fig. 3 for adsorption on the active surface both in the absence and presence of Cs. The surface concentration of Cs was 1.2 ± 0.1 × 10^{14} atoms cm^{-2} (~0.08 monolayers); this alkali coverage was chosen because it corresponds to the point of maximum promotion of ethylene epoxidation by Cs (*10*). It can be seen that Cs causes some increase in the initial rate of ethylene oxide adsorption; no other changes in the adsorption/desorption behaviour were observed.

TABLE 1

Mass Spectrometer Fragmentation Patterns

Mass (a.m.u.)	C_2H_4O		CH_3CHO	
	Gas phase	TDS	Gas phase	TDS
44	100	100	100	100
43	32	28	66	70
29	200	190	263	250

Note. Gas-phase spectra recorded at 10^{-9} Torr.

Batch Reactor Studies

The isomerisation of ethylene oxide to

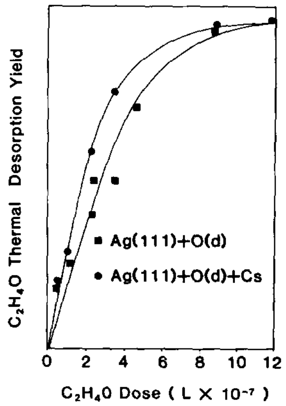


FIG. 3. Uptake of ethylene oxide on active Ag(111) in the absence and in the presence of preadsorbed Cs (θ = 0.08).

acetaldehyde was investigated at a pressure of 1 Torr over the temperature range 300–500 K working at conversion levels of ≤15%. The reaction was monitored by following the 29-a.m.u. signal (CHO^+) which increases by 16% upon complete conversion to acetaldehyde. At no stage were any signals observed other than those characteristic of C_2H_4O and CH_3CHO. A number of control experiments were performed in order to ascertain the importance of any contributions to the isomerisation rate from the tantalum crystal support wires.

(1) The rate of isomerisation was obtained under two different heating regimes: (a) Steady resistive heating by a current of ~10 A; under these conditions the support wires were at approximately the same temperature as the silver crystal. (b) Pulse resistive heating, controlled by a computer, with a current pulse of ~23 A and a frequency of ~0.3 Hz. In this case the support wires attained temperatures much greater than the single crystal. The rate of isomerisation was independent of the method employed to heat the crystal.

(2) A cleaned tantalum wire of the same dimensions as those used to support the crystal was inserted into the pressure cell and exposed to the same experimental conditions as the single crystal. No reaction was detectable until the wire was at a temperature of ≥570 K when a *fall* in the intensity of the 29-a.m.u. signal was observed with a corresponding increase in intensity at 28, 27, and 26 a.m.u., fragments characteristic of C_2H_4. The increase in 28-a.m.u. intensity was greater than could be accounted for purely on the grounds of C_2H_4 formation, i.e., CO or CO_2 was also produced. At 700 K the rate of formation of C_2H_4 was $1.5 \pm 0.5 \times 10^{16}$ molecules s^{-1} cm^{-2} with an activation energy of 112 ± 4 kJ/mol and a preexponential factor of $\sim 6 \times 10^{23}$ s^{-1}. From these values it can be calculated that the rate of decomposition of ethylene oxide by the specimen supports at 400 K is immeasurably small; it is many orders of magnitude smaller than the observed isomerisation rates induced by the Ag specimen.

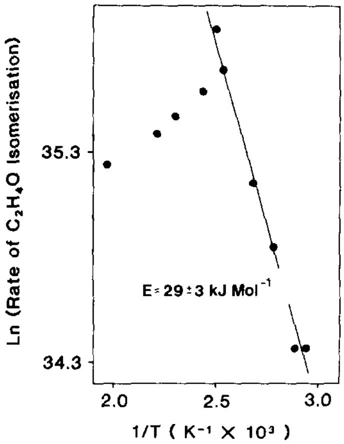


FIG. 4. Arrhenius plot for the isomerisation reaction on active Ag(111) at 1.0 Torr.

An Arrhenius plot of the single-crystal isomerisation rate data is shown in Fig. 4. A straight line corresponding to an activation energy of 29 ± 3 kJ/mol is obtained for reaction temperatures below ~410 K. Above this temperature the rate of isomerisation decreases with an apparent negative activation energy of 10 ± 3 kJ/mol. At 400 K, between 0.5 and 2.0 Torr, the pressure dependence of the isomerisation rate showed that the reaction was first order in ethylene oxide.

The effect of Cs was investigated by predosing the crystal surface with cesium from an evaporation source (SAES Getters). Control experiments showed that there was no subsequent loss of alkali from the surface under the conditions of the isomerisation reaction. Auger spectroscopy was used to monitor the relative concentration of surface Cs, and Fig. 5 shows the dependence of the isomerisation rate on alkali coverage. It can be seen that Cs markedly inhibits the reaction, a fourfold reduction in rate resulting from an alkali precoverage of ~0.1 monolayers. The Arrhenius rate parameters for the Cs-inhibited isomerisation at this alkali loading are 26 ± 4 kJ/mol and $\sim 3 \times 10^{19}$ s^{-1}. It was also found that subsurface

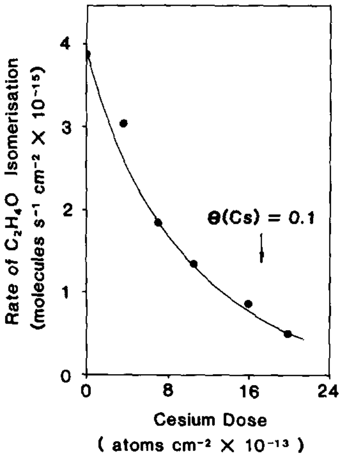


FIG. 5. Cs inhibition of the isomerisation rate at 1.0 Torr and 400 K.

oxygen substantially *accelerated* the isomerisation rate on the alkali-free surface. Typical results at 400 K and 1 Torr for three different surface conditions are summarised in Table 2.

DISCUSSION

The data in Fig. 3 can be used to obtain a value for the sticking probability of ethylene oxide provided that an estimate of the saturation coverage is available. Using the values obtained by Allen and Scaife (*11*) for the molecular cross-sectional area (18.9–30.1 Å^2) suggests that the fractional surface coverage at monolayer completion is ~0.36. This in turn leads to an initial adsorption rate on the alkali-free surface at 300 K and 1 Torr of ~7 × 10^{14} molecules s^{-1} cm^{-2}; the corresponding initial sticking probability is ~2.3 × 10^{-8}.

The coverage dependence of the ethylene oxide desorption spectra (Fig. 1) suggests that there are marked attractive lateral interactions between the adsorbed molecules, possibly due to intermolecular hydrogen bonding. This would lead to adsorbate island formation at low coverages. Desorption could then occur from within the islands (with a coverage-dependent activation energy) or from a dispersed phase in dynamic equilibrium with the islands (with fractional-order desorption kinetics); both possibilities would result in the observed shift of the desorption peak to higher temperatures with increasing coverage. The existence of such attractive lateral interactions is in keeping with the observation that ethylene oxide dimer formation occurs on oxidised silver foil at 520 K (*1*) and with the reported increase in adsorption enthalpy with increasing coverage (*11*). The desorption peak widths may reflect the effect of a significant lifetime for the precursor state to desorption. Under conditions similar to those of the present work, Kenson and Lapkin (*5*) obtained a heat of adsorption of ~13 kJ/mol at 550 K, i.e., in the low coverage limit. Combining this value with our own estimate of the activation energy to desorption leads to a value of 7 ± 5 kJ/mol for the activation energy to *adsorption* in the low coverage limit.

Preadsorbed atomic oxygen markedly increases the uptake of ethylene oxide by Ag(110) (*9*). Similar oxygen-induced adsorption on Ag has been observed for CH_2O (*12*) and CH_3CHO (*13*); the effect is understandable in terms of a "soft" acid/base interaction (*14–16*) between the oxygen atom of the organic molecule and an oxygen-induced $Ag^{\delta+}$ site. In the present case these $Ag^{\delta+}$ sites must have been created by the dissolved oxygen, because adsorbed oxygen was absent. This type of bonding mechanism is consistent with the UP spectrum of ethylene oxide adsorbed on the nonpolar

TABLE 2

Dependence of Isomerisation Rate on Condition of Surface

Surface condition	Rate of CH_3CHO formation (molecules s^{-1} cm^{-2})
Low O(d) Auger ratio = 0.002	0.8 × 10^{15}
High O(d) Auger ratio = 0.02	4.3 × 10^{15}
O(d) + Cs^a	0.9 × 10^{15}

[a] 1.7 × 10^{14} atoms cm^{-2}.

(11$\bar{2}$0) face of ZnO (*17*) and with the decrease in work function which accompanies C_2H_4O adsorption on Ag (*18*).

The apparent positive effect exerted by Cs on the rate of adsorption might in principle be explained by invoking a concomitant decrease in the activation energy to adsorption. However, this explanation does not seem acceptable in view of the likely bonding mechanism for adsorbed ethylene which was discussed above. An alternative possibility is that Cs leads to some accumulation of surface oxygen via the reaction

$$C_2H_4O(g) \rightarrow C_2H_4 + O(a)$$

and this oxygen could then enhance the effective number of $Ag^{\delta+}$ sites. Such a reaction has been observed on some Ag catalysts (*3, 5*) and similar behaviour seems to occur on Fe, Co, and Ni (*19, 20*). Whatever the origin of this effect of Cs, the most important conclusion is drawn by comparing the data in Fig. 3 with those in Fig. 5; Cs may exert some positive influence on the rate of adsorption; it has a very strong *negative* effect on the rate of isomerisation. It therefore seems reasonable to conclude that adsorption is *not* rate determining for the isomerisation reaction under these conditions.

The observed reaction order and the reaction rates for ethylene oxide isomerisation on the Ag(111) surface are in good agreement with the corresponding quantities measured for conventional supported Ag catalysts (*2*). The single-crystal value for the apparent activation energy lies somewhat lower (29 kJ/mol) than the range reported for supported catalysts (41–75 kJ/mol) (*2, 4, 5*), but this range is itself rather wide. On balance, it seems likely that the isomerisation behaviour of these practical catalysts is dominated by the metal component rather than the support.

A general reaction scheme for the reaction may be written as

$$C_2H_4O(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C_2H_4O(a)$$

$$C_2H_4O(a) \xrightarrow{k_2} CH_3CHO(a)$$

$$CH_3CHO(a) \xrightarrow{k_3} CH_3CHO(g)$$

As already mentioned, our data for the Cs-moderated reaction seem to rule out Kenson and Lapkin's suggestion (*5*) that step 1 is rate determining in the high coverage limit, i.e., at ≤410 K. If we take the alternative view (*4*) that step 2 is rate determining under these conditions, then the rate of acetaldehyde formation is given by

$$\text{Rate} = (k_2k_1/k_{-1})P(\text{EO}),$$

where $P(\text{EO})$ = ethylene oxide pressure. (Step 3 is unlikely to be rate limiting since CH_3CHO desorption is actually faster than C_2H_4O desorption at a given temperature (Figs. 1,2b).) The observed apparent activation energy is related to the activation energies of the individual reactions by

$$E_{\text{obs}} = E_1 - E_{-1} + E_2.$$

In the high coverage regime, the thermal desorption data yield $E_{-1} = 37 \pm 5$ kJ/mol; assuming the activation energy to adsorption to be independent of coverage leads to a value for E_2 of 59 ± 13 kJ/mol for the true activation energy of the isomerisation step 2. At a sufficiently high temperature (~410 K) k_{-1} dominates, and the adsorption step becomes rate limiting; this is the view adopted by Kenson and Lapkin. The rate expression for isomerisation is then

$$\text{Rate} = (k_1/k_{-1})P(\text{EO})$$

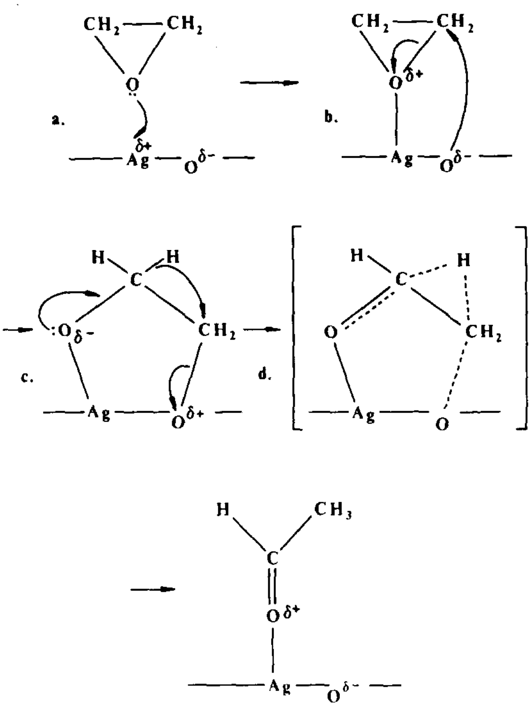
with an observed activation energy

$$E_{\text{obs}} = E_1 - E_{-1}.$$

Here we are operating in the low coverage regime with $E_{-1} = 20 \pm 5$ kJ/mol and $E_1 = 7 \pm 5$ kJ/mol. Substituting these values into the above expression for E_{obs} yields a value of -13 kJ/mol in good agreement with the experimental value of -10 ± 3 kJ/mol (Fig. 4).

The critical temperature of ~410 K (onset of negative apparent activation energy) correlates quite well with the temperature at which ethylene oxide desorption becomes fast at low coverages. There is thus both quantitative and qualitative accord between the low-pressure thermal desorption results for the reactant and product species and the observed reactive behaviour in the high-pressure batch reactor.

It is of interest to consider further the details of the reaction pathway by which the crucial isomerisation step occurs; the roles of dissolved oxygen and surface Cs in respectively enhancing and suppressing the isomerisation rate are of particular significance here. A possible mechanism might be as follows



(a) Adsorption of C_2H_4O at a "soft" $Ag^{\delta+}$ site is induced by electron withdrawal from neighbouring O(d); the epoxide ring is now activated towards nucleophilic attack at the carbon centres. This step is written by analogy with Brønsted acid-catalysed epoxide ring-opening reactions in solution (*21*). The lowest unoccupied molecular orbital of C_2H_4O will lie at a lower energy than in the gaseous molecule because of orbital relaxation following adsorption (*17*) and the polar nature of the adsorbed species. Attack by a hard nucleophile (i.e., with a relatively tightly bound highest occupied orbital) will therefore be favoured (*16*).

(b) Nucleophilic attack by O(d), a relatively hard nucleophile, now occurs.

(c) Epoxide ring opening is followed by a 1,2-hydride shift (*21*); this is driven by the lone pair of electrons on the epoxide oxygen and the ability of O(d) to act as a good "leaving group."

(d) The transition state for a concerted process has been drawn, but the reaction might equally well proceed in a stepwise fashion initiated by cleavage of the C–O bond on the right.

A merit of this model is that it accounts for the marked effect of O(d) in accelerating the isomerisation rate; this is the species which is postulated to initiate the ring-opening sequence. The mechanism can also be used to rationalise the moderating effect of adsorbed Cs. Cesium adsorption will lead to considerable charge transfer to the solid (*22*); much of this transferred charge is likely to reside on the electronegative oxygen, thereby raising the energy of the highest occupied orbital and making the oxygen a "softer" nucleophile. This in turn can reduce the rate of reaction (b). Such frontier orbital effects are known to operate for organic chemical reactions in solution; relatively small changes in the energies of frontier orbitals can induce large changes in the reaction rate (*16*).

CONCLUSIONS

Ethylene oxide isomerises on oxygen-containing Ag surfaces which are active for ethylene epoxidation; a reduction in the level of dissolved oxygen markedly inhibits the isomerisation rate. Preadsorbed Cs also strongly suppressed the isomerisation rate, although under the same conditions it exerts a small positive influence on the rate of C_2H_4O adsorption. These observations rule out the possibility that adsorption of the reactant is always rate limiting. A self-consistent analysis of the desorption and reaction rate data suggests that the nature of the rate-determining step changes at ~410 K. Below this temperature, isomerisation of the adsorbed molecule is rate determining; above it, the adsorption becomes rate limiting. The promoter and moderator effects of O(d) and Cs(a), respectively, can be understood in terms of a frontier orbital argument.

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