Products and mechanism of the reaction of Cl atoms with unsaturated alcohols

Ana Rodríguez [a,*], Diana Rodríguez [a], Amparo Soto [a], Iván Bravo [a], Yolanda Diaz-de-Mera [b], Alberto Notario [b], Alfonso Aranda [b]

[a] Faculty of Environmental Sciences and Biochemistry, University of Castilla La Mancha, Avenida Carlos III, s/n, 45071 Toledo, Spain
[b] Faculty of Chemistry, University of Castilla La Mancha, Avenida Camilo José Cela, n° 10, 13071 Ciudad Real, Spain

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ABSTRACT

The products of the chlorine atom initiated oxidation of different unsaturated alcohols were determined at atmospheric pressure and ambient temperature, in a 400 L teflon reaction chamber using GC−FID and GC−MS for the analysis. The major products detected (with molar yields in brackets) are: chloroacetaldehyde (50 ± 8%) and acrolein (27 ± 2%) from allyl alcohol; acetaldehyde (77 ± 11%), chloroacetaldehyde (75 ± 18%), and methyl vinyl ketone (17 ± 2%) from 3-buten-2-ol; acetone (55 ± 4%) and chloroacetaldehyde (59 ± 8%) from 2-methyl-3-buten-2-ol; chloroacetone (18 ± 1%) and methacrolein (8 ± 1%) from 2-methyl-2-propen-1-ol; acetaldehyde (20 ± 1%), crotonaldehyde (6 ± 3%), 3-choloro-4-hydroxy-2-butanone (2 ± 2%) and 2-chloro-propanal (4 ± 5%) from crotyl alcohol; and acetone (24 ± 3%) from 3-methyl-2-buten-1-ol. The experimental data suggests that addition of Cl to the double bond of the unsaturated alcohol is the dominant reaction pathway compared to the H-abstraction channel.

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1. Introduction

Surface O_3 background concentrations have been increasing since the industrial revolution as a result of increasing emissions of its precursors. Ozone can induce several health problems (e.g., Hazucha and Lefohn, 2007; Zelm et al., 2008) and it can also damage crops or vegetation (e.g., Gimeno et al., 2004; Fishman et al., 2010; Vlachokostas et al., 2010; Avnery et al., 2011a, 2011b), posing a major problem mainly in Mediterranean countries in Southern Europe, which are characterised by elevated levels of photochemical air pollution. Tropospheric O_3 is generated photochemically in the presence of NOx (NO + NO_2), solar radiation and volatile organic compounds, VOCs, including alcohols such as those studied in this work (Steiner et al., 2007; Chan et al., 2009). Within these photochemical processes, Cl + VOCs reactions may play an important role in the troposphere compared to the oxidation by OH. Under slightly elevated concentrations of Cl, e.g., in urban coastal environments, where Cl can reach levels of up to 1×10^4 molecule cm^{-3}, Cl-initiated VOCs oxidation can increase morning ozone concentrations by as much as 12 ppb (e.g., Knipping and Dabdub, 2003; Pechtl and von Glasow, 2007; Cohan et al., 2008; Ravishankara, 2009).

Generally, alcohols are directly emitted into the atmosphere from biogenic and anthropogenic sources. Thus, for example, 2-methyl-3-buten-2-ol (MBO232) has been measured from few specific species of pine and other trees and also from various types of vegetation (Harley et al., 1998; Kesselmeier and Staudt, 1999; Schade and Goldstein, 2002). The oxidation mechanism of alcohols leads to aldehydes, ketones, and organic nitrates as major products (Grosjean et al., 1993; Fantechi et al., 1998a; Ferronato et al., 1998; Alvarado et al., 1999; Noda et al., 2000). Nevertheless, only few kinetic and product studies are available in literature about the gas-phase reactions of unsaturated alcohols with Cl atoms (e.g., Fantechi et al., 1998b; Rodríguez et al., 2010 and Takahashi et al., 2010). In this paper we present the first determination of the reaction products for the reactions of Cl with 2-propen-1-ol (allyl alcohol), 3-buten-2-ol, MBO232, crotyl alcohol, 3-methyl-2-buten-1-ol (MBO321) and 2-methyl-2-propen-1-ol (MPO221). The selected alcohols may be regarded as methyl substituted derivates of the basic alcohol 2-propen-1-ol, thus the influence of the number of methyl groups and their position could be assessed. To the best of our knowledge, only a relative study carried out by Takahashi et al. (2010) for reactions of chlorine atoms with allyl alcohol, 3-buten-2-ol, and 2-methyl-3-buten-2-ol has been reported. They studied the degradation mechanism and obtained the molar yields for HCl production in 700 Torr of N_2.

In order to identify and quantify the reaction products, we have used GC−FID/MS as the sampling and detection technique. The

* Corresponding author.
  E-mail address: anamaria.rodriguez@uclm.es (A. Rodríguez).

results allow us to propose a mechanism for the studied reactions. Given the nature of the products identified, their atmospheric implications are briefly discussed.

2. Experimental

The experimental systems and the procedures used in this work have been described at great length previously (Rodríguez et al., 2010). Only details relevant to the present study are briefly described below. The experiments were conducted in a ∼400 L Teflon bag, which was placed inside an isothermal cabinet with 6 fluorescent lamps (Philips TUV G13. 36 W) mounted on the walls. Cl atoms were generated by photolysis of CCl_3COCl. Cl_2 was not used as source of Cl atoms since Cl_2 was found to react with the title alcohols at the concentrations used for this work (Rodriguez et al., 2007, 2008). The irradiation time was not continuous and the photolysis was typically carried out in steps of 60–300 s with a conversion of reactant between 80 and 92%. In addition, irradiation experiments were performed in absence of the source of chlorine atoms to verify that direct photolysis of the studied alcohols did not occur. The stability and wall losses of the individual alcohols were investigated by introducing them into the Teflon chamber and monitoring the concentration over time. The loss rate was insignificant compared to the rate of reaction in all cases.

The initial reactant concentrations were (1.6–6.0×10^{15} molecule cm^{-3}) for unsaturated alcohols and (1.3–9.8×10^{15} molecule cm^{-3}) for CCl_3COCl at atmospheric pressure of synthetic air and 298 ± 1 K. The products formed in the reaction of Cl atoms with the studied alcohols were measured during the experiments by GC–MS (Shimadzu QP 2010) for their identification and by GC–FID (Shimadzu, 2010) for their quantification. In both cases, the gas sample was directly introduced into the GC with an automatic 6 ways valve and a 1 mL loop evacuated with a vacuum pump. The temperature program used in both chromatographs on a 30 m Meta.X5 column was the following: 40 °C (8 min), 10 °C/min to 100 °C and hold 3 min.

The identification of the products was made by analysis of the mass spectrum and by comparison with a library of spectra. When possible, the identification was also performed by comparing with the retention time of a commercial sample of the detected product. When this identification was not possible a tentative assignment was proposed. In order to determine the concentrations of the different reactants and products detected, the GC–FID response factors of each compound were determined by introducing different known amounts of the commercial sample into the Teflon chamber and conducting several replicate analyses. Based on these analyses, the GC–FID measurement errors for the alcohols and products detected were typically 1–4%, except for MBO321 (10%) whose measurements were technically more difficult to make due to its lower vapor pressure. Product yields were obtained from plots of the amount of product formed against the amount of reactant lost. For compounds not commercially available, the yields were estimated using the effective carbon number method, ECN (Scanlon and Willis, 1985).

The chemicals used and their stated purities were as follows: Allyl alcohol (Fluka, ≥99.5%), 3-buten-2-ol (Aldrich, 97%), MBO232 (Aldrich, 98%), Crotyl alcohol (Aldrich, 96%), MBO321 (Acros, 99%) MPO221 (Fluka, 98%), Acetaldehyde (Aldrich, ≥99.5%), Acrolein (Fluka, ≥99.9%), Methyl-vinyl-ketone (Aldrich, 99%), Acetone (Aldrich, ≥99.9%), Crotonaldehyde (Aldrich, ≥99%), Methacrolein (Aldrich, 95%), Chloroacetone (Aldrich, 95%), 4-hydroxy-2-butanone (Aldrich, 95%). Synthetic air was supplied by a Peak Scientific Generator (model ZA035A), which has a hydrocarbon/methane content lesser than 0.01 ppm. He (Air Liquide, 99.998%) was used as the GC carrier gas. Liquid samples were degassed several times by trap-to-trap distillation before use.

3. Results

The degradation of unsaturated alcohols is expected to proceed predominantly through addition of the oxidant to the less substituted double bond carbon atom, forming the most stable radical (Wayne et al., 1990; Atkinson, 1997). Nevertheless, the addition to the more substituted double bond carbon atom and the H-abstraction have also been observed and need to be considered (Noda et al., 2000; Alvarado et al., 1999).

The chloroalkyl radicals formed in the Cl addition reactions add O_2 to form the corresponding chloroalkyl peroxy radicals. Under our experimental conditions, i.e., in absence of NO, the peroxy radicals can either undergo self-reaction or reaction with other peroxy radicals in the system, giving rise the corresponding chloroalkoxy radical. The later reactions of the alkoxy radicals are the crucial step to determine the product distribution, since these radicals can decompose by C–C bond scission or react with O_2 (Atkinson, 1997). The observed results in our work for the oxidation of unsaturated alcohols by Cl atoms are described below.

3.1. Allyl alcohol

In the reaction of Cl atoms with allyl alcohol, the compounds identified from the mass spectrum and the retention times of commercially available samples were chloroacetaldehyde and acrolein. In order to determine the yields of the main reaction products, Fig. 1(a) represents the formation of the observed products versus the loss of unsaturated alcohol. Primary products may also react towards Cl atoms. Thus, for example, in the case of acrolein, Fig. 1(a), a significant degree of curvature is observed for the larger extent of reaction values, revealing the occurrence of secondary chemistry. If such reactions were neglected, the yields on primary products would be underestimated. Thus, adjustments have been made to the experimental concentration values of the primary products to take into account the consumption resulting from secondary reactions with Cl atoms. The approach for determining corrections uses a two step mechanism, the formation of a product (P) due to reaction of Cl with the unsaturated alcohol followed by Cl reaction with P. Other processes are assumed to be negligible. This approach yields the following equation (Atkinson et al., 1982):

$$F = \frac{k_A - k_P}{k_A} \times \frac{1 - \dfrac{[\text{alcohol}]_t}{[\text{alcohol}]_0}}{\left(\dfrac{[\text{alcohol}]_t}{[\text{alcohol}]_0}\right)^{\frac{k_P}{k_A}} - \dfrac{[\text{alcohol}]_t}{[\text{alcohol}]_0}}$$

where F represents the correction, k_A the rate constant for the reaction of Cl atoms with the unsaturated alcohol, k_P the rate constant for the reaction of Cl + P, and $[\text{alcohol}]_t$ and $[\text{alcohol}]_0$ are the unsaturated alcohols concentrations at time $t = t$ and $t = 0$, respectively. The product $(F \times [P]_t)$ (where $[P]_t$ is the experimental concentration product profile) gives the concentration of the primary product at a time t if it was not consumed by the secondary reaction with Cl. Thus, the plot of $(F \times [P]_t)$ versus the consumed reactant $([\text{alcohol}]_0 - [\text{alcohol}]_t)$ provides the yield from the slope:

$$F \times [P]_t = \alpha([\text{alcohol}]_0 - [\text{alcohol}]_t)$$

This treatment was applied to the data obtained for all the studied compounds and the percentage of correction in each case is shown in Table 1. The plots of the corrected concentration products against the amount of reacted alcohol are shown in Figs. 1–6. In all cases, straight line plots with zero intercepts were obtained, what