Kinetic and Mechanistic Study of the Reactions of OH Radicals with Some Oxygenated VOC under Simulated Atmospheric Conditions

Guest contribution

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Introduction

For several years, anthropic emissions of oxygenated volatile organic compounds have increased. Alcohols, ethers and esters are widely used in paints and are employed in fuels as substitutes for lead alkyls or as alternative fuels. Hydroxyl radicals are the major sink of these compounds during the day. Their photo-oxydation chain contributes to the production of photo-oxidants such as ozone. However, models usually do not take them into account because too little is known about these compounds in the atmosphere. Therefore to assess their impact on tropospheric ozone production, a kinetic and mechanistic knowledge of the OH-induced oxidation of these species is needed. The few kinetic data available are often scattered (Wallington *et al.*, 1988, Le Calvé *et al.*, 1997, Veillerot *et al.*, 1996) and mechanistic studies are rare (Smith *et al.*, 1992).

The purpose of this work is, first, to determine rate constant data for the reaction of OH with some alcohols, ethers and esters, then to identify the reaction products in order to understand the photo-oxidation mechanisms. Methanol, ethanol, MTBE, ETBE, and ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, and *t*-butyl acetates were studied.

Experimental

Experiments were carried out at 298 ± 4 K and atmospheric pressure in a PFE film bag equipped with an irradiation system. Rate constants were determined by the relative rate technique and VOCs were analysed by gas chromatography.

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Analysis of carbonyl reaction products was also performed : the reactive mixture was sampled in bubbler containing 2,4 dinitrophenylhydrazine and analysed by HPLC with UV detection at 360 nm.

Hydroxyl radicals were produced by photolysis of hydrogen peroxide at 254 and 310 nm (a) or by photolysis of methyl nitrite at 370 and 420 nm (b).

a) $H_2O_2 + h\nu \rightarrow 2\ OH$

b) $CH_3ONO + h\nu \rightarrow CH_3O + NO$

$CH_3O + O_2 \rightarrow HO_2 + HCHO$

$HO_2 + NO \rightarrow OH + NO_2$

Reference compounds for relative kinetic studies were *n*-pentane, *n*-hexane and methanol. Their OH-oxidation rate constants are respectively 3.96, 5.55 and 0.93×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Atkinson, 1992, Atkinson *et al.*, 1997).

Kinetic results and discussion

An example of the kinetic plots, $\ln([X]_0/[X]_t)$ vs. $\ln([R]_0/[R]_t)$, (where $[X]_0$ and $[R]_0$, and $[X]_t$ and $[R]_t$ are, respectively, the concentrations of the selected compound and the reference compound at times 0 and *t*) is given in Fig. 1.

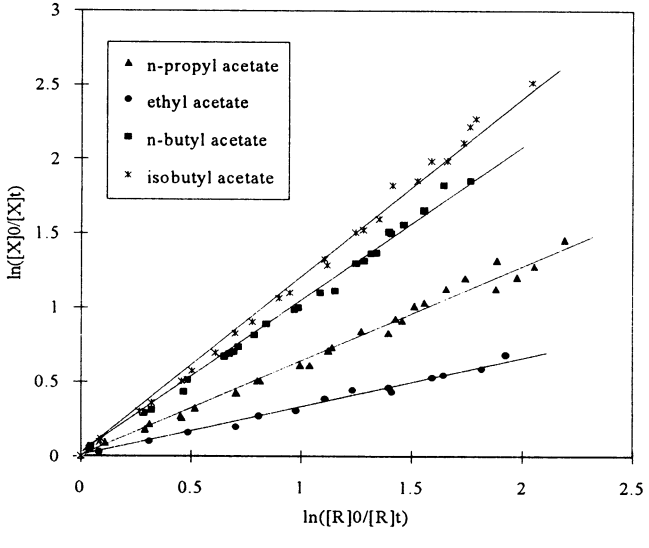

Fig. 1: Plots of relative kinetic experiments for some oxygenated VOCs.

The rate constants obtained are given in Table 1. The written error limits of our values represent 2σ from the linear least-squares analysis. These values have been compared to the previous data and to the calculated ones, using the structure-reactivity relationship (Kwok and Atkinson, 1995). The previous data are not given here but are discussed in a more complete paper, Picquet *et al.*

From the available values for each compound studied, we tried to point out coherent group of values in agreement, and when this was possible, we have suggested a recommended rate constant at 298 ± 4 K and at atmospheric pressure. These recommendations are based on a unit-weighted least-squares analysis of each correlated group of data. These values are given in Table 1. Concerning isobutyl and *t*-butyl acetates, the few available data do not allow us to suggest any recommended values.

Table 1: Experimental, recommended and calculated rate constants for the reaction of OH with some oxygenated VOC at 298 K and atmospheric pressure.

Compounds	$k_{experimental} \times 10^{12}$ [(a)]	$k_{recommended} \times 10^{12}$ [(a)]	$k_{SAR} \times 10^{12}$ [(a)]
methanol	0.90 ± 0.08 (*n*-pentane)	0.91 ± 0.24	0.48
ethanol	3.88 ± 0.11 (*n*-hexane)	3.4 ± 0.5	3.44
MTBE	2.98 ± 0.06 (*n*-pentane)	3.0 ± 0.5	1.64
ETBE	8.52 ± 0.61 (*n*-hexane)	8.8 ± 1.2	8.51
ethyl acetate	1.69 ± 0.13 (*n*-pentane) 1.83 ± 0.11 (*n*-hexane) 1.79 ± 0.17 (*n*-hexane) 1.61 ± 0.12 (methanol)	1.7 ± 0.2	1.76
n-propyl acetate	3.56 ± 0.15 (*n*-hexane)	3.5 ± 0.9	3.30
isopropyl acetate	3.96 ± 0.10 (*n*-hexane) 3.98 ± 0.18 (n-hexane)	3.6 ± 0.7	3.54
n-butyl acetate	5.78 ± 0.15 (*n*-hexane)	5.1 ± 1.4	4.70
isobutyl acetate	6.71 ± 0.15 (*n*-hexane) 6.83 ± 0.32 (*n*-hexane)	-	4.66
t-butyl acetate	0.56 ± 0.03 (methanol)	-	0.60

[(a)] In units of cm^3 $molecule^{-1}$ s^{-1}

From these results, we also notice that the agreement between experimental and calculated values is not good for methanol and isobutyl acetate. Concerning methanol, since many experiments are in good agreement, it is probable that the SAR is not reliable for that compound. Concerning the linear

acetates, the agreement between the calculated and the experimental rate constants decreases with the number of carbon (1.7 % for ethyl acetate and 18 % for *n*-butyl acetate).

Reaction products

For acetates, an identification of some reaction products has been performed. For linear acetates, large amounts of formaldehyde have been identified at the end of the experiment. Formaldehyde can be a primary product (from H abstraction on a primary carbon of the acetate) or a secondary one (from the photolysis of other aldehydes, for example). Acetaldehyde, propionaldehyde and butyraldehyde have also been detected in small amounts (depending on the compound studied).

Concerning the photo-oxidation of isopropyl and isobutyl acetates, acetone is the major carbonyl reaction product (around 80 % of the acetate). It indicates that the H-abstraction occurs mainly on the tertiary carbon. For *t*-butyl acetate, acetone and formaldehyde have also been detected in large amounts.

But to elucidate the mechanism, it is necessary to improve the budget of carbon by using other analytical devices like FTIR and DOAS.

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