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Secondary Chemistry in the Selective Oxidation of Ethylene: Effect of Cl and Cs Promoters on the Adsorption, Isomerisation, and Combustion of Ethylene Oxide on Ag(111)

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The adsorption/desorption, isomerisation, and combustion of ethylene oxide on single crystal Ag(111) have been studied under conditions which are pertinent to ethylene epoxidation. The effects of chlorine on the uptake and isomerisation of ethylene oxide are examined, as is the effect of Cs on the burning reaction. These data complement our earlier results and suggest that the observed promoter effects are largely electronic in origin. CO_2 strongly inhibits the combustion reaction, apparently by converting chemisorbed oxygen to a carbonate species. © 1987 Academic Press, Inc.

INTRODUCTION

The further conversion of ethylene oxide (EO) by isomerisation and burning is a process which significantly reduces the overall selectivity of Ag/α-Al_2O_3 ethylene epoxidation catalysts. Nevertheless, relatively little work has been carried out in this area of secondary chemistry. Allen and Scaife (*1*) found that EO adsorbed on Ag_2O both in a nonactivated and also in an activated manner, the latter process having an activation energy of 95 kJ/mol. On clean Ag(110), Backx *et al.* (*2*) carried out the adsorption at 110 K and found a weakly bound species which desorbed below room temperature. On the oxygen-precovered surface, they observed that the EO saturation coverage was enhanced and evidence was found for the existence of two distinct adsorbed states, one of which was induced to form by preadsorbed surface oxygen. These species, however, were relatively weakly bound as the activation energies for desorption were less than 53 kJ/mol. More recently, we reported the results from EO adsorption experiments performed on clean and Cs-precovered Ag(111) in which dosing pressures of ~1 Torr were employed (*3*). EO was found to adsorb reversibly without undergoing any surface reactions, and it desorbed in a broad peak with a peak maximum ranging between 426 and 500 K.

In the gas phase, EO is known to undergo an isomerisation reaction at 673 K to form acetaldehyde (*4*). The isomerisation reaction is rapid on a silver catalyst and has been shown to be the first step in the further combustion of EO to CO_2 (*3, 5, 6*). Although Kenson and Lapkin (*5*) have argued that EO adsorption is rate limiting in the isomerisation reaction, we have reported that this is only the case at elevated temperatures; for temperatures ≤410 K, the ring-opening step, yielding $CH_3CHO(a)$ from EO(a), was found to be rate determining (*3*). There is general agreement, however, that the rate of isomerisation displays first-order kinetics with respect to EO pressure (*3, 5*). In addition, work done in this laboratory and elsewhere has shown that Cs and Ba substantially decrease the rate of isomerisation (*3, 7*).

That EO can be further oxidised to CO_2 via acetaldehyde on a silver catalyst has been demonstrated by many workers (*3, 5,*

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6, 8–11). In addition, many have argued that since the observed rate of acetaldehyde combustion is greater than that of EO under similar conditions, EO isomerisation to acetaldehyde must be the rate-limiting step in its further combustion to CO_2 (*6, 9*). While much work has been published to show that the rate of EO combustion displays first-order kinetics with respect to EO pressure and zeroth-order kinetics with respect to oxygen pressure (*5, 6, 8, 12*), Stoukides and Vayenas (*8*) have shown that the kinetic order with respect to EO pressure is variable and dependent on the reaction temperature. Mikami *et al.* (*13*) have shown that the reaction is poisoned by the presence of CO_2.

Most of the work reported so far has been carried out on supported Ag so that observations refer to the combined effects of the metal and support phases. Vaabil *et al.* (*14*) have shown that the support can induce EO isomerisation, and it is known that burning of EO to CO_2 can occur over α-alumina (*15*). It would obviously be desirable to elucidate the role of Ag itself in this secondary chemistry, and we have already investigated the isomerisation of EO on single crystal Ag(111), both in the presence and absence of Cs (*3*). Likewise, we have described the overall effects of Cl and Cs in the oxidation of ethylene itself over Ag(111) (*16, 17*). The possible role of these important promoters in the further conversion, including burning, of ethylene oxide remains a virtually unexplored field. The present paper seeks to address the question of promoter effects on the secondary chemistry of EO over Ag(111) in the absence of any support material. It is found that Ag-catalyzed EO burning is a significant process and that Cl, Cs, and CO_2 can substantially affect the kinetics of the reaction.

METHODS

The ultrahigh vacuum/pressure cell-batch reactor apparatus used in this work has already been described (*16–18*). While surface characterisation of the single crystal wafer was performed by LEED/Auger analysis in ultrahigh vacuum, gas dosing of the specimen was achieved by translating the crystal to a pressure cell where dosing pressures of ~2 Torr were employed. In addition, TPD and TPR studies could be performed by returning the specimen to the UHV chamber after gas dosing. During the kinetic studies, the specimen was retained in the pressure cell which was filled with the appropriate gas mixture and operated as a differential batch reactor. To investigate the isomerisation of EO to acetaldehyde, the intensity of the 29 amu CHO^+ mass fragment of C_2H_4O/CH_3CHO was monitored as a function of time at a constant temperature. Upon complete isomerisation, this signal was found to increase by 41% as determined by separately calibrating the mass spectrometer with EO and acetaldehyde. EO combustion was similarly investigated by monitoring the variation in the intensity of the 44 amu mass spectrometer signal with time. Although both EO and CO_2 give rise to a 44 amu signal, separate calibrations showed that this latter signal increased by 220% after all the EO had been converted to CO_2. At the end of the reaction, the pressure cell could be rapidly evacuated and the specimen transferred back to the UHV chamber where TPD studies were carried out; the transfer from 10–10^{-9} Torr could typically be achieved within 60 s. An SAES getter filament was employed for Cs dosing while Cl dosing was achieved through an AgCl electrolysis cell as described earlier (*17*); the latter allowed *in situ* production of a molecular beam of Cl_2 gas in the UHV chamber. All exposures are quoted in Langmuirs (1 Langmuir = 1 L = 10^{-6} Torr s).

The specimen itself was a 99.999% purity (111)-oriented Ag wafer with a high face : edge ratio of 7 : 1. Furthermore, the specimen manipulator permitted preparation, examination, and dosing of both (111) crystal faces so that structural and chemical characterisation of the entire active surface area could be carried out. Research grade ethylene oxide and oxygen, of purity >99.7%, were used throughout the work.

As reported in earlier papers (*17*, *18*) and in agreement with the results of other workers (*19*) a minimum level of subsurface oxygen appears to be necessary for Ag to act as a selective oxidation catalyst towards ethylene. Accordingly, the experiments reported below were carried out in the presence of an appropriate stable level of subsurface oxygen characterised by an Auger intensity ratio O(515 eV)/Ag(356 eV) of 4%. Such a surface has previously been shown to be active for the selective oxidation of ethylene to EO and is therefore the pertinent system for present purposes. This surface, bearing some dissolved oxygen but no *chemisorbed* oxygen, will be referred to as the "clean surface."

RESULTS

Ethylene Oxide Uptake in the Absence and Presence of Cl

The clean crystal was dosed at room temperature with varying exposures of EO at a pressure of 2 Torr, and the uptake of the latter followed by TPD, monitoring the 29 amu CHO^+ fragmentation peak. Figure 1 shows that the sticking probability of EO on Ag(111) is low, as a relatively high exposure of 12 × 10^7 L was required to saturate the surface. As we reported earlier (*3*), the desorption peaks were observed to be very broad, centred around 400 K at low exposures, then further broadening and displaying an apparent shift in peak maximum as the exposure increased (Fig. 2). When the crystal (previously exposed to a saturation dose of EO) was allowed to remain in UHV for some minutes before the temperature sweep was performed, the resulting TPD spectrum revealed that the broad peaks observed in Fig. 2 apparently consist of two poorly resolved peaks at ~400 and ~573 K (Fig. 3). These broad desorption spectra reflect specific properties of EO and are not a general characteristic of the apparatus or technique (compare the "normal" O_2 spectra presented later in Fig. 10). We will re-

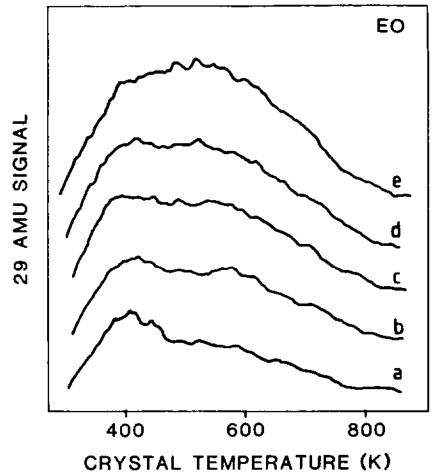


FIG. 2. Temperature-programmed desorption of EO as a function of exposure at 300 K. (a)–(e) refer to exposures of 1, 3, 5, 6, and 12 × 10^7 L, respectively.

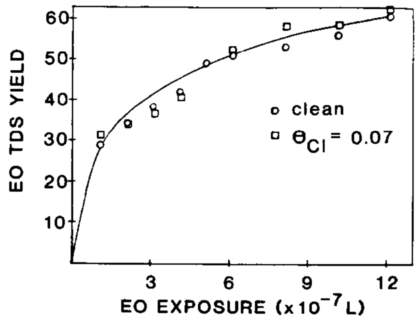


FIG. 1. EO uptake on Ag(111) at 300 K in the presence and absence of preadsorbed chlorine. Dosing pressure 2 Torr.

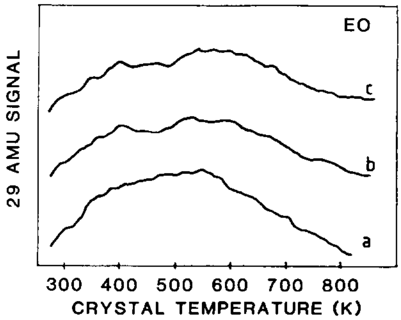


FIG. 3. Temperature-programmed desorption of EO as a function of standing time in ultrahigh vacuo. (a)–(c) refer to 0, 5, and 10 min, respectively.

turn to this point in the Discussion; note however in Fig. 2 that as a function of EO exposure, the more weakly bound state of EO appears first, while the data of Fig. 3 suggest that at relatively high EO surface coverages, at least two distinct EO adsorbed species are present on the crystal. The lower temperature state seems to be relatively more unstable in UHV as its thermal desorption yield decreases more rapidly than that of the higher temperature state, allowing the two to be resolved after the crystal had been left for some time in UHV. Backx *et al.* (*2*) have also found evidence for the existence of two adsorption states of EO on Ag(110); their adsorption experiments were conducted at very low temperatures on the oxygen-free crystal and the two EO(a) species were found to desorb below room temperature. That the lower temperature state observed here can be "pumped away" is therefore not surprising in view of the expected weakness of the Ag–EO(a) bond. Control experiments were performed to show that these desorbing EO species observed did not arise from adsorption on the crystal support rods and heating wires. It was further verified that under these conditions, EO adsorbed and desorbed reversibly on the Ag(111) surface; detailed mass spectrometric TPD measurements revealed that the only detectable fragment ions were ascribable to EO in good quantitative agreement with the fragmentation pattern of the gaseous molecule.

On a surface predosed with 0.07 monolayers of chlorine, the EO uptake curve was seen to be essentially identical to that on the clean surface (Fig. 1), indicating that Cl(a) does not significantly affect either the sticking probability or the maximum uptake of EO. Furthermore, when varying coverages of chlorine were preadsorbed on the surface prior to saturating the crystal with EO, no change in the thermal desorption yield was observed even with a Cl(a) precoverage of $\theta_{Cl} = 0.45$. (A monolayer of Cl(a) on Ag(111) corresponds to $\theta_{Cl} = 0.5$ (*17*).) This indicates that Cl(a) does not block EO adsorption; Auger spectroscopy also showed that Cl(a) was not displaced after EO adsorption. When the experiment was performed in the reverse sequence, i.e., when the crystal was first saturated with EO prior to exposure to chlorine, the Cl uptake curve on the EO-covered surface saturated at a lower Cl(a) coverage as measured by Auger spectroscopy (Fig. 4). This observation was confirmed by repeating the chlorine uptake experiment on both the clean and EO saturated surfaces, monitoring the Cl(a) coverage through the 35 amu Cl^+ TPD yield: the saturation Cl(a) uptake on clean Ag(111) was once again found to be greater than that on the EO presaturated crystal, as previously observed by AES. Furthermore, the thermal desorption yield of EO after chlorine adsorption showed no change, even after a relatively large chlorine exposure of 6 L ($\theta_{Cl} = 0.5$). Thus, it would appear that although Cl(a) does not block EO adsorption at all, a surface presaturated with EO is able to subsequently adsorb less Cl as compared to the clean crystal. It is also evident that adsorbed EO is not displaced by chlorine.

EO Isomerisation

The rate of EO isomerisation on clean Ag(111) increases linearly with increasing EO pressure, accurately obeying first-order reaction kinetics; Figs. 5a and 5b illustrate data taken at 400 K. For $T \geq 520$ K the rate becomes undetectably small in this pres-

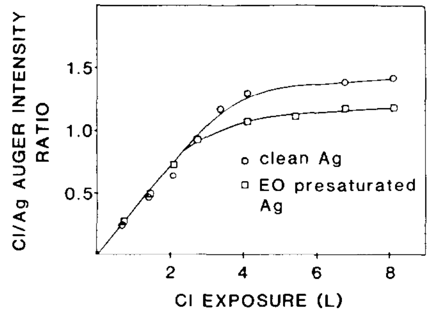


FIG. 4. Chlorine uptake at 300 K on clean and EO-presaturated Ag(111).

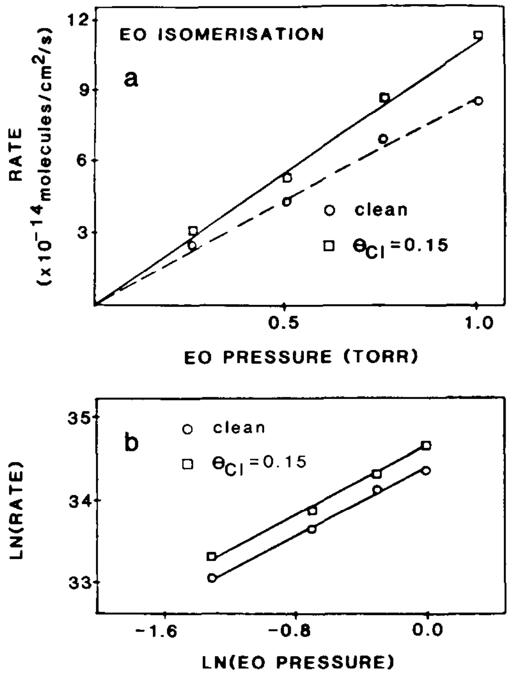


FIG. 5. EO isomerisation at 400 K showing the effect of Cl on rate and kinetic order.

sure regime, indicating that the isomerisation rate is limited by the short surface lifetime of EO under these conditions (*3*, *5*). On a surface predosed with 0.15 monolayers of Cl(a), the isomerisation rate again displays first-order reaction kinetics with respect to EO pressure, but the overall activities are seen to be *higher* as compared to the clean surface (Fig. 5). That Cl(a) accelerates the isomerisation of EO to acetaldehyde is seen more clearly in Fig. 6 which shows that the reaction rate increases as a function of increasing Cl(a) precoverage. We have already reported the related observation that preadsorbed Cs strongly *inhibits* the rate of EO isomerisation (*3*). It thus appears that electropositive and electronegative promoters have opposite effects on this reaction. Control experiments were also performed to ensure that the observed isomerisation did not take place on the Ta crystal support rods and heating wires. Two Ta wires (of the same dimensions as those used to support the crystal) and a thermocouple were inserted into the pressure cell and exposed to 1 Torr of EO. When the Ta wires were heated to temperatures between 350 and 520 K, no EO isomerisation could be detected under these conditions.

EO Combustion

The combustion of 0.5 Torr of EO was carried out with varying pressures of oxygen on the clean surface and the reaction displayed zeroth-order reaction kinetics with respect to oxygen pressure (Fig. 7). In addition, the apparent activation energy for the combustion reaction was found to be constant at 50 kJ/mol as a function of increasing oxygen pressure. With 0.5 Torr of oxygen and increasing pressures of EO, the kinetic order on the clean surface was found to be zero with respect to EO pressure at 507 K, increasing to 0.6 and 0.8 at 543 and 580 K, respectively (Fig. 8). The

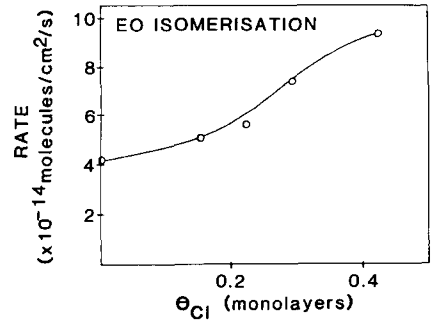


FIG. 6. EO isomerisation at 400 K and 0.5 Torr showing acceleration of rate by preadsorbed chlorine.

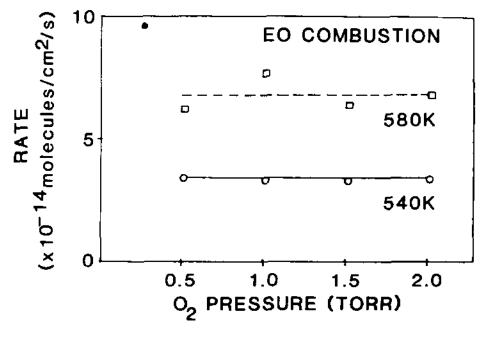


FIG. 7. Combustion of 0.5 Torr EO showing kinetic order in oxygen pressure.

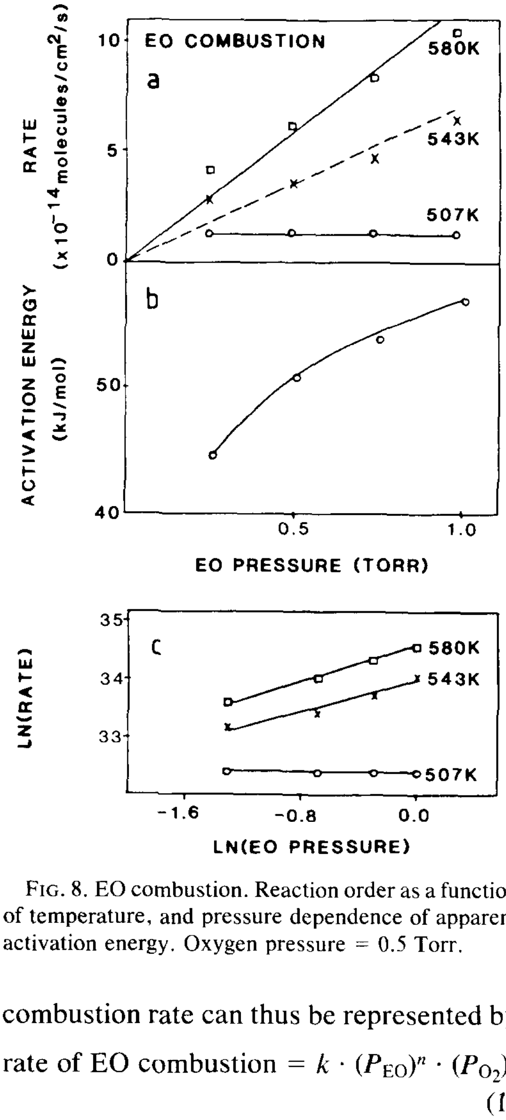


FIG. 8. EO combustion. Reaction order as a function of temperature, and pressure dependence of apparent activation energy. Oxygen pressure = 0.5 Torr.

combustion rate can thus be represented by

$$\text{rate of EO combustion} = k \cdot (P_{\text{EO}})^n \cdot (P_{\text{O}_2})^0 \quad (1)$$

where P_{EO} and P_{O_2} are the respective pressures of EO and O_2; $0 \leq n \leq 0.8$ for the temperature range 507 K $< T <$ 580 K. In addition, the apparent activation energies in the latter experiment (with 0.5 Torr of oxygen and varying EO pressures) increased as a function of increasing EO pressure (Fig. 8). These results show that the measured activation energy for combustion is dependent on the experimental conditions employed and rationalises the large range of activation energies reported in the literature, ranging from 41 to 85 kJ/mol (*5, 6, 8, 9, 20*).

A number of other workers have reported the reaction kinetics to be first order with respect to EO pressure and zeroth order with respect to oxygen pressure (*5, 6, 20*) which is in reasonable agreement with our findings at 580 K. Only one other work quotes evidence for a variable kinetic order in EO pressure with temperature; in broad agreement with the present results, Stoukides and Vayenas (*8*) found that the rate of EO combustion on a zirconia-supported Ag film could be represented by Eq. (1) with $0 \leq n \leq 2$ for the temperature range 593 K $\leq T \leq$ 673 K. It is also to be noted that all the work reported so far for EO combustion has been performed on Ag foils or supported catalysts at very high pressures (*5, 6, 20*). This is the first time that an investigation of this nature has been carried out on a clean, well-characterised single crystal of Ag, and the fact that there is general agreement between the results of this study and those previously published in the literature strongly suggests that EO combustion takes place principally on the Ag metal component and not on the support material of practical high-area catalysts.

The effect of Cs on the rate of EO combustion was investigated by first predosing both faces of the crystal with varying coverages of Cs and then exposing it to a mixture of 0.5 Torr of EO and 0.5 Torr of O_2. From the data presented in Fig. 9, it is evident that Cs retards the rate of EO combustion. This result is not unexpected given

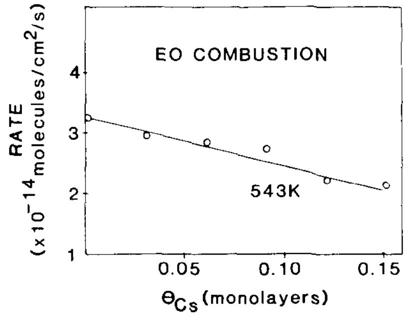


FIG. 9. Retardation of EO combustion rate by preadsorbed caesium.

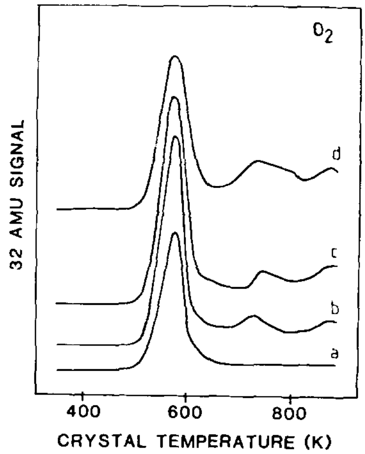


FIG. 10. Postreactor O_2 desorption spectra showing the effect of increasing Cs loading. (A)–(D) refer to θ_{Cs} = 0, 0.04, 0.08, and 0.12, respectively.

that Cs also inhibits EO isomerisation to acetaldehyde (*3*), a process often postulated as the rate-determining step in the combustion of EO to CO_2 (*6, 9*). In addition, postreaction 32 amu O(a) desorption spectra, shown in Fig. 10, display complicated desorption features above 580 K in the presence of high loadings of Cs(a), suggesting that Cs/oxygen complex formation had taken place on the surface (*16, 21*). The activation energy for combustion was also seen to increase on a Cs-precovered surface: for a 1 : 1 mixture of EO : O_2 at a total pressure of 1 Torr, the activation energy for combustion on a clean surface was 50 kJ/mol rising to 72 kJ/mol on a surface preadsorbed with 0.06 monolayers of Cs.

Finally, to investigate the effect of CO_2 poisoning on the combustion of EO in the absence of Cs, varying pressures of CO_2 were added to a reaction mixture consisting of 0.5 Torr of O_2 and 0.5 Torr of EO. Figure 11 shows that the rates of EO combustion decrease monotonically as the initial CO_2 pressure increases; with initial CO_2 pressures which were ≥ 0.2 Torr, the combustion rates at both 543 and 580 K decreased to less than 10^{13} molecules/cm²/s. Also shown in Fig. 11 is the variation in the postreactor O(a) desorption yield with increasing initial CO_2 pressures. These 32 amu yields derive not only from the associative desorption of free O(a) species, but also from O(a) species formed through the decomposition of CO_3(a) in the course of the temperature-programmed sweep.

DISCUSSION

Ethylene Oxide Uptake and Desorption

The data in Fig. 1 show that the clean Ag(111) surface becomes saturated with EO only after extended exposure (~1.2×10^8 L) at 300 K. Assuming that this condition corresponds to full monolayer coverage, published values (*1*) for the cross-sectional area of the adsorbed molecule may be used to estimate an upper limit to the initial sticking probability of ~10^{-8}. Figure 1 also shows that preadsorbed chlorine does not materially affect the sticking probability of EO. At first sight this may appear surprising since it might be expected that $Ag^{\delta+}$ sites created by Cl(a) would lead to an en-

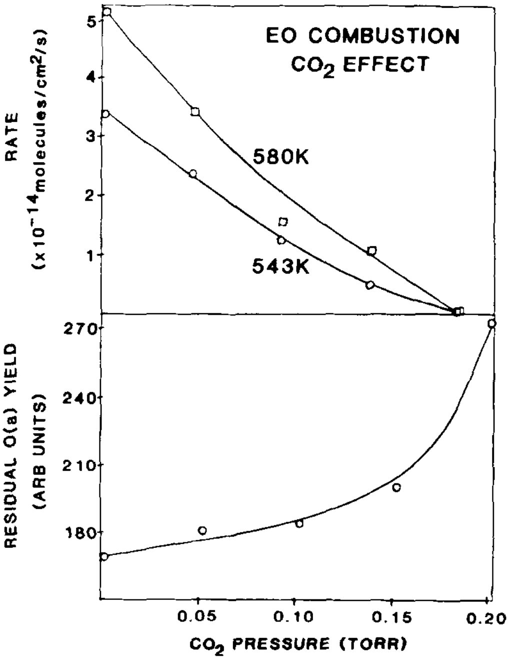


FIG. 11. CO_2 retardation of EO combustion showing the effect on rate (top) and postreactor O(a) desorption yield (bottom).

hanced adsorption probability for EO via the adsorbate oxygen lone pairs. However, earlier work on Ag(110) (*22*) has shown that such Cl-induced effects are rather weak even in the case of ethylene itself. More interesting is the observation that preadsorbed Cl(a) does not appear to inhibit the maximum extent of uptake of EO (Fig. 1); on the other hand, the maximum uptake of chlorine *is* partially suppressed by preadsorbed EO (Fig. 4). Preadsorbed EO is not displaced by chlorine.

If it is assumed that all the Cl(a) resides at the surface, then one would expect that on Ag(111) no free Ag sites would remain at a precoverage corresponding to $\theta_{Cl} = 0.5$ (*17*). In these circumstances, the only way to accommodate the EO layer would be on top of the Cl overlayer. However, the TPD results clearly indicate that the desorption kinetics of EO are not significantly affected by such chlorine precoverages; the above explanation therefore appears untenable. These observations could however be rationalised in terms of a model in which at least some of the adsorbed chlorine species exist coplanar with or even below the topmost Ag layers. Recent work (*23, 24*) has indeed shown that very substantial penetration of the metal lattice by Cl occurs on Ag(111) even at room temperature. There is therefore no particular difficulty in envisaging how free Ag adsorption sites can persist at chlorine loadings of $\theta_{Cl} \sim 0.5$: a substantial amount of the Cl is located below the surface (*23, 24*). (This view is not inconsistent with our own finding that *subsurface* oxygen on Ag(111) can be displaced by the subsequent chemisorption of chlorine (*17*)). Conversely, since EO is presumably exclusively a surface species, its ability to inhibit the dissociative chemisorption of chlorine is not unexpected; nevertheless, substantial amounts of chlorine can still be accommodated because of the ability of Cl atoms, once formed, to penetrate the metal lattice.

The unusually broad EO desorption spectra are thought to reflect at least two effects. Firstly, the slow pumping speed of the apparatus for EO at low pressures gives rise to a pronounced "tailing" to high temperatures; this is an unavoidable experimental artefact. Secondly, it seems very possible that the kinetics of EO desorption are intrinsically complicated by the presence of interadsorbate attractive interactions (hydrogen bonding?) (*3*). That such effects do operate is suggested by the observation that the high temperature EO desorption feature seems to grow *after* the low temperature feature.

Kinetics and Mechanism of Ethylene Oxide Isomerisation

The overall reaction may be represented by the following scheme:

$$\mathrm{EO(g)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{EO(a)}$$

$$\mathrm{EO(a)} \xrightarrow{k_3} \mathrm{CH_3CHO(a)}$$

$$\mathrm{CH_3CHO(a)} \xrightarrow{k_4} \mathrm{CH_3CHO(g)}$$

Assuming that the surface reaction (k_3) is rate limiting under the conditions employed (*3, 16*), and under the additional simplifying assumption that the system can be approximated by Langmuir kinetics, it is readily shown that

$$\text{isomerisation rate} = \frac{(k_3k_1/k_2)P_{\mathrm{EO}}}{1 + (k_1/k_2)P_{\mathrm{EO}}(1 + (k_3/k_4))}. \quad (2)$$

If we assume that

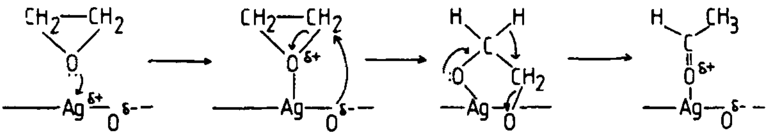
$$(k_1/k_2)P_{\mathrm{EO}}(1 + (k_3/k_4)) \ll 1$$

Eq. (2) reduces to

$$\text{isomerisation rate} \simeq (k_3k_1/k_2)P_{\mathrm{EO}}. \quad (3)$$

The latter approximation would appear to be justified since the data show that the adsorption probability of EO is very small (k_1 small) whereas the Ag–EO chemisorption bond is weak (k_2 large) so that the condition $k_1/k_2 \ll 1$ is fulfilled under reaction conditions. The first-order kinetics predicted by Eq. (3) are in good agreement with the observed behaviour for both the clean and the Cl-precovered surface (Fig. 5). This kinetic behaviour agrees well with earlier observations on supported Ag catalysts (*5*, *9*); the single crystal turnover frequencies are also in reasonable agreement with the supported catalyst results (*9*).

Given the opposite effects of Cs (*3*) and Cl promoters (this work) on the EO isomerisation rate (inhibition and acceleration, respectively) it seems likely that electronic effects are of significance here. A plausible mechanistic scheme for the catalysed isomerisation of EO may be written as follows (*3*) (subsurface oxygen is explicitly included in Scheme 1 because it is present under the experimental conditions):



SCHEME 1

The EO/chlorine coadsorption results indicated that the Ag–EO bond strength was not materially affected by the presence of Cl; they also showed that Cl does not block the adsorption of EO. Thus the overall kinetic behaviour of the isomerisation reaction on the Cl-dosed surface should still be described by Eq. (3), which is in agreement with experiment (Fig. 5). Now EO adsorption on Ag leads to a decrease in work function (*25*), suggesting charge donation from the oxygen atom to the metal (see Scheme 1 above). This would lead to the creation of an electron deficient, destabilised EO(a) species. The presence of Cl(a) would be expected to give rise to increased electronic charge deficiency (larger δ^+) on the O atom of the EO(a) species, because of charge transfer from metal to halogen. Such an effect, coupled with the concomitant weakening of the C–O bond might be expected to render the EO(a) species more susceptible to the ring-opening nucleophilic attack: an enhanced isomerisation rate should result. These arguments, though speculative, are consistent with the facts presented here *and* with the opposite behaviour observed with Cs promoter (*3*); in the latter case, the presence of an electropositive species naturally leads to the opposite prediction for the effect on the isomerisation rate.

Ethylene Oxide Combustion

The reactor data show that EO burning is zeroth order with respect to oxygen pressure at both 543 and 580 K (Fig. 7), suggesting that O(a) is relatively strongly bound under reaction conditions, as expected. This agrees well with earlier work on Ag films and supported Ag catalysts (*5*, *6*, *8*, *9*, *12*). Although some earlier workers have found the kinetic order in EO to be unity (*5*, *6*, *12*) we find a variable order which is dependent on reaction temperature; Stoukides and Vayenas (*8*) have made a similar observation. The Ag–EO bond strength is such that at 507 K EO adsorption is not rate determining under our conditions, and zeroth-order kinetics result. Increasing temperature eventually leads to an increase in kinetic order as surface depletion by EO desorption becomes significant: this is the usual explanation for such behaviour. Our results suggest, therefore, that the EO combustion reaction occurs via a Langmuir–Hinshelwood mechanism. Similar behaviour was reported for EO *isomerisation* over Ag(111) (*3*), and it is interesting to note that in this case the transition temperature for the kinetic order was significantly lower than for the burning reaction. The difference amounts to about 100 K.

This difference is understandable when it is recalled that the burning reaction (unlike the isomerisation) necessarily was studied in the presence of a large amount of chemisorbed oxygen. Backx *et al.* (*2*) have shown that coadsorbed oxygen leads to a substantial increase in the strength of the Ag–EO(a) bond. This naturally accounts for the higher transition temperature observed for the combustion reaction when combustion and isomerisation are investigated under comparable conditions. Such an explanation is also consistent with our observations that no isomerisation could be detected above 520 K whereas the burning rate was still quite high even at 580 K.

Figure 9 shows that preadsorbed Cs inhibits the rate of EO burning; this is unsurprising given that we have already shown that Cs suppresses the rate of EO isomerisation (*3*), a reaction which is thought to be the rate-limiting initial step of the combustion process (*5, 8, 9*). Cs does *not* operate by a simple site blocking effect (*3*) and comparison with the effects produced by Cl led to the "electronic" hypothesis proposed above. It is again instructive to make a quantitative comparison between the isomerisation and burning reactions under similar conditions. In the former case (*3*), 0.13 monolayers of Cs decreased the rate by ~80%. In the present case, a similar Cs loading decreased the combustion rate by only ~30%. This difference may reflect the ability of Cs to enhance the steady state coverage of O(a) (*16, 21*), an effect that would tend to offset electronic inhibition described above.

Finally, the effect of CO_2 in poisoning the combustion reaction (Fig. 11) is most readily understood in terms of the formation of a surface carbonate species (*26, 27*)

$$CO_2(g) + O(a) \rightarrow CO_3(a)$$

With increasing CO_2 pressure reactive oxygen species are converted to unreactive carbonate species which themselves may interfere with the chemisorption of reactants. These carbonate species can be decomposed to yield gaseous CO_2 and, eventually, gaseous oxygen. The postreactor oxygen TPD measurements (Fig. 11) clearly indicate that increasing CO_2 levels in the reactor feed results in progressively larger amounts of O(a) being rendered unreactive.

CONCLUSIONS

1. At 300 K ethylene oxide chemisorbs relatively weakly on clean Ag(111) with a very low sticking probability. The broad desorption spectra are due, at least in part, to the existence of attractive interactions in the adsorbate layer. Preadsorbed chlorine does not materially affect either the sticking probability or the maximum uptake of EO.

2. EO isomerisation to acetaldehyde occurs with first-order kinetics on both the clean and Cl-dosed surfaces. This is consistent with the adsorption/desorption parameters of the reactant. Preadsorbed Cl accelerates the isomerisation rate, in contradistinction to the effect of Cs, indicating that these promoters act mainly by electronic perturbation of the system. It is suggested that this electronic effect involves modification of the degree of charge transfer in the EO → Ag chemisorption bond.

3. EO burning occurs *via* a Langmuir–Hinshelwood mechanism in which EO → CH_3CHO is thought to be the rate-limiting step at sufficiently low temperatures. Under such conditions the combustion rate is zeroth order in both O_2 and EO. At higher temperatures the order in EO rises towards unity, reflecting the relative strengths of the Ag–O and Ag–EO chemisorption bonds. Cs inhibits the burning reaction, though its effect is significantly less pronounced than it is for the isomerisation reaction in the absence of oxygen. This is understandable in terms of the dual role played by Cs in the presence of oxygen. CO_2 effectively suppresses the burning rate, apparently by converting reactive O(a) sites to unreactive CO_3(a) sites.

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