Chlorination reactions relevant to the manufacture of trichloroethene and tetrachloroethene; Part 2: Effects of chlorine supply

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ABSTRACT

The behaviour of 1,1,2,2-tetrachloroethane and trichloroethene in chlorination reactions where the supply of chlorine is varied, either by change in chlorocarbon: Cl_2 feed ratio or the quantity of supported copper(II) chloride catalyst or by the use of an anhydrous hydrogen chloride/dioxygen feed as the source of chlorine, i.e. oxychlorination conditions, is described. Depending on the exact conditions used, the products are trichloroethene, pentachloroethane or tetrachloroethene. The products and the conditions under which they are observed are both in harmony with a previously proposed reaction scheme in which there is interplay between heterogeneous and homogeneous reactions. It is possible to define sets of reaction conditions which lead to improvements in selectivity towards the formation of either $CHCl=CCl_2$ or $CCl_2=CCl_2$ without significant formation of oligomeric species.

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1. Introduction

The term Industrial ecology [1], though controversial [2], encapsulates an approach which emphasizes the connectivity among different large scale chemical processes, for example in which the waste product of one process could act as the feedstock for another. The concept is well exemplified by anhydrous hydrogen chloride. This is a major waste product from the industrial synthesis of aryl isocyanates for polyurethane production; it is potentially also a feedstock for chlorohydrocarbon synthesis, via its oxidation to dichlorine, the Deacon reaction [2]. Waste HCl from polyurethane production can be used for the catalysed oxychlorination of ethene to give 1,2-dichloroethane and thence by dehydrochlorination, vinyl chloride [2,3]; this system has been examined in detail [4–7]. Active catalysts have been developed for the purpose [8–15]. However the fraction of waste HCl available that can be used for this outlet is limited increasingly by the mis-match between increasing, year-on-year tonnage of polyurethanes produced and the capacity of HCl to be used in the (mature) market for PVC [3]. For this reason there has been recent activity designed to improve the classical Deacon reaction [16–19,4,20–22] to oxidize HCl to Cl_2, using new catalysts [23–28] developed from work announced previously by

Sumitomo [29]. Moreover, Over and Schomäcker have considered the stability of Deacon catalysts and identify promising catalyst materials for the Deacon process [30].

An attractive possibility to utilize unwanted HCl would be in syntheses of poly-chlorinated hydrocarbons under oxychlorination conditions. In Part 1 of this series of two papers, we reported the results of a study designed to establish a reaction scheme connecting 1,1,2,2-tetrachloroethane with hexachloroethane, trichloroethene and tetrachloroethene. That work included experiments performed under static and continuous flow conditions, with aspects of the study examining the influence of a commercial oxychlorination catalyst (Cu^{II}/KCl/attapulgite). Pathways for the chlorination and dehydrochlorination reactions involved were proposed [31], the reaction conditions being either homogeneous flow conditions in which dichlorine is the initiator for dehydrochlorination of $CHCl_2CHCl_2$, or heterogeneously in the presence of the conventional copper(II)-supported Deacon catalyst. Although the results were broadly consistent with earlier studies [32,33], conditions for selective formation of either $CHCl=CCl_2$ or $CCl_2=CCl_2$ have been defined more precisely, bearing in mind the need to avoid the formation of oligomeric side-products. Specifically, the proposed reaction scheme identified pentachloroethane as a reaction intermediate. A role for Lewis acid site promoted chemistry was also considered [31].

The reactions reported in the initial study, Part 1: reaction pathways [31], were investigated under conditions where the dichlorine

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in the feed was insufficient for chlorination to be complete (a chlorocarbon: Cl_2 ratio of 3:1 was used). The present work, Part 2, builds on the previous study and examines (i) the effects of operation under chlorine-rich conditions (a chlorocarbon: Cl_2 ratio of 1:3 is used) and (ii) the effect of alteration of the chlorine supply when operating under oxychlorination conditions.

2. Experimental

Details of the flow apparatus, on-line analyses and the protocols used for flow experiments have been described previously [31]. Feedstocks were those used for experiments carried out under chlorine-lean conditions [31] with the addition of anhydrous hydrogen chloride (Linde, 99.5%), and dioxygen (BOC, 5% O_2/N_2). Pressure was limited via a pair of mercury-filled lutes to ensure that the reactor pressure did not exceed 0.5 bar g. Reaction data are reported as feed conversions, product yields and selectivities, defined according to standard practice [34]. Carbon mass balances were determined in all chlorination/dehydrochlorination reactions; they are reported explicitly when they contain features of note The analytical procedure described previously [31] to obtain chlorine mass balances (relative error ± 10%) was used to measure yields of Cl_2 from the catalytic oxidation of HCl to Cl_2.

The catalyst under consideration here is the same commercial grade oxychlorination catalyst [35] as examined in Part 1 [31]. Briefly, the catalyst comprises copper(II) chloride supported on the clay mineral, attapulgite, that is doped with a promoter, KCl. Prior to use, it was calcined at 673 K in flowing N_2 for 4 h and is characterized by a BET surface area of 71.6 $m^2 g^{-1}$ and a pore volume of 0.25 $cm^3 g^{-1}$ [31].

The experiments reported in Part 1 [31] established the importance of certain reaction pathways accessible at elevated temperatures even in the absence of a catalyst. A mixing vessel, packed with quartz beads (diameter 2 mm), was fitted within the furnace immediately before the reactor. This arrangement ensured complete mixing and thermalization of the reactant gases. Similar measurements are undertaken here and, as before, the catalyst was replaced with ground quartz. These experiments, which ensure comparable contact times, are useful in defining non-catalytic pathways. Previously we have referred to non-catalyst assisted processes as being 'homogeneous' [31], however we acknowledge that the quartz does provide some form of 'hold-up' in the hot zone, which could possibly influence reaction probabilities. Thus, these type of reactions could more correctly be called 'quasi-homogeneous', however, for completeness and additionally recognising the caveat described above, we will continue to use the term 'homogeneous' in this context.

3. Results and discussion

The results from the previous study [31] establish the reaction pathways connecting 1,1,2,2-tetrachloroethane with tri- and tetrachloroethene under chlorine-lean conditions (3:1 chlorocarbon: Cl_2 mol ratio). One of the reaction parameters that potentially might control the selectivity of the system is the chlorine supply. Although radical chlorinations, for example chlorination of 1,1,2,2-tetrachloroethane to give pentachloroethane, appear to be disfavoured kinetically compared with dehydrochlorinations, for example 1,1,2,2-tetrachloroethane to trichloroethene, increasing the chlorine supply might reverse this situation. To test the role of the supply of chlorine on reaction selectivity and outcomes, the effect of increasing the relative chlorine concentration was examined. Specifically, the chlorocarbon feed ($CHCl_2CHCl_2$ or $CHCl=CCl_2$) to dichlorine mol ratio was changed from 3:1 (i.e. chlorine-lean), as used in our previous study [31], to 1:3, i.e. a chlorine-rich regime.
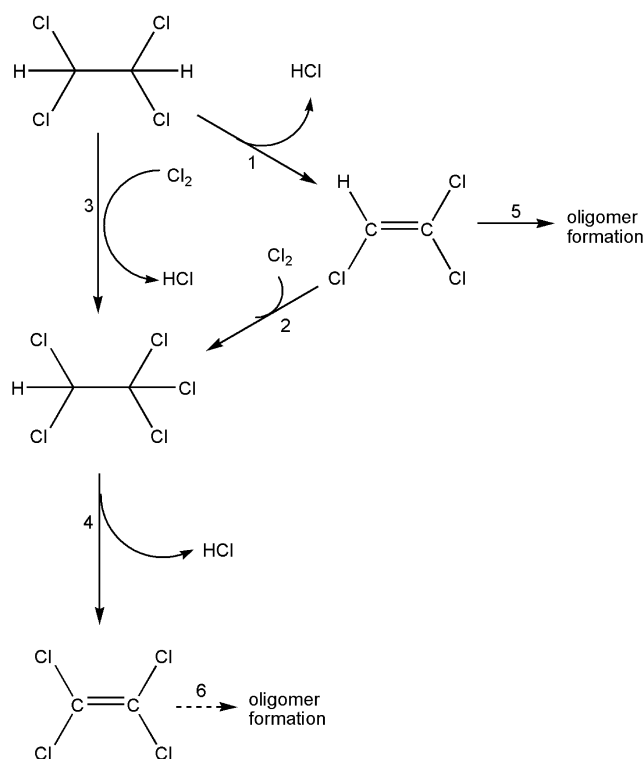

Fig. 1. The dehydrochlorination ((1) and (4)) and chlorination ((2) and (3)) processes that connect $CHCl_2CHCl_2$ with $CHCl=CCl_2$ and $CCl_2=CCl_2$. Possible oligomer formation ((5) and (6)). A pathway for reaction (5) is identified in Section 3.1.1. A pathway for reaction (6) is inferred in Section 3.1.2.

Nitrogen was used as a carrier gas for the chlorocarbon and a diluent for the feedstream to give a total volumetric flow rate of 25 ml min^{-1}. The chlorination and oxychlorination roles of the copper(II)/KCl/attapulgite catalyst were then examined over a range of conditions that have direct connectivity with an industrial process, as they potentially constitute external control parameters.

The changes in conditions have an implication for the reaction scheme that was reported earlier [31], notably an increased role for the chlorination route occurring via $CHCl=CCl_2$ (reactions (1) then (2) in Fig. 1) compared with the direct chlorination of $CHCl_2CHCl_2$ (reaction (3) in Fig. 1). They have also allowed clarification of conditions under which oligomerization, with its undesirable environmental and economic effects (reactions (5) and (6)), may occur.

3.1. Reactions under chlorine-rich conditions

3.1.1. 1,1,2,2-Tetrachloroethane with dichlorine (1:3 mol ratio) under homogeneous conditions, i.e. in the absence of Cu^{II} catalyst

The temperature relationships for mean conversions of $CHCl_2CHCl_2$ and mean carbon mass balances for 1,1,2,2-tetrachloroethane + $3Cl_2$, total volumetric flow 25 ml min^{-1}, are contained in Fig. 2(a) and (b), respectively.

The reaction profile is similar to that observed under chlorine lean conditions in that $CHCl=CCl_2$ is the only product observed, however, mean conversions of $CHCl_2CHCl_2$ at a given temperature, Fig. 2(a) are higher than those observed under a chlorine-lean regime [31]. The most significant difference is that the carbon mass balance shows a significant deficit (ca. 20%) at 623 K and above, Fig. 2(b). It is suggested that, when conversion of $CHCl_2CHCl_2$ becomes significant, the high concentration of carbon-centred radicals present, leads to the chlorine atom initiated formation of dimeric and oligomeric species, which being relatively involatile, results in the carbon mass imbalance observed. These results