

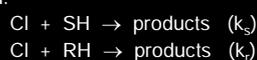
K. Hemavibool, T. Malkin, P. Seakins, A. Goddard, D. Glowacki, M. Pilling, and D. Heard
 University of Leeds, Leeds, LS2 9JT, UK. chmkhe@leeds.ac.uk

Introduction

Esters are one important class of VOCs used in plastic industry and manufacture of food flavoring and perfumes. They are also present in fruits and are emitted to the atmosphere naturally. The reaction of esters with Cl atoms could be significant in areas where high level of Cl atoms has been present, such as coastal regions.

In this study, relative rate measurements have been used to provide further information concerning the kinetics of Cl atom reactions with a series of acetates. In the previous work from Notario et al.¹ and Cuevas et al.² absolute rate studies of Cl atoms with ethyl acetate, *n*-propyl acetate and *n*-butyl acetate have a systematic discrepancy of approximately 30–40%, providing an objective for our study.

The relative rate method is a relative determination of the reactions of a reactive species with two hydrocarbon compounds. One is a reference compound (RH), which the rate coefficient is known so that the rate coefficient for study compound (SH) can be determined.



The rate of disappearance can be expressed by:

$$-d[\text{SH}]/dt = k_s[\text{Cl}][\text{SH}]$$

$$-d[\text{RH}]/dt = k_r[\text{Cl}][\text{RH}]$$

Combining these rate expressions and integrating:

$$\ln([\text{SH}]_0/[\text{SH}]_t) = k_s/k_r \ln([\text{RH}]_0/[\text{RH}]_t)$$

Hence the absolute calibration and direct measurement of highly reactive radicals is not required for this method.

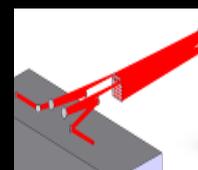
Instruments

HIRAC³ is a 2 m³ stainless steel cylindrical reactor capable of operating at a range of pressures and temperatures with 8 rows of photolysis lights. The experiments were carried out at room temperature in the chamber at 1000 mbar of total pressure of N₂. Kinetic data were derived by monitoring loss of acetates and reference compounds using GC-FID and FTIR.

HIRAC chamber



Multipass FTIR



Bruker IFS/66; Modified Chernin cell operates (120 m path length).

Gas Chromatography

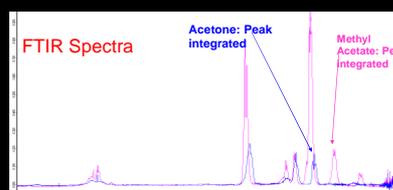
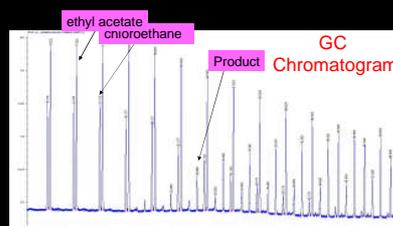
- Temp controlled oven with FID (HP6890)
- 40 m, 0.18 mm i.d., column coated with 100% Dimethylpolysiloxane (J&W, DB-1)
- Gas sampling valve with 5 ml sample loop
- Isothermal analysis

Relative rate measurements of Cl with acetates

Conditions

Acetates: 3 ppm
 Reference standards: acetone, chloroethane, ethane, *i*-butane, cyclohexane 3 ppm
 Precursor: Cl₂ 6 ppm, (COCl)₂ 20 ppm
 $\text{Cl}_2 + h\nu \rightarrow 2\text{Cl} \quad (\lambda > 300 \text{ nm})$
 $(\text{COCl})_2 + h\nu \rightarrow 2\text{CO} + 2\text{Cl} \quad (\text{UV})$
 Reactants Ratio: 1:1, 1:3, 3:1

Good agreement independent technique, precursor, reference or reactant ratio



Relative rate plot

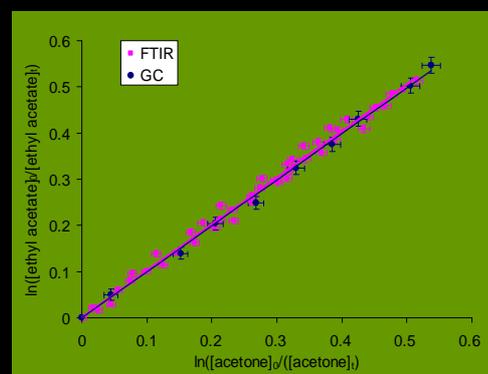


Table 1 Summary of rate constants for the reaction of Cl atoms with acetates: comparison between the experimental results and the calculated values using the SAR method

Compound	$k_r/10^{11}$ $\text{cm}^3/\text{molecule} \text{ s}^{-1}$	Technique	Reference	$k_{\text{calc}}^a/10^{11}$ $\text{cm}^3/\text{molecule} \text{ s}^{-1}$	$k_{\text{calc}}^b/10^{11}$ $\text{cm}^3/\text{molecule} \text{ s}^{-1}$
Methyl Acetate	0.21 ± 0.04	RR	This Work	0.20	0.20
	0.29 ± 0.04	PLP-RF	Notario et al., 1998		
	0.22 ± 0.03	RR	Christensen et al., 2000		
Ethyl Acetate	0.28 ± 0.03	PLP-RF	Cuevas et al., 2005		
	2.20 ± 0.29	RR FTIR	This Work	2.92	2.19
	2.01 ± 0.25	PLP-RF	Notario et al., 1998		
<i>n</i> -Propyl Acetate	1.35 ± 0.20	PLP-RF	Cuevas et al., 2005		
	7.88 ± 0.41	RR-FTIR	This Work	9.48	7.64
	7.76 ± 0.92	PLP-RF	Notario et al., 1998		
<i>n</i> -Butyl Acetate	4.60 ± 0.41	PLP-RF	Cuevas et al., 2005		
	15.8 ± 1.3	RR-FTIR	This Work	14.7	11.4
	17.4 ± 2.0	PLP-RF	Notario et al., 1998		
	12.3 ± 3.4	PLP-RF	Cuevas et al., 2005		

^a Calculated values using factors $F(\text{-CO})$ and $F(\text{C}(\text{O})\text{O-})$; ^b Calculated values using factors $F(\text{-C}(\text{O})\text{OCH}_3)$.

The results show that the rate constant increases with the number of CH₂ groups in the ester molecule and reactivity of methyl acetate is much lower than others. The low k_r value confirms the strong deactivating effect of -C(O)O- group on CH₃ in the α position as observed with ketones⁵.

The structure-activity relationship (SAR) method developed by Atkinson⁶ has been applied to the reactions of esters with Cl atoms. As proposed by previous workers^{1,2}, the SAR calculated using substituent factors $F(\text{-CO})$ and $F(\text{C}(\text{O})\text{O-})$ is in good agreement with only methyl acetate. It seems that the C(O)O- group has also a deactivating effect on the carbon group in the β position which is not accounted for in SAR method. A better agreement between experiment results and calculated values by using this substituent factor are shown in the last column of Table 1.

Summary

From a high precision instrument, relative rate studies can obtain excellent quantitative agreement of rate constant for acetates and Cl atoms between GC and FTIR. The results are consistent with Notario et al. study but are approximately 20% higher than the results from the results from Cuevas et al.

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