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The reaction of 1,2-dichloroethane with copper

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The decomposition of 1,2-dichloroethane on polycrystalline copper has been studied using a microreactor. The reaction is found to have an activation energy of 81 ± 5 kJ mol^{-1} generating gaseous ethene and chemisorbed chlorine. The reaction terminates on completion of a monolayer of chemisorbed chlorine and is followed by a much slower reaction. The rate limiting step is thought to be $C_2H_4Cl_{2(phys)} \rightarrow C_2H_4Cl_{(ads)} + Cl_{(ads)}$. The reaction is compared with a UHV study of the same molecule on Cu(111) and the possibility of a negative ion transition state is discussed.

Keywords: Copper; dichloroethane; microreactor; electron attachment

1. Introduction

In this paper we present a microreactor study of the decomposition of DCE on polycrystalline copper to gaseous ethene and chemisorbed chlorine and a discussion, using electron attachment studies, of the possibility that the transition state involved is formed by electron capture from the metal Fermi level. Halocarbon adsorption is of current interest for a number of reasons: (i) halocarbons are used as refrigerants and propellants; (ii) they are involved in the mechanism of ozone depletion; (iii) they are retained by soils long after their use as fumigants; (iv) they are used in the dry etching of semiconductors and copper in integrated circuit construction. More specifically, many halocarbons are industrially important, particularly

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1,2-dichloroethane (DCE) which is produced by the oxychlorination reaction using a copper chloride catalyst. DCE is a precursor to vinyl chloride monomer [1] and hence polyvinyl chloride, and is also used in the epoxidation of ethene. Academically, mono-halo substituted hydrocarbon adsorption on metals in ultra-high vacuum (UHV) is a convenient method of generating organic groups at a surface by dissociation of the carbon–halogen bond while the various conformers, orientations and reactions of the adsorbed molecules are now open to investigation using a range of techniques.

The thermal decomposition of DCE has been studied for many years, starting with Barton [2], under both homogeneous and heterogeneous conditions. Holbrook et al. [3] showed that although vinyl chloride is the major reaction product in homogeneous gas phase reaction, ethene is also a primary reaction product. It was suggested that the ethene came from a surface-dependent reaction which is consistent with the results found in this work. Studies have also been conducted on the chlorine catalysed pyrolyses [4,5] and on the laser induced thermal decomposition [6,7] of DCE. Both the thermal and the laser induced decompositions involve a similar step (1):

$$C_2H_4Cl_2 \rightarrow C_2H_4Cl^* + Cl \quad \text{thermal} \tag{1a}$$

$$C_2H_4Cl_2 + h\nu \rightarrow C_2H_4Cl^* + Cl \quad \text{photo} \tag{1b}$$

$$C_2H_4Cl^* \rightarrow C_2H_4 + Cl \tag{2}$$

$$Cl + C_2H_4Cl_2 \rightarrow CH_2ClCHCl + HCl \tag{3}$$

$$CH_2ClCHCl \rightarrow CH_2CHCl + Cl \tag{4}$$

plus other reactions.

The photo-activated chain initiation reaction ((1b) and (2)) was found to be complete, generating 2 Cl atoms per absorbed photon. The thermal initiation step (1a) has an enthalpy of 335 kJ mol^{-1} [7] necessitating high temperatures (>770 K) in commercial plants which produce vinyl chloride by thermal decomposition.

Gas phase DCE, in common with other halocarbons, also has an extensive electron attachment chemistry. It has a large electron capture cross section for electron kinetic energies <1 eV [8,9], forming an excited negative ion, MCl_x^{-*}, which can decompose promptly via a number of routes [8]:

$$C_2H_4Cl_2 + e^- \rightarrow C_2H_4Cl_2^{-*} \tag{5}$$

$$C_2H_4Cl_2^{-*} \rightarrow C_2H_4Cl + Cl^- \tag{6a}$$

$$C_2H_4Cl_2^{-*} \rightarrow C_2H_4Cl^- + Cl \tag{6b}$$

$$C_2H_4Cl_2^{-*} \rightarrow C_2H_4 + Cl_2^- . \quad (6c)$$

The route forming Cl^-, (6a), is dominant and in negative ion mass spectroscopy of DCE the $C_2H_4Cl_2^-$ ion is never observed [8,10].

1,2-dichloroethane adsorption on Cu(111) has been studied under ultra-high vacuum conditions using a range of surface sensitive techniques [11,12]. No adsorption or reaction appears to occur at room temperature and above, but at low temperatures reversible molecular adsorption does occur:

$$C_2H_4Cl_{2(g)} \rightleftharpoons C_2H_4Cl_{2(phys)} . \quad (7)$$

The physisorbed molecule is thought to be in the trans conformation [11], adsorbed with the Cl–C–C–Cl plane perpendicular to the copper surface, with one chlorine slightly higher (0.5 Å) than the other [12]. The physisorbed monolayer undergoes an electron stimulated reaction to produce chemisorbed chlorine in a $(\sqrt{3} \times \sqrt{3})R30^O$ structure uncontaminated by carbon; the carbon in the molecule is thought to be desorbed promptly as ethene:

$$C_2H_4Cl_{2(phys)} + e^- \rightarrow 2Cl_{(ads)} + C_2H_{4(g)} + e^- \downarrow . \quad (8)$$

These results should be compared with those of DCE on a rough silver surface studied using electron energy loss spectroscopy (EELS) and surface enhanced Raman spectroscopy (SERS) [13]. SERS showed some decomposition of DCE on the silver surface at 55 K, together with both the trans and gauche conformers of the adsorbed molecular species. EELS, however, showed only molecular DCE with no decomposition. It was concluded that EELS monitored the majority of the surface, while SERS showed a minority reaction at the SERS active sites.

2. Experimental

The work was carried out at 1 bar absolute using a microreactor at the Catalysis Research Centre at ICI Billingham. A similar microreactor has already been described [14]. The stainless steel catalyst column, length 19 cm, diameter 4 mm, was packed with a 1 : 2 mixture of glass beads (Phase separations Ltd., 80–100 mesh) and copper(II) oxide (98%, BDH) and plugged with glass wool. The tube temperature could be held between 873 and 77 K, and ramped at a constant rate. A bypass loop could be used to avoid flowing gases through the catalyst column. The carrier gas was helium and a constant flow rate of 25×10^{-6} m^3 min^{-1} was used for all gas mixtures (measured using a bubble meter). The 1,2-dichloroethane was held in a molecular sieve at 273 K (vapour pressure = 26.77 mbar, [15]), through which the helium carrier gas was passed.

The gaseous products from the reactor were passed through a micro-katharometer held at a temperature of 375 K and its change in resistance recorded on a y–t chart recorder. The katharometer was calibrated by injecting known volumes of the gases used into the system and using a loop to bypass the reactor tube. The areas

under the resistance time plots were found to be proportional to the number of moles injected. The gaseous products were also analysed in a quadrupole mass spectrometer (Supavac, V G-gas Analysis Ltd., 1–100 amu range), controlled by a personal computer and capable of monitoring up to 10 masses simultaneously.

3. Results

The copper(II) oxide was reduced to copper using carbon monoxide and a temperature of 523 K. Reduction was presumed to be complete when evolution of CO_2 ceased and the reactor was then flushed with helium as it cooled, to remove any remaining CO. The surface area of the copper was then measured using the N_2O reactive frontal chromatography method [16]. The sample was held at 333 K and a 6% mixture (by volume) of N_2O in helium was passed through the reactor to give first nitrogen, then nitrous oxide after completion of the reaction. In this method, mild oxidation of the copper surface occurs to form Cu(I) as follows:

$$N_2O_{(g)} + 2Cu_{(s)} \rightarrow N_{2(g)} + Cu{-}O{-}Cu_{(s)} .$$

The reaction is quantitative, giving a half monolayer coverage of oxygen (5×10^{18} O atoms m^{-2}) i.e. 2×10^{-19} m^2 per oxygen atom. Note that the ideal packing densities of the three low index faces of copper are 1.77, 1.53 and 1.08×10^{19} copper atoms m^{-2} for the (111), (100) and (110) respectively. Two separate runs gave values of 3.81 and 3.57 $m^2\ g^{-1}$. As a further check on surface area one oxidised sample was then titrated with CO (6% by volume in helium) at 523 K, yielding a surface area of 4.14 $m^2\ g^{-1}$. This slightly higher figure may be due to reduction of some oxide remaining from the original Cu(II) oxide used to form the metal [17]. The three values give an average of 3.8 ± 0.3 $m^2\ g^{-1}$.

The reaction of 1,2-dichloroethane (1.06×10^{-3} mol dm^{-3}) with the clean copper surface was monitored using the mass spectrometer, fig. 1. Four mass peaks were monitored: $C_2H_3Cl^+$ ($m/e = 62$) and Cl^+ ($m/e = 35$) due to unreacted 1,2-dichloroethane and $C_2H_4^+$ ($m/e = 28$) and $C_2H_3^+$ ($m/e = 27$) which can originate from either DCE or ethene. Initially, pure ethene ($m/e = 28$ and 27) was produced due to the reaction

$$C_2H_4Cl_{2(phys)} \rightarrow 2Cl_{(ads)} + C_2H_{4(g)} , \qquad (9)$$

$C_2H_3Cl^+$ ($m/e = 62$) due to unreacted 1,2-dichloroethane was unobservable. After completion of this reaction the 28 amu peak dropped in intensity simultaneously with an increase in the 62 amu peak. The cracking patterns of these later product gases are compared with that of pure unreacted DCE (via the bypass loop) in table 1, and show a small relative increase in the 27 and 28 amu peaks for the reacted gases. This suggests that after the initial reaction, most of the DCE came through unreacted but that a second, slower reaction between the chlorine covered copper and the DCE does occur which produces some ethene.

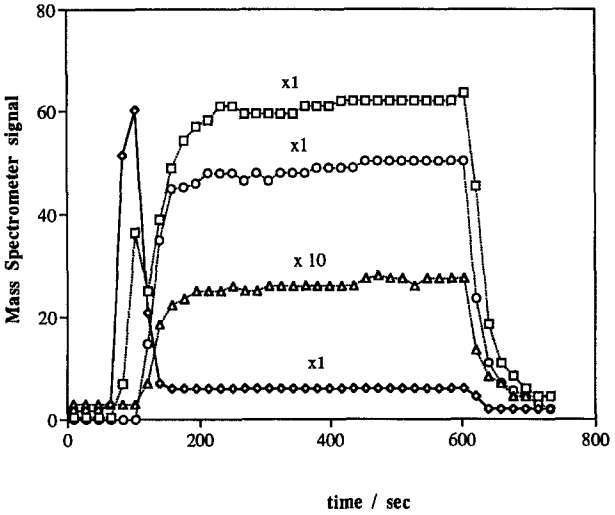

Fig. 1. The reaction of DCE with polycrystalline copper. m/e values of 27 (□, ×1 gain), 28 (◇, ×1 gain), 35 (△, ×10 gain) and 62 amu (○, ×1 gain), monitored using a mass spectrometer with respect to time after initiation of the DCE front in the microreactor.

Under the temperature and pressure conditions used here, the dichloroethane undergoes numerous adsorption/desorption events at the copper surfaces. The physisorbed lifetime, τ_{phys}, on each adsorption delays the DCE gas front with respect to where it would be if no physisorption occurred. If the activation energy for chemical reaction with the surface is E, then the lifetime for the reaction, τ, is given by

$$\tau = \tau_0 \exp(E/RT),$$

where τ_0 is the reciprocal of the preexponential term for the first order reaction and has a value $\sim h/kT$, in the region of vibrational frequencies. Thus, after an accumulated physisorption time τ, reaction will occur between DCE and the surface. The product molecule, ethene, is assumed to have zero residence time on subsequent collisions with clean copper, so it represents a front travelling at the no-reaction speed, but delayed by τ. The no-reaction time was 19.5 s (this was measured by passing DCE through the reactor a second time, when only the very

Table 1

Species	m/e	Intensity relative to $C_2H_3Cl^+$	
		DCE through bypass	DCE through reactor
$C_2H_3Cl^+$	62	1.0	1.0
$C_2H_3^+$	27	0.99	1.23
$C_2H_4^+$	28	0.08	0.11

slow reaction occurs between the chlorine covered copper surface and DCE, trace 1 of fig. 2) while the time taken for the ethene pulse to appear was 31.5 s (trace 2 of fig. 2), giving $\tau = 12$ s. For $T = 301$ K and τ_0 in the range $10^{-12} < \tau_0 < 10^{-14}$ s (the exact value will depend on the partition functions involved) the activation energy is found to be 81 ± 5 kJ mol^{-1}. The uncertainty in τ_0 exceeds the experimental uncertainties.

An approximate chlorine coverage can be calculated from the area of the ethene peak recorded in the katharometer measurements, fig. 2. If we assume initially that the sensitivity of the katharometer to ethene is the same as for nitrogen (for which we have a calibration sensitivity), then the amount of ethene can be used to calculate the number of chlorine atoms left on the copper from the reaction stoichiometry: two Cl_{ads} per $C_2H_{4(g)}$. Using this and the number of copper atoms per gram, the surface was found to consist of 0.56 chlorine atoms per copper atom or 0.56 ML (monolayer). The katharometer sensitivity to ethene was not known, but the temperature change of the thermistor in the katharometer, ΔT_{th}, is given by the following equation [18]:

$$\Delta T_{th} = x\Delta T(k_g/k_s - 1)$$

where ΔT is the temperature difference between the thermistor and the cell wall, x

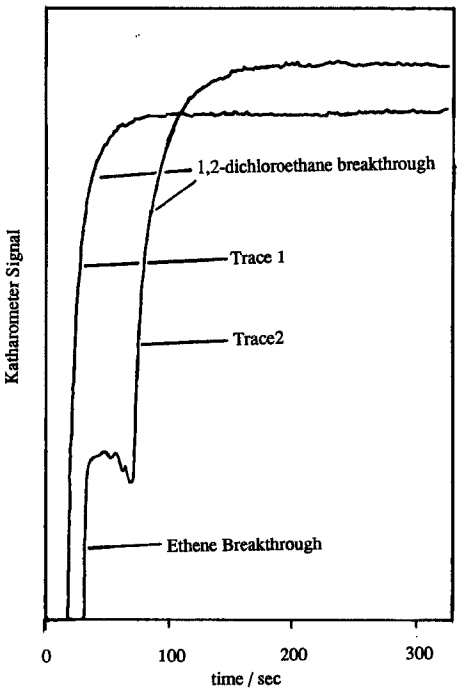

Fig. 2. Katharometer traces for DCE passing through the microreactor for the first time (trace 2) when the fast reaction occurs, and for the second time (trace 1) when only the very slow reaction occurs. Trace 1 represents a no-reaction trace.

is the mole fraction of dilutant and k_s and k_g are the thermal conductivities of the solute and the carrier gas respectively. The thermal conductivities of He, N_2 and ethene at 373 K are 17.2×10^{-2}, 3.07×10^{-2} and 3.02×10^{-2} W m^{-1} K^{-1} [19], the last value being extrapolated from 333 K. From this it can be seen that the thermal conductivity of nitrogen is very similar to that of ethene, so the sensitivity of the katharometer to the two gases is about the same. It should be noted that although the thermal conductivities of He and N_2 are reasonably consistent in the literature, the value for ethene varies by about 10%.

The chlorine coverage was also estimated from the quantity of DCE that had passed over the copper, prior to DCE emerging unreacted after the ethene pulse, fig. 2. Using 48 s, the flow rate of 25×10^{-6} m^3 min^{-1} and a DCE pressure of 26.77 mbar (saturated vapour pressure), the coverage of chlorine was found to be 0.42 ± 0.04 ML. This is in reasonably good agreement with the value of 0.56 above.

4. Discussion

1,2-dichloroethane reacts with polycrystalline copper to form chemisorbed chlorine and gaseous ethene as the only products. The reaction has an activation energy of 81 ± 5 kJ mol^{-1} and leaves a copper surface with a coverage of ~ 0.42 ML of chlorine. Once this reaction has ceased, a much slower reaction continues to occur which we assume leads to the formation of bulk chloride on the copper. A similar study has been carried out on silver powder [20] with the same qualitative results.

Rather surprisingly, DCE on Cu(111) has been found to be totally unreactive under UHV conditions at room temperature [11]. These two statements are now easily resolved. The physisorption energy of DCE on Cu(111) is ~ 52 kJ mol^{-1} [11] while the activation energy for chemical reaction is ~ 81 kJ mol^{-1}. In the microreactor study the physisorbed layer was complete which means that the activation energy for reaction from the physisorbed state is the same as the experimental value, ~ 81 kJ mol^{-1}. Therefore, the probability of chemical reaction for a physisorbed molecule relative to desorption is $\exp[-(81000 - 52000)/RT]$, which is 9×10^{-6} at 300 K. To form 0.38 ML of chlorine on a Cu(111) surface [11], $\sim 10^5$ monolayers of DCE must impinge. This is easily achieved in a microreactor using 26.77 mbar (20 Torr) of DCE (flux at the surface $\approx 20 \times 10^6$ ML s^{-1}), but unfeasible using 10^{-7} mbar of DCE in UHV (flux ≈ 0.1 ML s^{-1}, about 11 days to form 0.38 ML of chemisorbed chlorine). This illustrates rather nicely the "pressure gap" between UHV and real catalytic pressures.

In UHV, physisorbed dichloroethane on Cu(111) undergoes an electron stimulated reaction under the incident beams used for Auger electron spectroscopy and low energy electron diffraction [11] which appears to be identical in its reaction products (chemisorbed chlorine and ethene gas) with the thermal reaction on the copper surface reported here.

The very low energy electrons in the secondary electron yield are thought to be responsible, as gas phase DCE has a large capture cross section for such electrons. We propose that the electron stimulated (9) and the thermal reaction (10) at the copper surface have the following steps:

$$C_2H_4Cl_{2(phys)} + e^- \rightarrow C_2H_4Cl^{-*}_{2(phys)} \rightarrow C_2H_4Cl_{(ads)} + Cl_{(ads)} + e^-_{(to\,metal)} \quad (9)$$

$$C_2H_4Cl_{2(phys)} \rightarrow C_2H_4Cl_{(ads)} + Cl_{(ads)} \quad (10)$$

with the same subsequent step which forms the ethene product

$$C_2H_4Cl_{(ads)} \rightarrow Cl_{(ads)} + C_2H_{4(g)}\,. \quad (11)$$

The rate limiting step for the thermal decomposition of DCE on copper is expected to be (10), and hence the activation energy of (10), from this study, is 81 ± 5 kJ mol^{-1}.

In the gas phase electron attachment reaction, the electron is thought to go into a C–Cl σ^* orbital which is on a repulsive potential and leads to dissociation. The same process must occur for electron attachment in the physisorbed molecule. It is interesting to speculate how similar the $C_2H_4Cl^{-*}_{(phys)}$ species is to the transition state of the surface thermal reaction (10).

A thermodynamic cycle can be established, shown in fig. 3A, which is closed by the activation energy E_a if DCE^-_{phys} is the transition state. We assume the negative ion has approximately the same physisorption component, due to dispersion forces etc., as the neutral molecule. Johnson et al. [8] have reviewed the electron affinities of chlorine containing radicals and molecules, and conclude that the electron affinity of a molecule containing several chlorine atoms is about 1.5 eV. Tikhamirov and German [21], using MNDO calculations for DCE^-, arrive at a value of about 1 eV. When such a negative ion at infinity is brought up to a metal surface, it induces an image charge to which it is then attracted. The energy of the negative ion/positive image combination is given by simple electrostatics as $-14.4/d$ eV where d is the separation in Å. Using an electron affinity of 1.5 eV for DCE, a work function change for a saturated monolayer of DCE on Cu(111) of -0.55 eV [11], a work function for the clean Cu(111) surface of 4.98 eV [22] and a value for d of 6.88 Å (see below), then E_a is exactly 0.84 eV (81 kJ mol^{-1}), the activation energy for the thermal reaction. Normal incidence standing X-ray wave studies of DCE on Cu(111) give two heights for the chlorine atoms at 3.08 and 3.68 Å above the surface plane of copper atoms, ref. [12] and fig. 3B. This is an average of 3.38, which is fortuitously close to $6.88/2 = 3.44$ Å and would place the image plane at the surface copper atoms. The major errors in this calculation are the electron affinity, which may be ± 0.5 eV wrong, and the position of the image plane, which is not known and could alter the image energy by ± 0.35 eV for a change of ± 1 Å either side of 6.88 Å. So for the case of DCE on Cu(111) it seems reasonable to speculate that the transition state for the surface thermal reaction (10) may be formed by thermal excitation of electrons from the Fermi level of the metal to the antibonding C–Cl σ^*

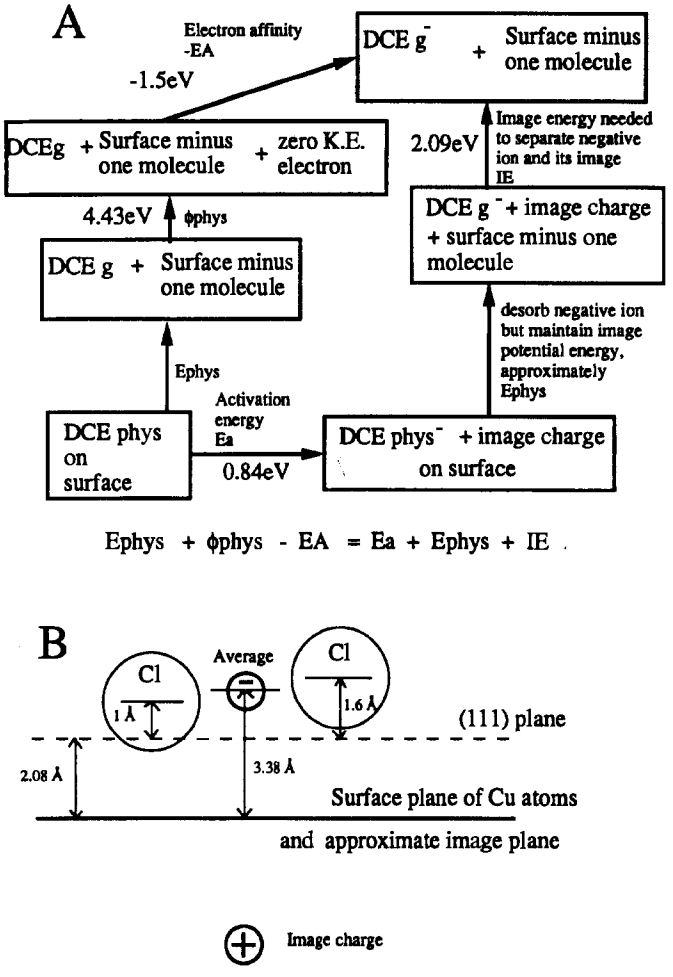

Fig. 3. (A) Thermodynamic cycle showing the energies of gas phase and physisorbed DCE and DCE^-, the electron affinity of DCE, the image potential at the surface for a separation of 3.44 Å from the image plane and the work function for DCE_{phys}. (B) diagram showing the heights of the two chlorine atoms for physisorbed DCE [13], and their average value of 3.34 Å which we assume is a good estimate of the centre of gravity of the charge on the DCE^- ion.

orbital, to form DCE^-_{phys} which is virtually the same as the $C_2H_4Cl^{-*}_{2(phys)}$ formed by electron attachment. We are currently carrying out studies using 1-bromo-2-chloroethane to test this theory.

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