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THE PARTIAL OXIDATION OF NORBORNENE OVER A SILVER CATALYST UNDER STEADY STATE CONDITIONS

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The continuous oxidation of norbornene (C_7H_{10}) by molecular oxygen over a silver catalyst at 500-573 K has been investigated. In contrast to that observed during the temperature programmed reaction of norbornene and oxygen adsorbed on Ag(110) no norbornene epoxide is formed. Instead benzene is the sole partial oxidation product. A stable selectivity of 20 to 25% with fractional conversions up to 0.8 at 573 K could be obtained by inclusion of 15 to 30 ppm dichloroethane in the feed. Separate experiments with *exo*-norbornene epoxide showed that in the absence of oxygen it was almost completely isomerised to 3-cyclohexene-1-carboxyaldehyde with production of lesser amounts of norcamphor and norbornene. With oxygen present carbon dioxide and small amounts of benzene were also produced. It is concluded that norbornene epoxide cannot be a gas phase intermediate in the production of benzene from norbornene.

Keywords: Norbornene, oxidation, silver, norbornene epoxide, 3-cyclohexene-1-carboxyaldehyde

1. Introduction

Silver metal is uniquely effective as a catalyst for the direct oxidation of ethylene to ethylene oxide on an industrial scale [1]. However the corresponding reaction with propene gives very low epoxide yields [2] and this behaviour extends to higher olefins in general [3]. It is usually attributed to the ready total oxidation of species formed by the abstraction of γ-hydrogens. There are three very interesting recent reports which show that higher olefins lacking readily removed γ-hydrogens can be epoxidised over particular single crystal planes of silver, at least under transient conditions. Roberts and Madix [4] reported that norbornene epoxide was desorbed at 310 K when an Ag(110) surface containing a coadsorbed layer of norbornene and atomic oxygen was heated from 120 K to 700 K.

Similarly, Hawker et al. [5] observed epoxidation of styrene during temperature programmed reaction over Ag(111) and Mukoid et al. [6] demonstrated that 3,3-dimethyl-1-butene reacts in the same way. The selectivity to the epoxide in [5] was approximately 60% increasing to 93% when the surface contained adsorbed chlorine and decreasing to zero in the presence of adsorbed potassium. In all

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these studies the transient conditions used were very different from those employed for ethylene oxidation on an industrial scale (i.e. continuous operation at 470 K to 570 K). Here we wish to describe results for the oxidation of norbornene under such conditions.

2. Experimental

The catalytic measurements were carried out at atmospheric pressure in a single pass flow reactor using norbornene (2 to 20 Torr), oxygen (50 to 200 Torr), balance helium at a total flowrate of 50 to 100 cm^3 (STP)/min. The norbornene (Aldrich, 99% pure) was supplied from a three arm saturator in which a helium stream passing through the liquid at 50 ° C was diluted at the exit of the saturator by a second helium stream. The catalyst used was an unsupported silver sponge (surface area 0.5 m^2/g) prepared by the reduction of silver nitrate by hydrazine hydrochloride in a manner similar to that described by Kulifay [7]. Details of its performance for the epoxidation of ethylene have been given previously [8]. Testing with norbornene was carried out using 0.15 g of the silver contained in a Pyrex tube of 3 mm ID or with 2 to 4 g packed into the bulb of a shortened 5 mL Pyrex pipette. In each case the tube containing the catalyst was located in an aluminium block in an electrically heated furnace and maintained to ±1 K. The catalyst samples were reduced in 10% H_2/He for some hours at a temperature of 513 to 563 K and then cooled in helium prior to exposure to the feed stream. The 1,2-dichloroethane was obtained as a 90 ppm mixture in helium (CIG Ltd) and diluted as needed.

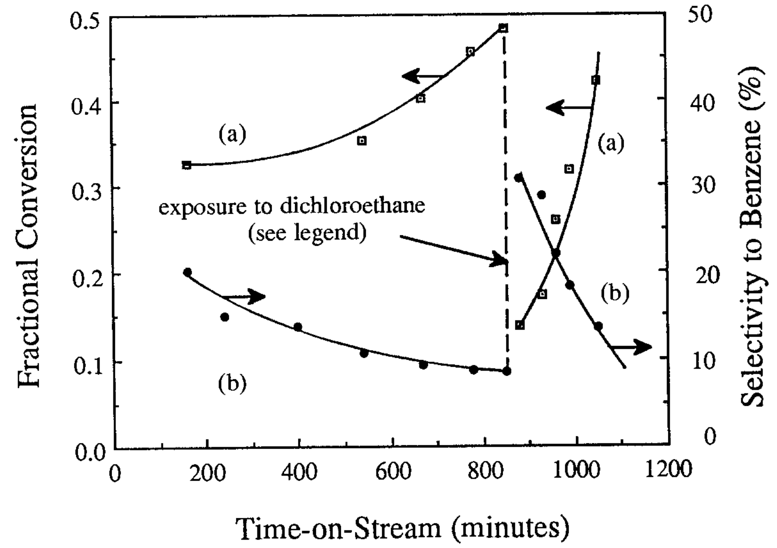
The product (or feed) streams were analysed by on-line gas chromatography using a Porapak Q column for separation of oxygen and carbon dioxide and a 2 m 10% AT-1000 on Chromosorb W-AW column (Alltech Inc.) for organic analysis. At a column temperature of 80 ° C the retention time of norbornene was 1.04 min compared to 9.3 min for *exo*-norbornene epoxide. The latter was obtained from Aldrich or prepared by the reaction of norbornene with m-chloroperbenzoic acid according to the procedure of Brown et al. [9] and its structure verified by proton NMR at 200 MHz using a Varian XL 200 spectrometer. Infrared measurements of product streams were performed with a Perkin-Elmer Model 580 spectrometer using a flow through gas cell of pathlength 16 cm. The GC-MS analyses used a Kratos MS25 instrument fitted with a 50 m BP-1 column programmed from 10 ° C or 30 ° C at 4 ° C/min.

3. Results

Initial tests involved a comparison of the oxidation rates of ethylene and norbornene at 513 K with approximately 20 Torr of olefin and 80 Torr of oxygen in helium and a total flowrate of 40 cm^3/min. Under these conditions the fractional conversion of ethylene was about 0.65 and the selectivity to ethylene oxide about 37%. Using norbornene the conversion was very low with traces of carbon dioxide as the only product. Conversion increased with temperature and an additional product was just observable above 553 K. The rate of reaction appeared to increase with oxygen pressure and decrease with increase in norbornene pressure. Thus the reaction seemed inverse order in norbornene presumably because the olefin is strongly adsorbed to the point of inhibiting oxygen adsorption. This behaviour is also observed with C_4 and C_5 olefins [3] but is opposite to that observed using ethylene over the same catalyst when the reaction is positive order in olefin [8]. Strong adsorption of norbornene was confirmed by co-reacting the two olefins. At 240 ° C the conversion of ethylene was then 0.15 compared to 0.65 in the absence of norbornene.

Most subsequent tests employed 2 to 4 g of catalyst with approximately 4 Torr of norbornene and 150 Torr of oxygen. In experiments at 533 to 573 K the additional product was clearly apparent as a peak with retention time of 1.42 min, well removed from that due to unreacted norbornene or that expected for norbornene epoxide. No reaction of norbornene occurred in blank tests using an empty reactor. The retention time of the product observed with the silver catalyst corresponded to that of benzene and this identification was confirmed in three ways. Firstly, in an experiment at 573 K the product gas stream was dried by passage through a drierite (calcium sulfate) trap and its infrared spectrum recorded on-line. After subtraction of the contributions of unreacted norbornene and product carbon dioxide, absorption bands were apparent at 3090 cm^{-1}, 3050 cm^{-1} and 672 cm^{-1}. They closely matched those for gaseous benzene measured under the same conditions. In a second experiment the product stream was trapped at 195 K for a period of 4 hours. A GC-MS analysis of the collected fraction showed a peak with the mass spectrum of benzene. The proton nmr spectrum of the fraction was recorded as a solution in $CDCl_3$. The presence of benzene was obvious from a large peak at 7.24 ppm. Integration of the benzene peak relative to those of unreacted norbornene showed that the ratio of benzene to norbornene was 0.67, identical to that calculated from gas chromatographic peak areas. There was no trace of *exo*-norbornene epoxide. However the spectrum did reveal small amounts of a compound also present in trace quantities in the starting norbornene. It is probably a norbornene isomer and indistinguishable from norbornene itself by gas chromatography under our conditions.

The selectivity to benzene varied with time-on-stream. Fig. 1 illustrates the behaviour for a catalyst sample which had been reduced at 513 K. The selectivity fell from approximately 21% after a reaction time of 120 min to 8% after 840 min. Over the same period the fractional conversion of norbornene rose from 0.33 to 0.48. It appears that these changes may be due to the gradual removal of chlorine occluded in the catalyst during preparation and not removed by the mild reduction procedure. A sample reduced at 563 K gave an initial selectivity below 10%. Also, as shown in fig. 1, selectivity and conversion could be largely restored



Variation in (a), fractional conversion of norbornene and (b), selectivity to benzene with time-on-stream for 2.2 g of silver catalyst reduced at 513 K. Tests with norbornene pressure of 4.6 Torr, oxygen pressure of 155 Torr, balance helium with total flowrate of 58 cm^3 (STP)/min. Only data for 551 K is shown but other temperatures were also tried in the test period (see text and fig. 2). After 840 min the catalyst was exposed to 40 ppm dichloroethane in helium for 12 hours at 423 K and flushed for 60 min in helium before recommencement of reaction at 551 K.

to their starting values if the catalyst was treated with 40 ppm of dichloroethane in helium overnight and flushed with helium prior to recommencement of reaction (i.e. reduction was omitted). The subsequent decline in selectivity (during

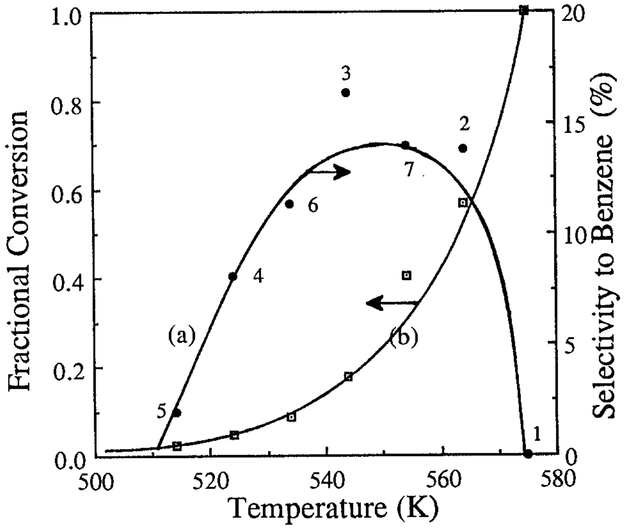


Fig. 2. Fractional conversion, (a) and selectivity, (b), as a function of temperature. Tests were made during the time interval 220 to 420 min of fig. 1 with the same test conditions. Points obtained in numbered order shown.

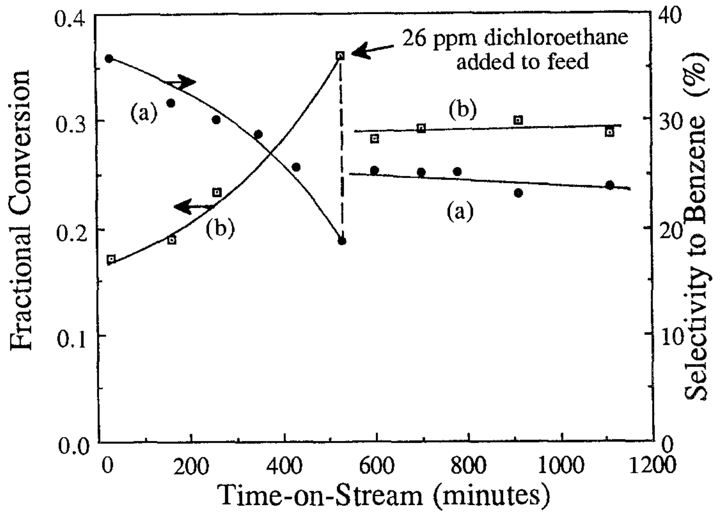


Fig. 3. Effect of inclusion of 26 ppm dichloroethane in feed on time-on-stream behaviour of (a), fractional conversion and (b), selectivity. Tests at 551 K with norbornene pressure of 3.8 Torr, oxygen pressure of 177 Torr, balance helium to total flow rate of 96 cm^3 (STP)/min over 3.8 g of silver reduced at 513 K.

the period 840 to 1040 min on stream) was much steeper than that with the starting catalyst. This is expected since exposure to dichloroethane will deposit chlorine on the surface alone. That will be removed more readily than any bulk chlorine in the fresh catalyst which will be transfered to the surface only over an extended period of time. If the reaction was allowed to run on longer than shown

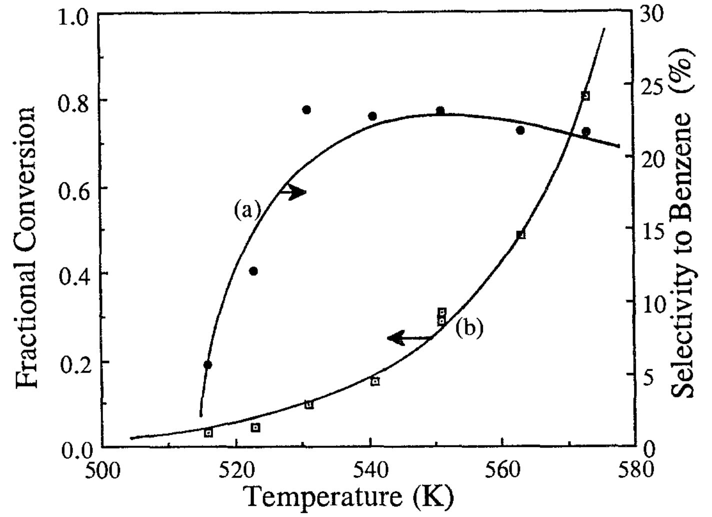


Fig. 4. Temperature dependence of (a), fractional conversion and (b), selectivity with 26 ppm dichloroethane in feed. Test made during the time interval 720 to 1000 min of fig. 3 with the same test conditions.

in fig. 1 then the selectivity to benzene eventually fell to 5%. This is similar to the selectivity with which propene can be converted to propene oxide over an unchlorinated silver catalyst [2].

Fig. 1 shows data for measurements made with the catalyst at 551 K alone but they were actually interspersed with measurements under other conditions. Fig. 2 shows the temperature dependence of selectivity and conversion, measured over the interval 220 to 420 min on-stream, with the points obtained in the numbered order. With this catalyst the selectivity dropped to near zero at 573 K as the fractional conversion approached unity but largely returned when the temperature was lowered again. The selectivity also appeared to decline below 530 K but this may have reflected some experimental inaccuracies at the low conversions then applying.

Stable catalytic behaviour could be achieved by inclusion of some dichloroethane in the feed as demonstrated by the data of fig. 3. The test conditions (with the temperature at 551 K throughout), and the catalyst batch, was different to that employed to obtain the data of fig. 1. The initial selectivity was higher at 36% and it declined rather more slowly to 18% after 480 min. Introduction of 26 ppm of dichloroethane then increased this to a stable value of 24% with a fractional conversion of 0.3. Levels of dichloroethane below 15 ppm failed to stabilise the catalyst whilst values much above 30 ppm led to significant losses in activity. These concentrations are much above the 0.5 to 2 ppm required to optimise selectivity during the epoxidation of ethylene over silver [8,10]. Either norbornene is more efficient than ethylene in stripping surface chlorine or it is adsorbed so strongly that high levels of dichloroethane are required to adsorb in competition with it.

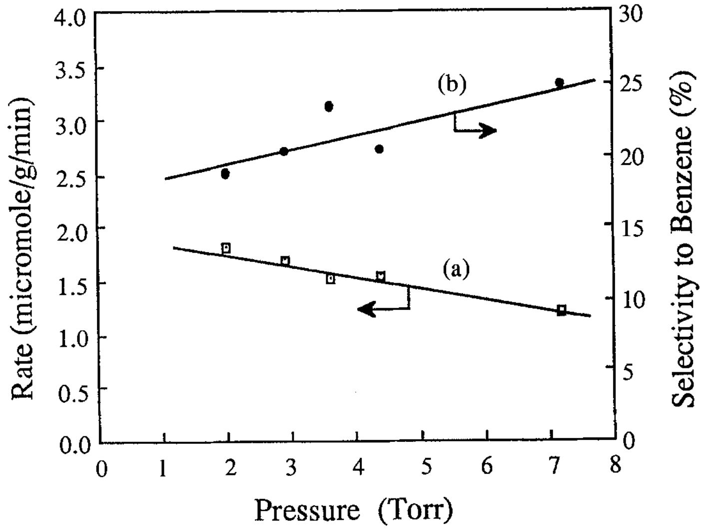


Fig. 5. Dependence of (a), rate and (b), selectivity on norbornene pressure at 551 K with 27 ppm dichloroethane in feed. Oxygen pressure and other test conditions as per fig. 3.

The effect of temperature on selectivity and conversion with 26 ppm dichloroethane in the feed was measured over the interval 720 to 1000 min of fig. 3 and gave the results shown in fig. 4. Unlike the situation without dichloroethane, selectivity was now maintained to 573 K with a fractional conversion of 0.8. Again the selectivity seemed to fall below 530 K but it is uncertain if that is really significant because of experimental inaccuracies at lower conversions. An apparent activation energy of 137 kJ/mol was obtained from an Arrhenius plot of rates calculated using the differential reactor approximation for the points with conversion below 0.3. A similar value was obtained from the corresponding points of fig. 2.

A determination of the dependence of selectivity and overall rate on norbornene pressure with 27 ppm dichloroethane in the feed gave the results shown in fig. 5. The corresponding conversion ranged from < 0.02 at the highest pressure to ≈ 0.3 at the lowest pressure and rates are calculated according to the differential reactor approximation. The selectivity seems to increase slightly with

Table 1
Relative ion yields for GC-MS of the reaction products of *exo*-norbornene epoxide over 3.8 g of silver at 551 K.

m/e	relative ion yields (%) [a]				
	major [b,c] product	minor [b] product	*exo*-norbornene [d] epoxide (I)	norcamphor [d] (II)	3-cyclohexene-1-carboxyaldehyde (III) [e]
54	61	185	60	188	30
66	37	370	28	270	20
67	65	370	47	270	34
77	67	15	25	13	36
79	108	26	78	22	140
81	100	100	100	100	100
91	39	10	21	11	29
92	56	15	22	19	48
95	44	26	32	22	33
109	11	14	8	13	7
110	89	207	5	168	110

[a] Expressed relative to $m/e = 81$ to facilitate comparison with data of Roberts and Madix [4].

[b] The relative amounts of these compounds and their retention times on the on-line chromatograph are given in table 2.

[c] The ^{13}C nmr line positions relative to TMS for this compound in $CDCl_3$ solution were as follows:
$C_1 = 45.9$ ppm
C_2, C_5, $C_6 = 21.9$, 23.6, 24.1 ppm (unassigned)
C_3, $C_4 = 124.6$, 127.0 ppm (unassigned)
$C_7 = 204.3$ ppm.

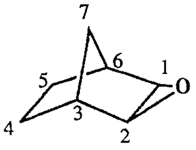
[d] Authentic samples-the fragmentation patterns are similar to those given by Roberts and Madix [4].

[e] Data from library spectra [11] for different instrument to that used here.

norbornene pressure but, as noted before, the rate decreased as the pressure was raised. The apparent kinetic order (from the slope of a log-log plot) was -0.4. Other measurements indicated that the rate increased with oxygen pressure with an order of about 0.5.

The formation of benzene, rather than norbornene epoxide, as the sole partial oxidation product was quite unexpected given the temperature programmed reaction results of Roberts and Madix [4]. There are two possibilities. Either norbornene epoxide never forms at the higher temperatures used here, or alternatively, it does form but is then further oxidised. The latter possibility was checked by feeding norbornene epoxide itself. This was done as follows. A few hundred milligram of solid *exo*-norbornene oxide was held at room temperature between two glass wool plugs in a 4 mm ID Pyrex tube upstream of the catalyst and helium passed through it at a flow rate of 40 cm^3 (STP)/min. The resultant epoxide pressure was approximately 2 Torr reducing to 1.5 Torr if oxygen (100 to 150 Torr) was added.

With or without oxygen no reaction of *exo*-norbornene epoxide was observed in empty reactor tests to 573 K. Reaction over unchlorinated silver at 551 K in the absence of oxygen resulted in almost complete conversion of the epoxide to two products with longer retention times on the on-line chromatograph. GC-MS analysis of a bulk sample collected over an interval of 1 to 3 hours on stream also showed the two products with relative ion yields as shown in table 1. Both compounds have parent ions of 110 like the epoxide (I)



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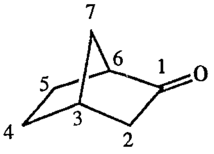
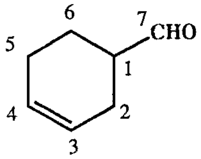


II



III

but their fragmentation patterns are very different. The pattern for the lesser product closely matches that for an authentic sample of norcamphor (II). Comparison of the pattern for the major product against a mass spectral library [11] gave a reasonable match to 3-cyclohexene-1-carboxyaldehyde (III). This identification was confirmed by ^1H and ^{13}C NMR spectroscopy. The number of protons on adjacent carbons was established by sequential proton decoupling and the existence of an aldehydic carbon proven by ^{13}C NMR using the DEPT pulse sequence. The ^{13}C line positions are given in the footnote to table 1.

Reaction of *exo*-norbornene epoxide over unchlorinated silver in the presence of oxygen also gave 3-cyclohexene-1-carboxyaldehyde and norcamphor as the major products. As shown in table 2 the minor products included some carbon dioxide and benzene with somewhat more norbornene to that produced in the absence of oxygen. With oxygen present approximately 20% of the input epoxide

Table 2
Comparison of product distributions for the reaction of *exo*-norbornene epoxide in the presence and absence of oxygen over 4.3 g of silver at 551 K.

	without oxygen	with oxygen
Input pressures, Torr [a]		
oxygen	nil	100
exo-norbornene epoxide	2.0	1.5
Output pressures, Torr [b,c]		
exo-norbornene epoxide (9.3)	~ 0.06	~ 0.02
carbon dioxide	nil	2.3
benzene (1.42)	nil	0.1
norbornene (1.04)	0.02	0.1
3-cyclohexene-1-carboxyaldehyde (13.1)	1.6	0.6
norcamphor (18.8)	0.3	0.1

[a] Balance helium with total flow rate of 40 cm^3 (STP)/min (no oxygen) and 50 cm^3 (STP)/min (with oxygen).

[b] The distributions shown were obtained after 3 hours of reaction. The initial distribution contained somewhat less norcamphor and unreacted *exo*-norbornene epoxide.

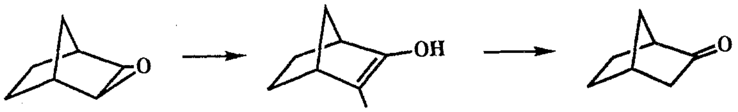
[c] Retention times (min) on AT-1000 column in parentheses.

was converted to a higher molecular weight material which was observable on the on-line chromatograph but could not be identified.

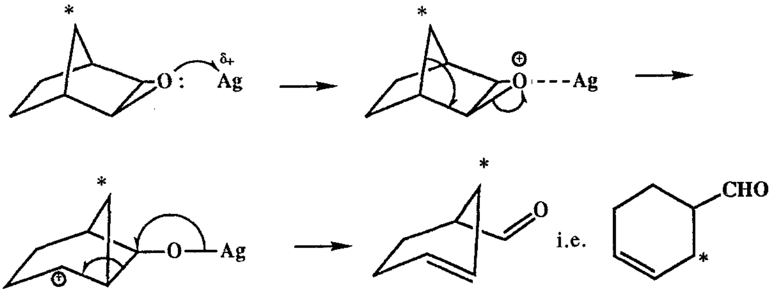
Similar experiments to those detailed in table 2 were carried out using chlorinated silver. The distribution amongst the products formed was similar but the conversion of epoxide was much less. With 26 ppm dichloroethane in the feed the fractional conversion declined to 0.4 after some hours operation at 551 K in the absence of oxygen. Over a still more heavily chlorinated catalyst it was 0.3 in the absence of oxygen but considerably higher with oxygen present.

4. Discussion

The current study has made two quite unexpected findings concerning reactions of olefins and epoxides over silver. Firstly, benzene is a significant product of the oxidation of norbornene and secondly, norbornene epoxide isomerises to 3-cyclohexene-1-carboxyaldehyde. Neither observation is expected on the basis of the findings of Roberts and Madix [4] that norbornene epoxide is the sole partial oxidation product of the temperature programmed reaction between norbornene and oxygen on Ag(110). It is clear that under the conditions used here norbornene epoxide is not even an intermediate in the conversion of norbornene to benzene since that would surely result in the formation of 3-cyclohexene-1-carboxyaldehyde whereas none was observed. The mechanisms for the observed transformations are problematic. The formation of norcamphor, the minor product of norbornene epoxide isomerisation, could occur by simple ring opening to form the unsaturated alcohol followed by a keto-enol interconversion:



This could proceed either by an initial coordination of the oxygen to electropositive silver or by acid catalysis as is observed during the isomerisation of ethylene oxide to acetaldehyde over oxides such as γ-Al_2O_3 and TiO_2 [12]. However the formation of 3-cyclohexene-1-carboxyaldehyde must involve a skeletal isomerisation in which C_7 of the epoxide becomes C_2 in the aldehyde unless one assumes movement of the oxygen which seems unlikely. Skeletal rearrangements of the above type are well known in systems in which a positive charge is developed [13]. In the present case the process could perhaps be written as



The conversion of norbornene to benzene presents a similar dilemma in respect of the carbon which is removed. It could be either C_7, with retention of the existing sixmembered ring, or one of the other carbons following a rearrangement. If the adsorption of norbornene occurred by π-coordination of the double bond then the geometry of the molecule is such that one of the hydrogens on C_7 will be tilted towards the surface. Abstraction of it by adsorbed oxygen could be followed by breakage of the bond from C_7 to C_3 (or C_4). Subsequent oxidation could remove C_7 and eventually form benzene after a further oxidative dehydrogenation. Alternatively, if the coordination of the double bond was asymmetric then abstraction of the hydrogen attached to C_3 (or C_4) would be more likely. In this case a rearrangement similar to the above might occur with the result that one of the olefinic carbons is removed.

Clearly some of the above postulates are amenable to checking by ^{13}C or ^{18}O labelling but the synthesis required are likely to be difficult and are beyond the scope of the present work. Here we simply wish to report the discovery of this interesting set of reactions.

Acknowledgments

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