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The partial oxidation of some cyclohexenes and branched chain olefins over a silver catalyst

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The oxidation of some cyclic and branched chain olefins over a silver catalyst effective for the conversion of ethylene to ethylene oxide has been investigated in a steady state flow system. The reaction of cyclohexene produces benzene and that of both 1-methylcyclohexene and 4-methylcyclohexene yields toluene. The selectivity to aromatics exceeds 20% for fractional conversions below 0.2, but it can be improved to almost 50% by inclusion of an optimum quantity of dichloroethane in the feed. Styrene is oxidised more slowly than the cyclohexenes and only carbon dioxide and water are produced. The oxidation of 3,3-dimethyl-1-butene and 3-methyl-1-butene occurs much faster than that of the cyclic molecules and some of the corresponding epoxides are produced. The selectivity with the dimethylbutene is 9–13% for conversions to 0.2. The methylbutene requires a higher temperature for reaction and the epoxide yield is lower. Factors influencing reactivity and product distribution are discussed.

Keywords: Silver; oxidation; cyclohexenes; branched chain olefins

1. Introduction

Silver-based catalysts have now been used for the commercial production of ethylene oxide from ethylene for over fifty years [1]. Despite some claims to the contrary [2] there is general recognition that the same catalysts are ineffective for the epoxidation of higher olefins. Certainly the survey of Akimoto et al. [3] indicates little, if any, epoxide formation during the oxidation of C_3–C_5 linear and singly branched olefins under steady state conditions. However, recent transient experiments employing individual planes of silver indicate that low selectivity is not inevitable. Roberts and Madix [4] reported a substantial yield of norbornene epoxide when norbornene and oxygen, coadsorbed on Ag(110), were heated. Similar transient experiments employing 3,3-dimethyl-1-butene and styrene with Ag(111) also produce epoxides [5,6]. Such selectivity has been

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attributed to the low reactivity, or total absence, of γ-hydrogens in these molecules. Roberts and Madix [7] have also shown that Ag(110) can selectively oxidise cyclohexene to benzene.

In recent work we have found [8] that under steady state conditions, a silver catalyst can selectively oxidise norbornene (C_7H_{10}) but the product is benzene rather than norbornene epoxide. This is surprising since it involves oxidative removal of one carbon in addition to the hydrogens. The reaction is continuous and selectivities over 30% are possible if the catalyst surface is suitably moderated with chlorine as in the commercial process for ethylene oxidation [1]. The present work concerns the oxidation of cyclohexenes and branched olefins over the same catalyst.

2. Experimental

The general procedure was similar to that described previously [8]. The hydrocarbons were fed by bubbling a helium stream through the liquid held at a suitable temperature in a saturator followed by further dilution with added oxygen, helium and, in some experiments, helium containing 90 ppm 1,2-dichloroethane. The standard stream comprised 10 Torr hydrocarbon, 150 Torr oxygen, balance helium to one atmosphere, at a total flow rate of 46 cm^3 (STP)/min. This was passed over 3.8 g of silver sponge, in the form of 300–600 μm particles, packed in the bulb of a shortened 5 cm^3 pyrex pipette. This was mounted in an aluminium block in a furnace maintained to ± 1 K. The catalyst was prepared by reduction of silver nitrate by hydrazine hydrochloride according to the procedure of Kulifay [9]. It was reduced at 513 K in 10% H_2/He for 2 h prior to commencement of reaction.

The stream leaving the reactor was analysed by on-line gas chromatography. Samples for NMR analysis were collected by condensing out the organic fraction from the stream in a trap held at -195 K. Proton NMR spectra were recorded at 400 MHz using a Varian XL400 spectrometer. The three cyclohexenes and 3,3-dimethyl-1-butene were all obtained from Aldrich (Wisconsin). The 3-methyl-1-butene was from Koch-Light and the styrene from Ajax Chemicals. Toluene and benzene were standard laboratory grade reagents. Authentic samples of the epoxides of some of the olefins were prepared according to the procedure of Brown et al. [10].

3. Results

Initial tests were carried out using streams containing approximately 10 Torr of hydrocarbon and 150 Torr of oxygen. With all three cyclohexenes reaction became detectable above 500 K and gave rise to one product in addition to

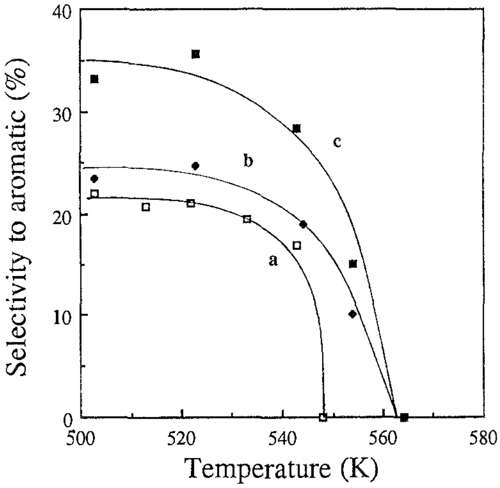

Fig. 1. Temperature dependence of selectivity during oxidation over 3.8 g of silver using standard feedstream; (a) cyclohexene; (b) 1-methylcyclohexene; (c) 4-methylcyclohexene.

carbon dioxide and water. The retention time of this product corresponded to the aromatic with the same carbon number as the starting cyclohexene (i.e. benzene from cyclohexene and toluene from the two methylcyclohexenes). These identifications were confirmed by proton NMR analysis of liquid samples obtained by condensing out the organic fraction of the exit stream. A specific search was made for epoxides of the cyclohexenes and none was detected. These results show that the findings of Roberts and Madix [7] for the temperature programmed reaction of coadsorbed cyclohexene and oxygen on Ag(110) can be extended both to steady state catalysis and to substituted cyclohexenes.

The temperature dependence of selectivity to the aromatic, and of conversion, for the three cyclohexenes is shown in figs. 1 and 2 respectively. In each case the selectivity was fairly constant below 540 K but then declined steeply with higher temperature as conversion rose above 25%. It Is likely that the fall in conversion is due to oxidation of the aromatic products since, in a separate test (fig. 2d), benzene was oxidised at a slightly greater rate than the cyclohexenes under the same conditions. Similar tests were also carried out with styrene (fig. 2e). Its oxidation rate was much less than that of the cyclohexenes and of benzene. The only products detected were carbon dioxide and water with no evidence of epoxide formation.

Pressure dependencies for the oxidation of cyclohexene under differential conditions at 513 and 533 K were determined. The reaction to benzene and total oxidation products combined was negative order in cyclohexene (order ≈ -0.5) and positive order in oxygen (order ≈ 0.6). These orders are similar to those found for norbornene [8] and are best interpreted in terms of standard Langmuir–Hinshelwood behaviour. The hydrocarbon is adsorbed relatively strongly and oxygen relatively weakly so that an increase in hydrocarbon pressure

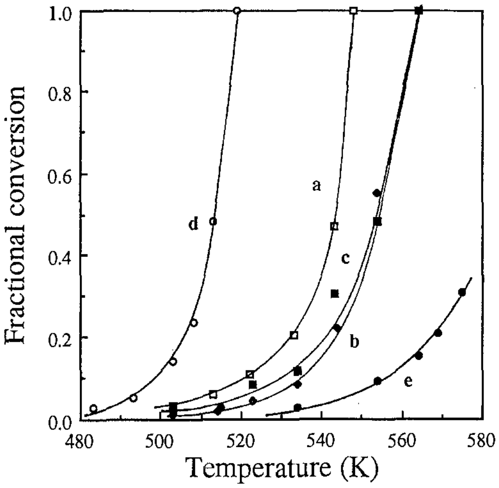

Fig. 2. Temperature dependence of conversion during oxidation over 3.8 g of silver using standard feedstream; (a) cyclohexene; (b) 1-methylcyclohexene; (c) 4-methylcyclohexene; (d) benzene; (e) styrene.

depresses oxygen coverage and lowers the probability of a bimolecular surface reaction between the two adsorbed species. Although both benzene formation and total oxidation were negative order in cyclohexene and positive order in oxygen, the orders were not exactly the same for the two pathways leading to changes in selectivity with pressure. As shown in fig. 3, selectivity increased with

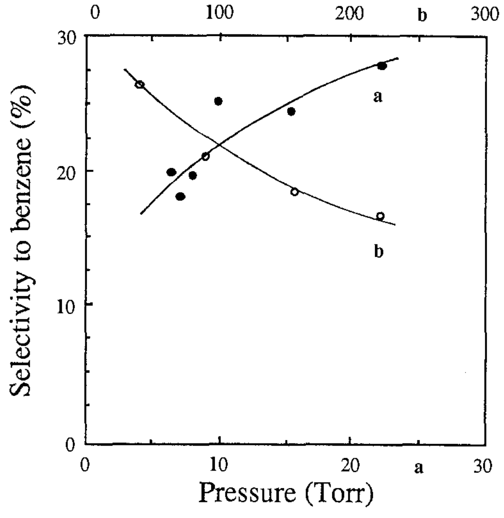

Fig. 3. Effect of pressure on selectivity to benzene during oxidation of cyclohexene at 533 K: (a) dependence on cyclohexene with oxygen pressure of 145 Torr; (b) dependence on oxygen with cyclohexene pressure of 7.3 Torr.

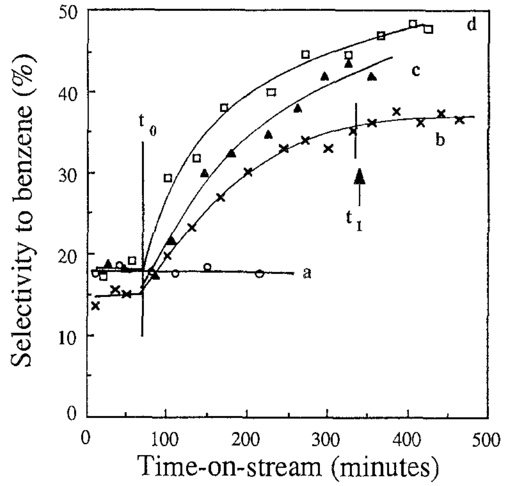

Fig. 4. Time-on-stream behaviour of selectivity following introduction of dichloroethane during oxidation of cyclohexene of 3.8 g of silver under standard conditions at 533 K: (a) no added dichloroethane; (b) 10 ppm dichloroethane; (c) 18 ppm dichloroethane; (d) 36 ppm dichloroethane. The dichloroethane flow was started at t_0 and turned off (for experiment (b) only) at t_1.

cyclohexene pressure but declined with increase in oxygen pressure. A possible cause is that increases in oxygen coverage relative to cyclohexene coverage increase the likelihood of additional hydrogen abstractions and hence total oxidation. Again the oxidation of norbornene over the same catalyst shows similar behaviour [8].

Additional experiments were carried out to see if the selectivity of cyclohexene oxidation could be enhanced by the inclusion of chlorine-containing compounds in the feed as is the case for norbornene oxidation [8] and for the epoxidation of ethylene over silver [1,11]. The time-on-stream behaviour of selectivity and conversion with three different concentrations of added dichloroethane is shown in figs. 4 and 5, respectively. In the control experiment in the absence of dichloroethane selectivity was constant at 18% with a fractional conversion of 0.37. With 10 ppm dichloroethane present the selectivity rose steadily to 35% over a period of six hours while the conversion halved. With 36 ppm of dichloroethane included the decline in conversion was faster and to a lower value while the final selectivity approached 50%. Inclusion of 18 ppm dichloroethane gave an intermediate result. It is likely that the added dichloroethane is adsorbed in chromatographic fashion with the final surface coverage dependent on the dichloroethane concentration (and on temperature). If the dichloroethane flow was stopped then the catalyst gradually regained activity and eventually lost selectivity. However the return to starting values was very slow as may be seen in figs. 4 and 5 for the experiment using 10 ppm dichloroethane. Reduction in flowing hydrogen for in excess of four hours at 540 K was necessary to fully restore catalyst behaviour to the untreated state.

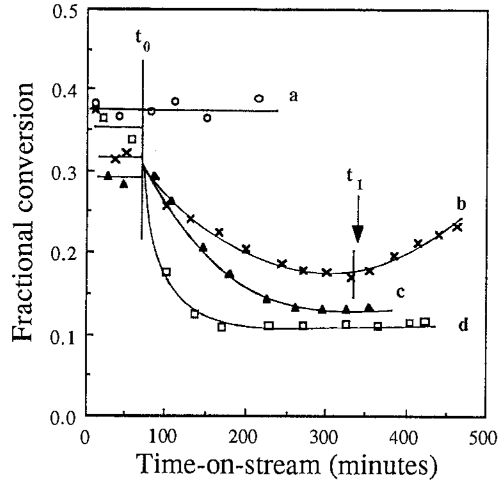

Fig. 5. Time-on-stream behaviour of conversion following introduction of dichloroethane during oxidation of cyclohexene over 3.8 g of silver under standard conditions at 533 K: (a) no added dichloroethane; (b) 10 ppm dichloroethane; (c) 18 ppm dichloroethane; (d) 36 ppm dichloroethane. The dichloroethane flow was started at t_0 and turned off (for experiment (b) only) at t_1.

Branched olefins

Tests were carried out with 3,3-dimethyl-1-butene and 3-methyl-1-butene. The former has a methyl group in place of the single γ-hydrogen on the latter. With both molecules oxidation over the silver catalyst was detectable at a temperature more than 70 K below that required for the cyclohexenes. Both compounds produced one product in addition to carbon dioxide and water whose retention time corresponded to that expected for the epoxide of the

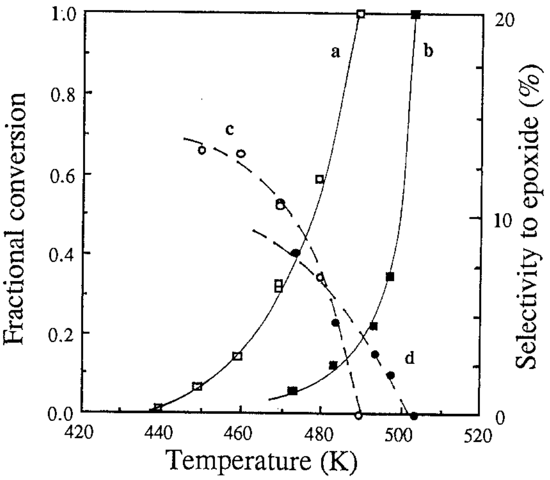

Fig. 6. Temperature dependence of selectivity during oxidation over 3.8 g of silver using standard feedstream; (a) conversion with 3,3-dimethyl-1-butene; (b) conversion with 3-methyl-1-butene; (c) selectivity with 3,3-dimethyl-1-butene; (d) selectivity with 3-methyl-1-butene.

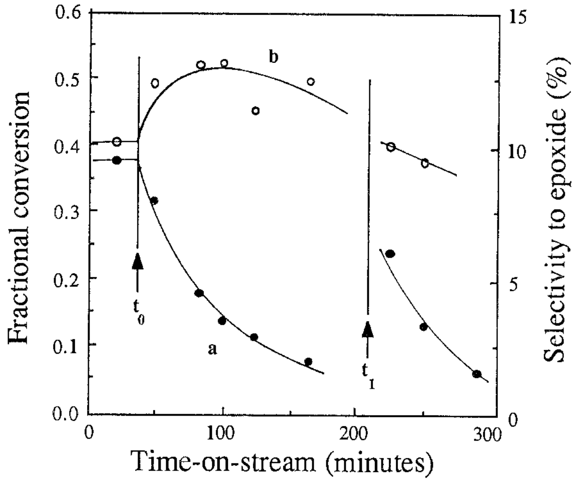

Fig. 7. Time-on-stream behaviour of conversion (a) and selectivity (b) following introduction of 10 ppm dichloroethane during oxidation of 3,3-dimethyl-1-butene over 3.8 g of silver using standard feedstream at 473 K. The dichloroethane was introduced at the time denoted t_0 and the temperature raised to 503 K at t_1.

reactant molecule. In the case of the dimethylbutene the amount formed was sufficient to be collected and analysed by proton NMR. The spectrum corresponded exactly to that of an authentic sample of 3,3-dimethyl-1,2-epoxybutane. The amount of product formed from the methylbutene was too small to be analysed in the same way but is believed to be 3-methyl-1,2-epoxybutane. Fig. 6 shows the temperature dependence of conversion and selectivity to epoxide for the two molecules. With 3,3-dimethyl-1-butene the selectivity to its epoxide remains above 10% until conversion exceeds 0.3. The 3-methyl-1-butene is less reactive by a factor of at least five and the fall-off in epoxide selectivity with temperature is pronounced even for conversions below 10%. Akimoto et al. [3] did not detect any epoxide formation when using 3-methyl-1-butene, probably because the temperature they used (503 K) was higher still. Conversely Hawker et al. [5] in temperature programmed experiments with 3,3-dimethyl-1-butene at a lower effective temperature found much more epoxide than observed here.

Experiments were also carried out with the dimethylbutene to see if selectivity to the epoxide could be enhanced by inclusion of dichloroethane in the feed. Results are shown in fig. 7 for addition of 10 ppm of dichloroethane. The conversion at 473 K fell to a low value after just two hours. It continued to fall steeply when the temperature was raised to 503 K. The selectivity remained constant at 11 $\pm 2\%$ throughout. The continuing decline in conversion, unlike the stabilisation with cyclohexene, probably reflects the fact that at the lower temperature required with the two butenes even 10 ppm dichloroethane will eventually produce a surface chlorine concentration sufficient to block all activity. A further experiment was carried out with 2 ppm dichloroethane which

Table 1

Reaction rates, selectivities and kinetic orders for oxidation of olefins and aromatics over silver sponge catalysts

Unsaturate	Reaction rate [a] (μmol g^{-1} min^{-1})	Selectivity [b] (%)	Kinetic orders	
			in hydrocarbon	in oxygen
ethylene	68 [c], 99 [d]	47 (E) [c]	0.5	0.3
propylene	29 [c], 62 [d]	3 (E) [c]	0.2	0.3
3-methyl-1-butene	3 [c], 32 [d]	4 (E) [e]	−0.5	0.9
3,3-dimethyl-1-butene	24 [e]	11 (E) [e]	–	–
benzene	0.74 [e]	–	–	–
cyclohexene	0.21 [e]	20 (B) [e]	−0.5	0.6
norbornene	0.08 [f]	10 (B) [f]	−0.4 [f]	> 0.5 [f]
1-methylcyclohexene	0.10 [e]	22 (T) [e]	–	–
4-methylcyclohexene	0.14 [e]	30 (T) [e]	–	–
styrene	0.02 [e]	nil [e]	–	–

[a] For reaction at 500 K using 10 Torr hydrocarbon and 150 Torr of oxygen. Considerable extrapolation is involved for some reactants.

[b] To epoxide (E), benzene (B) or toluene (T) at fractional conversion of ≈ 0.2.

[c] Data from ref. [12].

[d] Data from ref. [3].

[e] This work.

[f] Data from ref. [8]. The selectivity to benzene was somewhat dependent on catalyst history.

is close to the optimum value when using ethylene [11]. This level produced a much slower activity decline but again with no selectivity improvement. Thus it appears that chlorine moderation does not enhance selectivity. However, it is just possible that the results obtained may reflect the difficulty in achieving an optimum dichloroethane concentration when equilibration times are very long.

Table 1 provides a summary for the reaction parameters measured here. It is supplemented by other values calculated from the results of Cant and Hall [12] for the same catalyst and Akimoto et al. [3] for a somewhat different type of silver sponge. It is clear that the cyclic compounds are much less reactive than the linear ones. There is a distinct trend for reaction rate to decrease with increase in molecular size and for the corresponding kinetic orders in olefin to become more negative despite the need for a higher reaction temperature. A possible explanation for this is that strength of adsorption increases with size and this causes the fraction of surface covered by olefin to grow at the expense of that occupied by oxygen. In such a situation the number of adjacently adsorbed reactants will be depressed and rate will fall even if intrinsic reactivity is unaffected. As described by Roberts and Madix [7] the intrinsic reactivity of many organic species towards oxygen atoms adsorbed on silver seems related to the gas phase acidity of the reactant. That effect is not apparent here. Propylene and cyclohexene, both with allylic hydrogens, have quite similar gas phase acidities (391 kJ/mol [13] and 387 kJ/mol [14] respectively) but very different reaction rates. On the other hand propylene and 3,3-dimethyl-1-butene have fairly similar rates but very different acidities (391 kJ/mol [13] and 409 kJ/mol [15]). Intrinsic reactivity may be expected to operate in a situation such as temperature programming of species coadsorbed at low temperature. Under our conditions of steady state catalysis it may be masked by the effects of competitive adsorption.

Whilst the trend in reactivity relates to size that in selectivity clearly does not. With the non-cyclic olefins epoxidation is related to the presence or absence of abstractable hydrogens on nearby carbons. Ethylene has none and the epoxide yield is high; 3,3-dimethyl-1-butene also has no allylic hydrogens (but there are many abstractable ones on the next carbon) and some epoxide is made; 3-methyl-1-butene and propylene have one and three allylic hydrogens, respectively, and the yields are lower still. The cyclohexenes, with two allylic hydrogens, give no epoxide. However, the corresponding aromatics do provide a relatively stable product short of complete oxidation. This is only possible at relatively low conversions since, as shown by fig. 2, benzene is more easily oxidised than cyclohexene. Once its concentration approaches that of cyclohexene it will be oxidised rapidly and selectivity will fall as shown in fig. 1. Cyclohexadiene may be a transient species but is oxidised much faster than cyclohexene and therefore not seen at all. The previously rather surprising result that oxidation of norbornene (with one allylic hydrogen) yields benzene is now more easily understood. Its bicyclic framework is subject to ready rearrangement. If a configuration that allows oxidative removal of one carbon is reached then the remaining ring can follow the cyclohexadiene to benzene pathway. It is not possible for styrene to follow this route since it lacks the required number of aromatic hydrogens for conversion to benzene. No epoxide could be observed in our experiments either, which is a bit surprising given the relatively high yields found in the temperature programmed reaction experiments of Mukoid et al. [6]. The very high temperature required for styrene oxidation under our conditions may have led to complete oxidation of any epoxide initially formed. This point may bear checking under substantially different conditions.

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