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Gas-phase reactivity of acyclic α,β-unsaturated carbonyls towards ozone

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We evaluated different approaches to discuss the reactivity of α,β-unsaturated carbonyls comparative to alkene analogues. It was found that the reactivity factors x_r, defined as the relative ratio between the rate coefficient of the carbonyl and a core structure, allow a semi-quantitative estimation of substituent effects in α,β-unsaturated acids, aldehydes and esters when the carbonyl containing substituent is replaced by a hydrogen atom. By contrast, it can be shown that the reactivity of the corresponding ketones differs from the other carbonyls. A linear correlation is presented between the x_r – values and the number of carbon atoms of the alkyl group of the unsaturated esters, which can be used to predict ozonolysis rate coefficients. For this systematic analysis the following rate coefficients (in 10^{-18} cm^3 molecule^{-1} s^{-1}) have been determined at 298 ± 2 K and 990 ± 15 mbar and under dry conditions using the relative rate method: $k(O_3$ + methyl methacrylate) = 7.0 ± 0.9, $k(O_3$ + methyl crotonate) = 5.5 ± 1.4, $k(O_3$ + methyl 3-methyl-3-butenoate) = 1.3 ± 0.3, $k(O_3$ + methyl tiglate) = 65 ± 11, $k(O_3$ + 3-penten-2-one) = 31 ± 7, $k(O_3$ + 3-methyl-3-penten-2-one) = 80 ± 19, $k(O_3$ + 4-methyl-3-penten-2-one) = 8.4 ± 0.8.

Introduction

Unsaturated carbonyls are a particular class of OVOCs (Oxygenated Volatile Organic Compounds) emitted into the atmosphere from biogenic and anthropogenic sources. Esters like methyl methacrylate are important intermediates in the polymer industry.[1] Unsaturated ketones are mainly used in the food and fragrances industry.[2,3] 4-Methyl-3-penten-2-one is also utilized for the production of methyl isobutyl ketone (MIBK), a common polar solvent with wide applications in the manufacturing of pharmaceuticals, paints and coatings.[4]

Once released into the atmosphere, the α,β-unsaturated carbonyls are removed by the reaction with atmospheric oxidants like OH and NO_3 radicals, O_3 or halogen atoms. Considering the time profile of atmospheric concentrations for these species the oxidation by OH radicals will be the dominating process during the daytime[5] whereas NO_3 radical reactions can only contribute during the night due to their rapid photolysis. The ozonolysis reactions potentially play a role during both day and night. In depth investigation of these processes is relevant for completion of data sets to be used in chemical modelling.

Several studies have shown that unsaturated carbonyls exhibit an unexpected high reactivity towards OH radicals indicating a mechanism other than the simple addition to an olefinic bond.[6,7] The kinetics of the ozonolysis reactions of a moderate number of α,β-unsaturated carbonyls have been studied using both the absolute and relative rate method.[8–27] However, the systematic analysis of their reactivity towards O_3 is at best at the beginning.[28]

It is quite common to relate a target compound to the reactivity of its core structure in order to explain and/or predict its behaviour towards one of the atmospheric oxidants. In literature, these core structures were obtained by replacing the substituent of interest with –H, –CH_3 or the elimination of the carbonyl group as the most common approaches. However, in the case of ozonolysis reactions the resulting conclusion is usually just that carbonyls are less reactive then their core structure due to the deactivating inductive effect of the carbonyl moiety upon olefinic bonds. Neither a comparison of the different approaches nor a systematic analysis of different functional groups has been carried out yet.

In this work a critical comparison of the various selection methods for the core reference structure was performed and tested on the quantification of substituent effects in series of α,β-unsaturated acids, aldehydes, ketones and esters.

In order to enlarge the kinetics data base for reactivity and modelling studies we determined the rate coefficients for the compounds summarised in Table 1 using the relative rate technique and FTIR spectrometry. This work, to the best of our knowledge, represents the first determination of the rate coefficients for methyl 3-methyl-2-butenoate and methyl tiglate with O_3. For methyl crotonate and 3-methyl-3-penten-2-one we report here the first rate constant determination using FTIR spectrometry.

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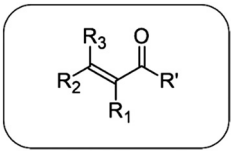
Table 1 General structure of α,β-unsaturated carbonyls and substitution pattern of the compounds studied within this work. Replacement of R′ with –H or –OH would lead to the corresponding α,β-unsaturated aldehydes and acids, respectively

Structure	R′	R_1	R_2	R_3	Compound IUPAC nomenclature	Other name	Abbreviation
	$-CH_3$	–H	$-CH_3$	–H	Pent-3-en-2-one	3-Penten-2-one	3P2
	$-CH_3$	$-CH_3$	$-CH_3$	–H	(*E*)-3-Methylpent-3-en-2-one	3-Methyl-3-penten-2-one	3M3P2
	$-CH_3$	–H	$-CH_3$	$-CH_3$	4-Methylpent-3-en-2-one	4-Methyl-3-penten-2-one	4M3P2
	$-OCH_3$	–H	$-CH_3$	–H	Methyl (*E*)-but-2-enoate	Methyl crotonate	MCrot
	$-OCH_3$	$-CH_3$	–H	–H	Methyl 2-methylprop-2-enoate	Methyl methacrylate	MMA
	$-OCH_3$	$-CH_3$	$-CH_3$	–H	Methyl (*E*)-2-methylbut-2-enoate	Methyl tiglate	MTig
	$-OCH_3$	–H	$-CH_3$	$-CH_3$	Methyl 3-methylbut-2-enoate	Methyl 3,3-dimethylacrylate	M3M2B

Experimental

All experiments were carried out in a 1080 L quartz-glass reaction chamber in (990 ± 15) mbar of synthetic air at (298 ± 2) K. Only a brief description of the chamber will be given here as further details can be found in the previous literature.[29] The chamber is closed at both ends by metal flanges bearing several ports for the injection of reactants, addition of bath gases and coupling with analytical devices. The pumping system consists of a turbo-molecular pump backed by a double-stage rotary fore pump. The chamber can be evacuated to 10^{-4} mbar. Homogeneity of the reaction mixtures is achieved by three magnetically coupled Teflon mixing fans which are evenly placed in the chamber. A White-type mirror system is installed inside the chamber to monitor reaction mixtures *via* FTIR spectrometry in the spectral range 4000–700 cm^{-1} and a resolution of 1 cm^{-1}. The system whose base length is (5.91 ± 0.01) m was operated at 82 traverses which yields a total optical path length of (484.7 ± 0.8) m. Spectra were recorded using a Nicolet iS50 instrument equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector.

During each experiment 50–120 interferograms were co-added per spectrum which results in an averaging period of about 80–190 s. Typically, 15 spectra were recorded per experiment and the first five spectra were collected without oxidant over a period of 20–30 min to check for potential wall losses of the target compound and the reference. After that the reaction was started by single or multiple injection of O_3 which was generated by passing a stream of pure oxygen through an electrical discharge in a homemade device. The observed reaction time was usually 20–40 min.

The initial mixing ratios in ppmV (1 ppmV = 2.46 × 10^{13} molecules cm^{-3} at 298 K) were: 0.6–0.8 for methyl methacrylate (MMA), 0.6–0.8 for methyl crotonate (MCrot), 0.3 for methyl 3-methyl-2-butenoate (M3M2B), 0.6–0.7 for methyl tiglate (MTig), 1.0–1.2 for 3-penten-2-one (3P2), 1.3–1.8 for 3-methyl-3-penten-2-one (3M3P2), 1.2–1.8 for 4-methyl-3-penten-2-one (4M3P2), 1.3–1.7 for cyclohexene, 1.1 for isoprene, 0.8–0.9 for ethene, 0.9–1.9 for 2-methylpropene, 0.8–1.9 for *E*2-butene, 0.9–1.9 for 1,3-butadiene and 6000–17 000 for carbon monoxide.

Materials

The following chemicals were used without further purification (purities as stated by the suppliers): 2-methylpropene (Aldrich, 99%), ethene (Aldrich, 99.5%), *E*2-butene (Messer, >99%), 1,3-butadiene (Messer, >99%), cyclohexene (Aldrich, 99%), isoprene (Aldrich, 99%), carbon monoxide (Air Liquide, 99.97%), methyl methacrylate (Aldrich, 99%), methyl crotonate (Aldrich, 98%), methyl 3-methyl-2-butenoate (Aldrich, 97%), methyl tiglate (Alfa Aesar, 98%), 3-penten-2-one (Alfa Aesar, tech. 85%), 3-methyl-3-penten-2-one (Aldrich, tech. 90%), 4-methyl-3-penten-2-one (Aldrich, tech. 90%), synthetic air (Messer, 99.9999%), oxygen (Messer, 99.5%). The *cis*/*trans* isomer ratio for commercially available 3-penten-2-one is not specified.

Results and discussion

The rate coefficients for the gas-phase ozonolysis reactions of selected α,β-unsaturated carbonyls were determined relative to the O_3 reactions of at least two references for each target compound. The results are shown in Table 2. Preliminary results of *n*-butyl acrylate and *n*-hexyl methacrylate have been included in the discussion of reactivity trends. As these data will be part of a separate publication no experimental details are given here.

Rate coefficients

The relative rate technique relies on the assumption that both target compound and reference are solely removed by the oxidant as follows

$$\text{carbonyl} + O_3 \rightarrow \text{products}; \quad k_{\text{carbonyl}} \qquad (1)$$

$$\text{reference} + O_3 \rightarrow \text{products}; \quad k_{\text{reference}} \qquad (2)$$

However the unsaturated carbonyls are potentially subject of an irreversible first-order wall loss:

$$\text{carbonyl} + \text{wall} \rightarrow \text{wall}; \quad k_{\text{wall}} \qquad (3)$$

Considering all these processes the following equation can be derived:

$$\ln\left(\frac{[\text{carbonyl}]_0}{[\text{carbonyl}]_t}\right) - k_{\text{wall}} \times t = \frac{k_{\text{carbonyl}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) \qquad (4)$$

where $[X]_t$ is the concentration of the species X at time *t*. If the initial assumption is correct, a plot of $\left\{\ln\left(\frac{[\text{carbonyl}]_0}{[\text{carbonyl}]_t}\right) - k_{\text{wall}} \times t\right\}$ against $\left\{\ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)\right\}$ should yield a straight line where the slope represents the relative ratio between

Table 2 Ozonolysis of unsaturated carbonyls. Summary of the results of the relative rate study

Compound	Reference	No. of runs	Consumption/% min–max	$k_{carbonyl}/k_{reference}$	$k_{carbonyl} \times 10^{18}$/ cm^3 molecule^{-1} s^{-1}
Methyl methacrylate	2-Methylpropene	5		0.61 ± 0.03	6.9 ± 2.3
	Ethene	3		4.57 ± 0.30	7.3 ± 2.4
			31–53	**Average**	**7.0 ± 0.9**
Methyl crotonate	2-Methylpropene	3		0.45 ± 0.01	5.1 ± 1.6
	Ethene	3		3.88 ± 0.20	6.2 ± 1.9
	1,3-Butadiene	1		0.69 ± 0.03	4.4 ± 1.3
			41–60	**Average**	**5.5 ± 1.4**
Methyl 3-methyl-2-butenoate	1,3-Butadiene	3		0.19 ± 0.01	1.2 ± 0.4
	Ethene	3		0.90 ± 0.03	1.4 ± 0.4
			15–27	**Average**	**1.3 ± 0.3**
Methyl tiglate	Cyclohexene	4		0.87 ± 0.04	68 ± 11
	*E*2-Butene	3		0.32 ± 0.02	60 ± 22
			35–65	**Average**	**65 ± 11**
3-Penten-2-one	Cyclohexene	3		0.38 ± 0.02	30 ± 5
	2-Methylpropene	1		2.76 ± 0.06	31 ± 9
	Isoprene	1		2.64 ± 0.04	34 ± 9
			26–64	**Average**	**31 ± 7**
3-Methyl-3-penten-2-one	2-Methylpropene	3		6.33 ± 0.34	72 ± 22
	Cyclohexene	3		0.98 ± 0.04	77 ± 11
	*E*2-Butene	3		0.48 ± 0.01	92 ± 32
			32–67	**Average**	**80 ± 19**
4-Methyl-3-penten-2-one	2-Methylpropene	5		0.72 ± 0.02	8.1 ± 2.5
	1,3-Butadiene	3		1.39 ± 0.02	8.7 ± 2.7
			34–62	**Average**	**8.4 ± 0.8**

$k_{carbonyl}$ and $k_{reference}$. The relative rate plots of the investigated species are shown in Fig. 1. The loss rates were typically in the range of (1–4) × 10^{-5} s^{-1} for the wall loss and (1–7) × 10^{-4} s^{-1} for the loss due to the ozonolysis reaction. Only 3-penten-2-one and methyl crotonate showed a higher variability of the wall loss rate ranging from 0.6 × 10^{-4} s^{-1} to 2.4 × 10^{-4} s^{-1} and from 0.1 × 10^{-4} s^{-1} to 1.6 × 10^{-4} s^{-1}, respectively. Ozonolysis reactions are known to produce OH radicals with yields up to unity and beyond.[30] To scavenge any OH radical formed in the experimental system an excess of CO was added. The linear fit of all kinetic plots are going through the origin within a statistical error of 3σ resulting from the regression analysis. Both scavenger efficiency and insignificant intercepts lead to the conclusion that secondary reactions can be neglected in the present experimental set-up. Hence, the obtained relative ratios $\frac{k_{carbonyl}}{k_{reference}}$ listed in Table 2 solely result from the ozonolysis reaction. The errors represent the 2σ statistical error of the linear regression analysis.

The relative ratios were put on an absolute basis using the following rate coefficients for room temperature recommended by Calvert *et al.*[30] in 10^{-18} cm^3 molecule^{-1} s^{-1}: k(O$_3$ + ethene) = 1.59 ± 30%, k(O$_3$ + 2-methylpropene) = 11.3 ± 30%, k(O$_3$ + *E*2-butene) = 190 ± 35%, k(O$_3$ + 1,3-butadiene) = 6.3 ± 30% and k(O$_3$ + isoprene) = 12.8 ± 25%. For cyclohexene the latest recommendation given by Stewart *et al.*[31] has been used: k(O$_3$ + cyclohexene) = (7.8 ± 1.1) × 10^{-17} cm^3 molecule^{-1} s^{-1}. The rate coefficients for the target species determined with each reference are listed in Table 2. The errors represent the statistical error from the regression analysis and the uncertainty of the reference rate coefficient. For the final results given as the mean of all determinations the arithmetic and the weighted means were compared and found to be insignificantly different. However, the error of the weighted average becomes quite small in some cases. Therefore, to cover all experimental uncertainties we thus prefer to indicate the arithmetic mean together with the corresponding 2σ error.

The following rate coefficients (in 10^{-18} cm^3 molecule^{-1} s^{-1}) were determined: k(O$_3$ + MMA) = 7.0 ± 0.9, k(O$_3$ + MCrot) = 5.5 ± 1.4, k(O$_3$ + M3M2B) = 1.3 ± 0.3, k(O$_3$ + MTig) = 65 ± 11, k(O$_3$ + 3P2) = 31 ± 7, k(O$_3$ + 3M3P2) = 80 ± 19, k(O$_3$ + 4M3P2) = 8.4 ± 0.8. The rate coefficients for methyl methacrylate and 4-methyl-3-penten-2-one are in excellent agreement with previous determinations.[8–10,12] The ozonolysis of 3-penten-2-one has been subject of three previous studies.[11–13] While consistent with Greene and Atkinson[11] and Sato *et al.*[12] the rate coefficient determined in this work is around 30% higher than the first determination reported in literature.[13] However, as already pointed out by Greene and Atkinson,[11] the first determination *via* an absolute rate technique was probably affected by an impurity present in the samples, namely 4-methyl-3-penten-2-one. Thus, this value will not be considered further in the following discussion about reactivity trends.

The kinetics of 3-methyl-3-penten-2-one with ozone has been theoretically[14] and experimentally[15] investigated, once each. The theoretical investigation by RRKM theory[14] yielded a rate coefficient of 2.28 × 10^{-16} cm^3 molecule^{-1} s^{-1}, which

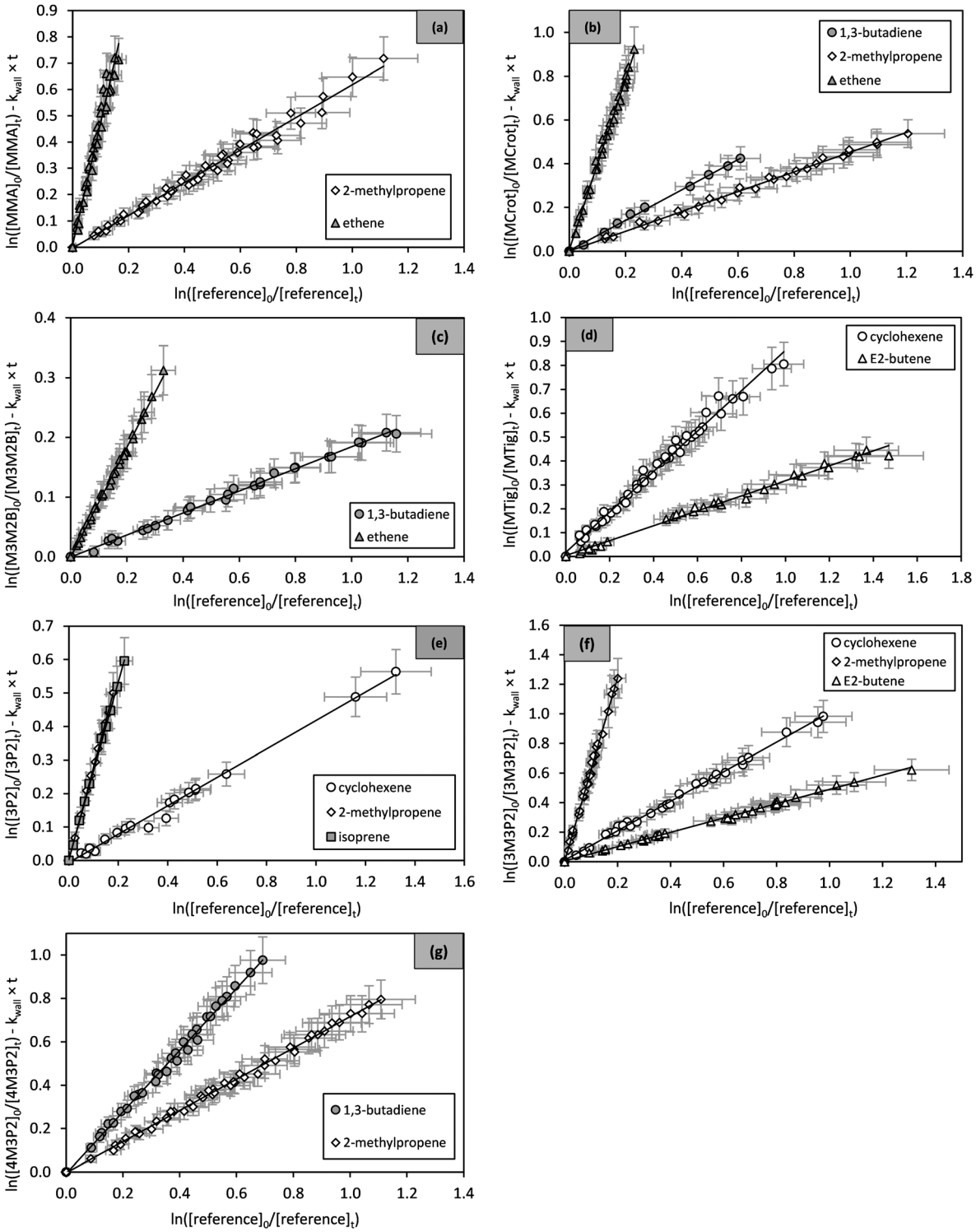


Fig. 1 Relative rate plots of (a) methyl methacrylate, (b) methyl crotonate, (c) methyl 3-methyl-2-butenoate, (d) methyl tiglate, (e) 3-penten-2-one, (f) 3-methyl-3-penten-2-one and (g) 4-methyl-3-penten-2-one. The error bars consist of a 10% systematic error estimated from evaluation uncertainties.

is around three times larger than the value of $(80.1 \pm 18.7) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} determined in this work. On the other hand, the rate coefficient reported by Wang and co-workers[15] is 50% smaller. They determined $k(O_3 + 3M3P2)$ with an absolute method by observing the decay of ozone, using a commercial O_3-analyzer, at different concentrations of 3-methyl-3-penten-2-one. Ozone monitors based on UV absorption are known to be affected by an interference caused by UV absorbing species.[32] Even when negligible under atmospheric conditions this effect becomes more relevant at higher

levels of the undesired absorber.[33–35] Preliminary tests in our laboratory have shown 3-methyl-3-penten-2-one to photolyze when irradiated at 254 nm. Besides, Wang and co-workers[15] do not report any test on possible interferences. Hence, this effect would have been undetected in their experimental set-up and subsequently have led to an underestimation of the decay of ozone. The same reason could apply for methyl crotonate. The rate coefficient determined in this work is, within the experimental uncertainties, still in satisfactorily agreement with the previous study by Grosjean *et al.*[8]

The rate coefficients for methyl 3-methyl-2-butenoate and methyl tiglate were experimentally determined within this work for the first time. Gallego-Iniesta and co-workers[36] predicted both to be 10.5×10^{-18} cm^3 molecule^{-1} s^{-1} using a SAR approach with group-reactivity factors given by Pfrang *et al.*[37] While their predictions overestimate the rate coefficients for methyl 3-methyl-2-butenoate by a factor of 8 they underestimate $k(O_3 + \text{MTig})$ by a factor of 6. A similar divergence is observed using the recent SAR approach by Jenkin *et al.*,[28] which yields a predicted rate coefficient of 6.5×10^{-18} cm^3 molecule^{-1} s^{-1} for both species. The reason for these differences will be tentatively explained in the following sections.

Reactivity trends

It is commonly accepted that ozonolysis reactions proceed *via* a concerted 1,3-dipolar cycloaddition with the electrophilic character of the dipole being dominant. Therefore the rate coefficients should be related to the electron density in the olefinic bond. Different groups were building SAR correlations in an attempt to fill the gaps where experimental determination of rate constants is missing. McGillen *et al.*[38] developed a SAR method for the prediction of ozonolysis rate constants for heteroatomic unsaturated species based on the summation of steric and inductive effects and concluded that, even when not negligible, the steric effects are of minor importance. Besides, the compounds studied here do not contain bulky alkyl substituents and differ only in the number and position of the methyl groups attached to the olefinic bond. Hence, it should be possible to explain the reactivity in terms of inductive effects only.

However, a weakness in reactivity discussions is identifying the core structure, to which the kinetics of the target compounds is related. Here, in order to identify the effect of the carbonyl containing substituent a useful approach is the comparison with the structural analogue alkene. As an attempt to quantify the substituent effects a non-dimensional reactivity factor x_r is used defined as the ratio between k_{carbonyl} and k_{alkene}.

$$x_r = \frac{k_{\text{carbonyl}}}{k_{\text{alkene}}} \quad (5)$$

However, in the literature different approaches for establishing analogue structures can be found by replacing the substituent of interest by either (a) a hydrogen atom[7,12,16] or (b) a methyl group[6] or by (c) elimination of the –C(O)– or –C(O)O– moiety.[5,10] In Fig. 2 these methods are explained using as examples methyl methacrylate and methyl crotonate. For both

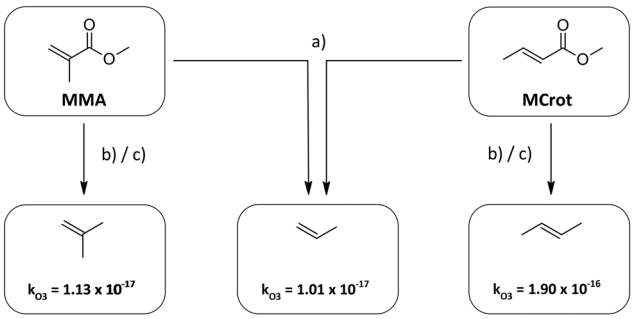


Fig. 2 Determination of the analogue structures of methyl methacrylate (MMA) and methyl crotonate (MCrot) according to the different methods. The rate constants for the alkenes are taken from Calvert *et al.*[30]

compounds the first method yields propene as analogue structure, thus (a) is not able to distinguish between certain substitution patterns. Nevertheless, a hydrogen atom would be the only neutral species without substituent effect.

According to method (b) and (c), on the other hand, the analogue alkenes are 2-methylpropene and *E*2-butene, respectively. Since $k(O_3 + \text{propene}) \approx k(O_3 + \text{2-methylpropene})$ all approaches yield the same x_r – value in the case of methyl methacrylate. For methyl crotonate though the results differ significantly due to the much larger rate coefficient of *E*2-butene compared to propene caused by the inductive effect of the *trans*-substituted methyl group. Thus method (b) potentially overestimates the deactivating effect of the carbonyl substituent.

Table 3 summarises reactivity factors calculated for a series of unsaturated esters, ketones and aldehydes using the rate coefficients obtained in the present study and literature data, where available. Only species where α- and β-position are substituted with either –H or –CH$_3$ are taken into account. The recommended values given by Calvert *et al.*[30] have been used for the rate coefficients of the analogue alkenes. To compare the different approaches, we considered that the analogue alkenes resulted from replacing the –C(O)R moiety by both (a) a hydrogen atom and (b) a methyl group. For the compounds listed here method (c), *i.e.* the elimination of the –C(O)– or –C(O)O– moiety, leads to the same structures as method (b) for the ketones and methyl esters and method (a) for the aldehydes, respectively.

Based on the electron-withdrawing inductive effect of the carbonyl group and the resonance (mesomeric effect) due to the conjugated olefinic bond one would expect α,β-unsaturated carbonyls to be less reactive than the analogue alkenes and thus $x_r < 1$ for both methods. Method (b) yields reactivity factors between 0.003 and 0.66. This large deviation can be observed even when aldehydes, ketones and methyl esters are treated separately. Besides that, there is no information on a tendency or strength of the deactivating effect of the carbonyl moiety to be gained from this method. Thus, the replacement of the substituent by a methyl group seems not to yield further conclusions.

On the other hand, the replacement by a hydrogen atom, method (a), leads to more consistent results. Except for methyl

Table 3 Summary of the rate coefficients of the gas-phase ozonolysis of α,β-unsaturated ketones, esters and aldehydes and their corresponding reactivity factors according to method (a) and (b). The errors of x_r represent the 2σ statistical error of the mean value. If only one determination is available, the error reflects the relative error of the rate coefficient

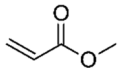
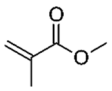
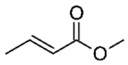
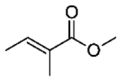
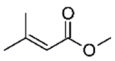
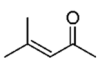
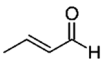
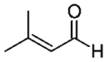
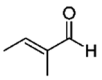
Compound	Reference	T/K	$k_{carbonyl} \times 10^{18}$/ cm^3 molecule^{-1} s^{-1}	Alkene analogue[a]	x_r[a]	Alkene analogue[b]	x_r[b] $\times 10^2$
methyl acrylate 	Grosjean and Grosjean[17]	291	1.05 ± 0.15	Ethene	0.6	Propene	10.4
	Al Mulla *et al.*[18]	298 ± 3	1.19 ± 0.11	Ethene	0.75	Propene	11.8
	Al Mulla *et al.*[18]	298 ± 3	1.00 ± 0.05	Ethene	0.63	Propene	9.9
	Bernard *et al.*[9]	294	0.95 ± 0.07	Ethene	0.60	Propene	9.4
	Average		**1.1 ± 0.2**		**0.66 ± 0.13**		**10.4 ± 2.1**
methyl methacrylate 	Grosjean *et al.*[8]	291	7.5 ± 0.9	Propene	0.74	2-Methylpropene	66.4
	Bernard *et al.*[9]	294	6.7 ± 0.9	Propene	0.66	2-Methylpropene	59.3
	Al Mulla *et al.*[18]	298 ± 3	5.75 ± 0.52	Propene	0.57	2-Methylpropene	50.9
	Al Mulla *et al.*[18]	298 ± 3	6.66 ± 0.60	Propene	0.66	2-Methylpropene	58.9
	Ren *et al.*[10]	291	6.63 ± 0.38	Propene	0.66	2-Methylpropene	58.7
	This work	298 ± 2	7.0 ± 0.9	Propene	0.70	2-Methylpropene	62.3
	Average		**6.7 ± 1.2**		**0.66 ± 0.11**		**59.4 ± 10.2**
methyl crotonate 	Grosjean *et al.*[8]	291	4.4 ± 0.3	Propene	0.44	*E*2-Butene	2.3
	This work	298 ± 2	5.5 ± 1.4	Propene	0.54	*E*2-Butene	2.9
	Average		**4.9 ± 1.5**		**0.49 ± 0.15**		**2.6 ± 0.8**
methyl tiglate 	**This work**	**298 ± 2**	**65 ± 11**	*Z*2-Butene	**0.52 ± 0.08**	2-Methyl-2-butene	**16.0 ± 2.6**
methyl 3-methyl-2-butenoate 	**This work**	**298 ± 2**	**1.3 ± 0.3**	2-Methyl-propene	**0.12 ± 0.03**	2-Methyl-2-butene	**0.3 ± 0.1**
methyl vinyl ketone 	Atkinson *et al.*[13]	296	4.77 ± 0.59	Ethene	3.00	Propene	47.2
	Treacy *et al.*[19]	298 ± 4	4.20 ± 0.40	Ethene	2.64	Propene	41.6
	Grosjean and Grosjean[17]	291	5.84 ± 0.39	Ethene	3.67	Propene	57.8
	Neeb *et al.*[20]	296 ± 2	5.4 ± 0.6	Ethene	3.40	Propene	53.5
	Al Mulla *et al.*[18]	298 ± 3	4.16 ± 0.33	Ethene	2.62	Propene	41.2
	Al Mulla *et al.*[18]	298 ± 3	4.48 ± 0.20	Ethene	2.82	Propene	44.4
	Average		**4.8 ± 1.4**		**3.02 ± 0.86**		**47.6 ± 13.5**
3-penten-2-one 	Greene and Atkinson[11]	296	36.6 ± 1.6	Propene	3.62	*E*2-Butene	19.2
	Sato *et al.*[12]	298	29.5 ± 4.1	Propene	2.92	*E*2-Butene	15.5
	This work	298 ± 2	31 ± 7	Propene	3.07	*E*2-Butene	16.3
	Average		**32.4 ± 7.4**		**3.20 ± 0.74**		**17.0 ± 3.9**
3-methyl-3-penten-2-one 	**This work**	**298 ± 2**	**80 ± 19**	*Z*2-Butene	**0.64 ± 0.15**	2-Methyl-2-butene	**19.9 ± 4.6**
4-methyl-3-penten-2-one 	Sato *et al.*[12]	298	8.3 ± 1.1	2-Methyl-propene	0.73	2-Methyl-2-butene	2.1
	This work	298 ± 2	8.4 ± 0.8	2-Methyl-propene	0.74	2-Methyl-2-butene	2.1
	Average		**8.3 ± 0.1**		**0.74 ± 0.01**		**2.1 ± 0.1**
acrolein 	Atkinson *et al.*[13]	296	0.28 ± 0.05	Ethene	0.18	Propene	2.8
	Treacy *et al.*[19]	298 ± 4	0.30 ± 0.04	Ethene	0.19	Propene	3.0
	Grosjean *et al.*[8]	286	0.26 ± 0.05	Ethene	0.16	Propene	2.6
	Al Mulla *et al.*[18]	298 ± 3	0.363 ± 0.035	Ethene	0.23	Propene	3.6
	Al Mulla *et al.*[18]	298 ± 3	0.336 ± 0.022	Ethene	0.21	Propene	3.3
	Average		**0.31 ± 0.08**		**0.19 ± 0.05**		**3.1 ± 0.8**
	Atkinson *et al.*[13]	296	1.12 ± 0.13	Propene	0.11	2-Methylpropene	9.9
	Treacy *et al.*[19]	298 ± 4	1.1 ± 0.2	Propene	0.11	2-Methylpropene	9.7
	Grosjean and Grosjean[17]	290	1.08 ± 0.20	Propene	0.11	2-Methylpropene	9.6
	Neeb *et al.*[20]	296 ± 2	1.3 ± 0.14	Propene	0.13	2-Methylpropene	11.5

Table 3 (*continued*)

Compound	Reference	T/K	$k_{carbonyl} \times 10^{18}$/ cm^3 molecule^{-1} s^{-1}	Alkene analogue[a]	x_r[a]	Alkene analogue[b]	x_r[b] $\times 10^2$
methacrolein 	**Average**		**1.2 ± 0.2**		**0.11 ± 0.02**		**10.2 ± 1.8**
crotonaldehyde 	Atkinson *et al.*[13]	296	0.90 ± 0.18	Propene	0.09	*E*2-Butene	0.5
	Grosjean and Grosjean[17]	290	1.74 ± 0.20	Propene	0.17	*E*2-Butene	0.9
	Sato *et al.*[12]	298 ± 2	1.58 ± 0.23	Propene	0.16	*E*2-Butene	0.8
	Average		**1.4 ± 0.9**		**0.14 ± 0.09**		**0.7 ± 0.5**
3-methyl-2-butenal 	**Sato *et al.*[12]**	**298 ± 2**	**1.82 ± 0.26**	2-Methyl-propene	**0.16 ± 0.02**	2-Methyl-2-butene	**0.5 ± 0.1**
tiglic aldehyde 	**Sato *et al.*[12]**	**298 ± 2**	**5.34 ± 0.73**	*Z*2-Butene	**0.04 ± 0.01**	2-Methyl-2-butene	**1.3 ± 0.2**

3-methyl-2-butenoate whose reactivity towards ozone is less than the analogue alkene by a factor of 10, for all unsaturated methyl esters in Table 3 the average x_r – value calculated with method (a) is 0.58 ± 0.19. For the α,β-unsaturated aldehydes a reactivity factor of 0.13 ± 0.11 can be obtained which has been similarly reported by Sato *et al.*[12] Tiglic aldehyde is at the lower limit of the reactivity range, however, up to date only one value was reported.[12]

It can be concluded that the –C(O)OCH$_3$ moiety reduces the reactivity of the olefinic bond towards ozone by 23–61% whereas the –C(O)H moiety yields a reduction of reactivity by 76–98%. These findings agree well with fundamentals of organic chemistry postulating that the strength of the $-I$ effect varies as following:

$$\text{–C(O)H} > \text{–C(O)–} > \text{–C(O)OR} \quad (6)$$

The x_r – values for 3-methyl-3-penten-2-one and 4-methyl-3-penten-2-one are 0.64 ± 0.15 and 0.74 ± 0.01, respectively, and thereby close to the reactivity of the methyl esters. For methyl vinyl ketone (MVK) and 3-penten-2-one (3P2) though the factors are 3.02 ± 0.86 and 3.20 ± 0.74. Hence, while consistent for α,β-unsaturated methyl esters and aldehydes, this approach seems not to be commonly valid for the unsaturated ketones. This is even more surprising as $x_r \gg 1$ indicates a significant enhancement of reactivity towards ozone compared to the structural analogue alkene. Intuitively, this is a contradiction to the well-known deactivating effect of a single carbonyl substituent. Earlier studies have shown that α,β-unsaturated ketones like 3-penten-2-one exhibit also an unexpected high reactivity towards OH radicals,[6] which was tentatively attributed to the formation of a hydrogen-bonded transition state.[39,40] However, the formation of such a complex is not possible in case of ozone.

One can argue that experimentally determined rate coefficients might be influenced by the secondary reaction of stabilized CI (= Criegee Intermediate) with carbonyl compounds. Higher than expected rate coefficients of ozonolysis reactions have been reported for acrylic and methacrylic acid when working without sufficient quantities of a CI scavenger.[20] By contrast, no such effect was detected for MVK.[20] For 3-penten-2-one no such experimental results are available but a similar behaviour toward CIs is expected. Hence it seems plausible to assume that the high rate coefficients obtained here and reported previously[11,12] are not the product of secondary consumption by CIs.

Several attempts have been made for the prediction of ozonolysis rate coefficients at room temperature. King *et al.*[41] used perturbation frontier molecular orbital theory (PFMO) and correlated the natural logarithm of the rate coefficients with the energy of the highest occupied molecular orbital (HOMO) over a small range of E_{HOMO}. Pfrang and co-workers updated this concept, originally developed for the prediction of OH, NO$_3$ and O$_3$ reactions of alkenes and conjugated dialkenes only, and extended its applicability to unsaturated ketones, esters, alcohols and ethers.[37,42–44] These studies yielded structure–activity relations with group-reactivity factors those predictability has been shown to be less accurate for O$_3$ than for OH and NO$_3$.[37] McGillen *et al.*[38] improved the predictability of rate coefficients for ozonolysis reactions of heteroatomic unsaturated species by parameterisation of steric and inductive effects which yielded the definition of a new SAR index (x_H). In the case of 3-penten-2-one the rate coefficient calculated based on Pfrang *et al.*[37] and McGillen *et al.*[38] is 3.9 × 10^{-18} cm^3 molecule^{-1} s^{-1} and 5.4 × 10^{-18} cm^3 molecule^{-1} s^{-1}, respectively. This would indicate a lower reactivity towards ozone than propene which is contradicted by the experimentally obtained values. Thus none of these approaches captures the significant increase of reactivity

compared to the alkene analogue (resulting from replacement of the carbonyl containing substituent by a hydrogen atom) as observed here for methyl vinyl ketone and 3-penten-2-one. By contrast, the very recent SAR method by Jenkin *et al.*[28] predicts both ketones to be more reactive than their alkene analogues. However, the authors stated that, in contrast to the SAR modifications for alkenes, generic rate coefficients had to be assigned for α,β-unsaturated carbonyls (referred to as "vinylic oxygenated compounds") simply based on the experimental data of these ketones.[28]

In the liquid phase, α,β-unsaturated carbonyls are known to exhibit a reactivity other than the reactivity of an olefinic bond or a carbonyl group, respectively, but characteristic conjugate addition reactions (see for example: Rossiter and Swinger[45] and references therein). Due to conjugation, the olefinic bond and the carbonyl group are examined as a unit where π-electrons are delocalised thus lowering the electron density in the olefinic bond and reducing the reactivity towards electrophiles. The delocalisation of π-electrons is though limited to planar or nearly planar conformations. Hence, if resonance besides inductive effects significantly impacts the reduced reactivity of the α,β-unsaturated aldehydes and methyl esters, it may be possible that in 3P2 and MVK non-planar conformations are energetically favoured and therefore their reactivity cannot be compared directly with the α,β-unsaturated esters. However, this is just speculation and detailed quantum mechanical calculations are needed to whether support or refuse this hypothesis.

One could intuitively also imagine that the reactivity of 3P2 and MVK indicates an ozonolysis mechanism other than a 1,3-dipolar cycloaddition yielding a 1,2,3-trioxoalane. Criegee already discussed the alternative formation of a σ-complex or a peroxy-epoxide in the liquid phase for systems in which epoxides have been observed.[46] However, if this is rate-determining for 3P2 and MVK it should be reflected in the product distribution. At least for MVK methylglyoxal and formaldehyde have been identified as main products, which is in agreement with the initially formed trioxolane.[47,48] This reasoning may thus be ruled out.

The outstandingly low rate coefficient for methyl 3-methyl-2-butenoate in comparison to the other α,β-unsaturated methyl esters indicates additional effects reducing its reactivity towards ozone. One could intuitively imagine that the *Z*-substituted methyl group and the $-C(O)OCH_3$ moiety could repel each other in the initially formed trioxolane. However, this effect cannot be observed in the ketone analogue (4-methyl-3-penten-2-one) whose reactivity is close to the other methyl esters. Besides, as previously mentioned, steric effects are expected to play a minor role. Currently there is no convincing explanation for the low reactivity of methyl 3-methyl-2-butenoate towards ozone.

Dependence of x_r on the alkyl chain length

Literature data are even scarcer for ozonolysis reactions of α,β-unsaturated carbonyls with larger linear alkyl substituents attached to the carbonyl moiety. Among α,β-unsaturated ketones only rate coefficients for ethyl vinyl ketone[8] and 4-hexen-3-one[21] have been reported up to date. In the case of esters kinetic data were published for C_2 (4 compounds),[9,10,16,22,23] C_3 (1 compound)[10] and C_4 (2 compounds).[10,16] These information are shown in Table 4. In addition, preliminary results on the kinetics of *n*-butyl acrylate and *n*-hexyl methacrylate performed were included for a more comprehensive analysis. Very recently, Ren *et al.*[10] reported the kinetics of C_1–C_4 alkyl methacrylates and concluded that longer alkyl substituents may enhance the reactivity of the olefinic bond towards ozonolysis. They further interpreted their results as a proof that the ozonolysis reaction is an electrophilic process.

In order to establish a possible relationship between the alkyl chain length and the kinetics of ozonolysis reactions reactivity factors have been calculated for α,β-unsaturated esters according to method (a) using averaged data derived from all available literature references. Following this rationale, the alkyl substituent with zero carbon atoms corresponds to the α,β-unsaturated acids. Up to now, only two studies[18,20] reported rate coefficients for acrylic and methacrylic acid. While consistent for acrylic acid the rate coefficients for methacrylic acid differ by a factor of two. Al Mulla and co-workers[18] pointed out that, based on the given experimental details, no error in the experimental set-up could be identified and the discrepancies remain unexplained. The latter compound is therefore not considered further. As for the C_1 esters, methyl 3-methyl-2-butenoate, as discussed previously, has been excluded.

A plot of the averaged x_r – values against the carbon number of the alkyl chain yields a straight line with a surprisingly high correlation coefficient (Fig. 3). For a better overview the average values of each substance are also included. The variation of x_r for C_4 is unsatisfactorily large for one reason mainly. The literature references for *n*-butyl methacrylate[10,22] agree well and yield and average of $x_r = 0.98$ which would be much closer to the regression line. For *n*-butyl acrylate the unpublished rate coefficient determined in our laboratory is around 30% smaller ($x_r = 1.19$) than previously reported by Gai *et al.*[16] ($x_r = 1.51$). This difference, even when acceptable within experimentally uncertainties, significantly increases the average reactivity factor for C_4 and its statistical error.

The consistency of the x_r – values observed for the α,β-unsaturated methyl esters is exhibited also in the case of the C_2 esters where besides C_1 esters most data are available. Their reactivity towards ozone can be explained in the way the carbonyl containing substituent adjacent to the olefinic bond affects it. Even when different approaches exist in literature for the interpretation and quantification of substituent effects the addition principle, first introduced by Taft[49] and related to inductive and steric effects, has been generally accepted. Resonance effects have been included later on.[50] Furthermore, resonance, if its influence on the reactivity is measurable in comparison to the inductive effects, results from the conjugation between the olefinic bond and the carbonyl group only and thus should be nearly the same for all α,β-unsaturated esters. This fact is supported by the x_r – values obtained here for methyl esters (Table 3). Hence, the increasing reactivity factors with the alkyl chain length solely result from the positive inductive effect of the alkyl group. Linear regression analysis

Table 4 Summary of the rate coefficients of the gas-phase ozonolysis of α,β-unsaturated acids and esters with longer *n*-alkyl chain. For each determination the error of x_r represents the relative error of the rate coefficient. The errors of the average x_r for each C_n are the 2σ statistical error of the average if more than one determination is available

Alkyl rest	Compound	Reference	*T*/K	$k_{carbonyl} \times 10^{18}$/ cm^3 molecule^{-1} s^{-1}	x_r[a]
Acid (n = 0)	Acrylic acid	Neeb *et al.*[20]	296 ± 2	0.65 ± 0.13	0.41 ± 0.08
		Al Mulla *et al.*[18]	298 ± 3	0.76 ± 0.05	0.48 ± 0.03
		Al Mulla *et al.*[18]	298 ± 3	0.79 ± 0.07	0.49 ± 0.04
					0.46 ± 0.09
Ethyl (n = 2)	Ethyl acrylate	Bernard *et al.*[9]	294	1.3 ± 0.1	0.82 ± 0.06
	Ethyl methacrylate	Gai *et al.*[16]	293 ± 1	7.68 ± 0.88	0.76 ± 0.09
		Ren *et al.*[10]	291	7.74 ± 0.41	0.77 ± 0.04
		Average		**7.71 ± 0.09**	**0.76 ± 0.01**
	Ethyl 3,3-dimethylacrylate	Gaona-Colman *et al.*[23]	298 ± 2	8.2 ± 1.9	0.73 ± 0.17
	Ethyl crotonate	Gaona-Colman *et al.*[22]	298 ± 2	8.0 ± 1.8	0.79 ± 0.18
					0.77 ± 0.08
n-Propyl (n = 3)	*n*-Propyl methacrylate	Ren *et al.*[10]	291	8.46 ± 0.36	**0.84 ± 0.04**
n-Butyl (n = 4)	*n*-Butyl acrylate	Gai *et al.*[16]	293 ± 1	2.40 ± 0.29	1.51 ± 0.18
		Preliminary results[a]		1.9 ± 0.2	1.19 ± 0.11
		Average		**2.2 ± 0.3**	**1.35 ± 0.45**
	n-Butyl methacrylate	Ren *et al.*[10]	291	9.78 ± 0.58	0.97 ± 0.06
		Gaona-Colman *et al.*[22]	298 ± 2	10.0 ± 3.0	0.99 ± 0.30
		Average			**0.98 ± 0.03**
					1.16 ± 0.51
n-Hexyl (n =6)	*n*-Hexyl methacrylate	Preliminary results[b]		13.6 ± 1.4	**1.35 ± 0.14**

[a] Ongoing study in our laboratory (measured relative to ethene and 1,3-butadiene). [b] Ongoing study in our laboratory (measured relative to propene, 1,3-butadiene and isoprene).

yields an intercept of 0.45 ± 0.09 (2σ). Consequently, the pure –C(O)O– moiety, present in the unsaturated acids, reduces the reactivity of the olefinic bond by 46–64%. Irrespective of the experimental uncertainties this deactivation is a factor of 1.3 larger than for the unsaturated methyl esters. This is in agreement with the previously mentioned conclusion by Ren *et al.*[10] and in contradiction to earlier findings by Pfrang and co-workers[37] who stated the influence of R being rather small.

The transmission of an inductive effect σ through a molecule has been discussed in two originally alternative mechanisms: by either transmission along bonds or interaction through space (as reviewed for example by Exner[51] and references therein). The magnitude of σ according to the latter mechanism, irrespective of its total strength, has been described in literature[51] by different functions in dependence of r^{-n} where r is the distance between the atom of interest and the reactive centre of the molecule. This is equivalent to the intuitive notion that the effect of a substituent becomes smaller the more remote it is located. Hence, a logarithmic-like correlation between x_r and the number of carbon atoms would be expected where the reactivity factors for the esters with $n > 3$ become indistinguishable. However, the correlation between x_r and the number of carbon atoms shows a remarkable linearity indicating an inductive influence up to C_6 for the α,β-unsaturated esters. It would furthermore imply that the influence of every added methylene group is independent from the distance to the olefinic bond and no attenuation of the inductive influence would be visible. It would thus be more general to say for the unsaturated esters that while a carbonyl group has an electron-withdrawing effect,

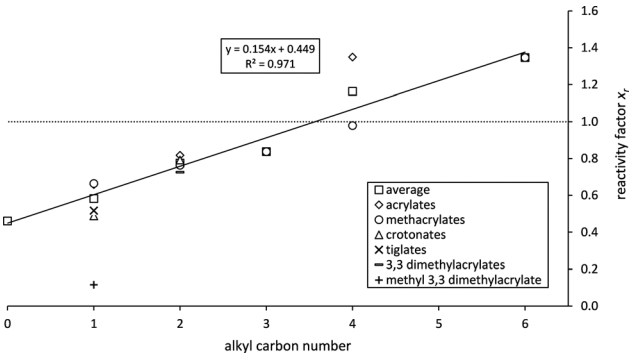


Fig. 3 Dependence of reactivity factors on the alkyl chain length. Error bars are not included for clarity. Methyl 3,3 dimethylacrylate (= methyl 3-methyl-2-butenoate) is, as discussed previously, not included in the correlation. The dashed line represents the alkene reactivity.

electron-donating alkyl groups are thus lowering the cumulative deactivating effect of the –C(O)OR substituent. The increase of the $+I$ – effect with the length of the alkyl group leads to an overcompensation of the electron-withdrawing effect in case of C_4 (= *n*-butyl) hence exceeding the reactivity of the alkene analogue (Fig. 3). It should be emphasized that these observations contradict our understanding of the inductive influence's transmission. The invariance of the reactivity of terminal alkenes towards ozone is well documented (see for example McGillen *et al.*[52] and references therein). Thus, longer alkyl groups attached to the olefinic bond do not further enhance the C=C double bond's reactivity. The presented correlation,

on the other hand, unambiguously shows the influence of longer alkyl substituents. Based on that, there seems to be a fundamental difference when the alkyl group is adjacent to the oxygen atom of the –C(O)O– moiety. This effect needs to be further investigated both experimentally and theoretically.

Structure–activity relations

The correlation in Fig. 3 allows to derive a formula for the group-reactivity factor of the carbonyl moiety:

$$f(\text{–C(O)OC}_n\text{H}_{2n+1}) = (0.154 \pm 0.026) \times n + (0.449 \pm 0.088) \quad (7)$$

where n is the number of carbon atoms attached to the oxygen atom and the errors represent the 2σ statistical error resulting from linear regression analysis. The rate coefficient of the ozonolysis reaction can be predicted using the relation:

$$k_{\text{O}_3} = k_{\text{basic}} \times f(\text{–C(O)OC}_n\text{H}_{2n+1}) \quad (8)$$

where k_{basic} is the rate coefficient of the alkene analogue resulting from replacing the –C(O)OR substituent by a hydrogen atom. This is a fundamental difference to previous SAR approaches where the basic structure reflects the number and position of all substituents and a methyl group is supposed to be neutral ($f(\text{–CH}_3) = 1$).[36,37] Table 5 summarises measured and predicted rate coefficients for all α,β-unsaturated carbonyls (except ketones) where literature data are available. Predicted values are given as well for a series of species where, to the best of our knowledge, no experimental data are available. To rate the predictability for each measured species a ratio r between the predicted and observed rate coefficient was calculated according to an equation previously used by McGillen and co-workers:[38]

$$r = (k_{\text{pred.}}/k_{\text{obs.}})^y \quad (9)$$

where $y = 1$ if $k_{\text{pred.}} > k_{\text{obs.}}$ and $y = -1$ if $k_{\text{pred.}} < k_{\text{obs.}}$.

For most of the listed species the predicted rate coefficients using the eqn (7) and (8) are similar to those based on the

Table 5 Predicted and observed rate coefficients (in 10^{18} cm^3 molecule^{-1} s^{-1}) of selected α,β-unsaturated carbonyls. If not indicated, the observed rate coefficients are taken from Tables 3 and 4

Compound (IUPAC nomenclature)	Other name	CAS	Alkene analogue	$k_{\text{obs.}}$	$k_{\text{pred.}}$ [a]	r [a]	$k_{\text{pred.}}$ [b]	r [b]
Prop-2-enal	Acrolein	107-02-8	Ethene	0.31	0.21	1.49		
2-Methylprop-2-enal	Methacrolein	78-85-3	Prop-1-ene	1.2	1.3	1.14	1.2	1.04
(*E*)-But-2-enal	Crotonaldehyde	123-73-9	Prop-1-ene	1.4	1.3	1.07	1.4	1.00
3-Methylbut-2-enal	3-Methyl-2-butenal	107-86-8	2-Methylprop-1-ene	1.8	1.5	1.24	1.8	1.01
(*E*)-2-Methylbut-2-enal	Tiglic aldehyde	497-03-0	(*Z*)-But-2-ene	5.3	16	3.05	5.7	1.07
2-Methylidenebutanal	2-Ethyl acrolein	922-63-4	But-1-ene[c]	1.1[d]	1.3	1.22	1.4	1.33
(*E*)-Pent-2-enal	*E*2-Pentenal	1576-87-0	But-1-ene[c]	1.4[e]	1.3	1.09	1.7	1.18
2-Methyl-2-pentenal[f]	2-Methyl-2-pentenal	623-36-9	(*Z*)-Pent-2-ene[g]	1.6[h]	17	10.87	6.8	4.29
			(*Z*)-Pent-2-ene	7.1[i]	17	2.42	6.8	1.05
(*E*)-Hex-2-enal	*E*2-Hexenal	6728-26-3	Pent-1-ene[c]	1.6[j]	1.3	1.19	1.9	1.25
(*E*)-Hept-2-enal	*E*2-Heptenal	18829-55-5	Hex-1-ene[c]	2.5[k]	1.3	1.90	2.2	1.12
(*E*)-Oct-2-enal	*E*2-Octenal	2548-87-0	Hept-1-ene[c]	2.4[k]	1.3	1.82	2.5	1.04
(*E*)-Non-2-enal	*E*2-Nonenal	18829-56-6	Octe-1-ne[c]	2.1[k]	1.3	1.58	2.7	1.33
Prop-2-enoic acid	Acrylic acid	79-10-7	Ethene	0.73	0.71	1.03		
2-Methylprop-2-enoic acid	Methacrylic acid	79-41-4	Prop-1-ene	4.1[l]	4.5	1.11	2.3	1.78
(*E*)-But-2-enoic acid	Crotonic acid	107-93-7	Prop-1-ene		4.5		2.3	
(*E*)-2-Methylbut-2-enoic acid	Tiglic acid	80-59-1	(*Z*)-But-2-ene		56		2.3	
(*E*)-Pent-2-enoic acid	*E*2-Pentenoic acid	13991-37-2	But-1-ene[c]	3.1[m]	4.5	1.46	2.7	1.12
Methyl prop-2-enoate	Methyl acrylate	96-33-3	Ethene	1.0	0.96	1.09	1.5	1.43
Methyl 2-methylprop-2-enoate	Methyl methacrylate	80-62-6	Prop-1-ene	6.7	6.1	1.10	6.5	1.03
Methyl (*E*)-but-2-enoate	Methyl crotonate	623-43-8	Prop-1-ene	4.9	6.1	1.24	6.5	1.32
Methyl (*E*)-2-methylbut-2-enoate	Methyl tiglate	6622-76-0	(*Z*)-But-2-ene	65	75	1.17	6.5	9.94
Methyl 3-methylbut-2-enoate	Methyl 3,3-dimethylacrylate	924-50-5	2-Methylprop-1-ene	1.3	6.8	5.21	6.5	4.96
Ethyl prop-2-enoate	Ethyl acrylate	140-88-5	Ethene	1.3	1.2	1.08	1.8	1.37
Ethyl 2-methylprop-2-enoate	Ethyl methacrylate	97-63-2	Prop-1-ene	7.7	7.7	1.01	7.7	1.00
Ethyl (*E*)-but-2-enoate	Ethyl crotonate	623-70-1	Prop-1-ene	8.0	7.7	1.05	7.7	1.03
Ethyl (*E*)-2-methylbut-2-enoate	Ethyl tiglate	5837-78-5	(*Z*)-But-2-ene		95		7.7	
Ethyl 3-methylbut-2-enoate	Ethyl 3,3-dimethylacrylate	638-10-8	2-Methylprop-1-ene	8.2	8.6	1.04	7.7	1.06
Propyl prop-2-enoate	Propyl acrylate	925-60-0	Ethene		1.5		2.1	
Propyl 2-methylprop-2-enoate	Propyl methacrylate	2210-28-8	Prop-1-ene	8.5	9.2	1.09	9.0	1.06
Butyl prop-2-enoate	*n*-Butyl acrylate	141-32-2	Ethene	2.1	1.7	1.26	2.4	1.10
Butyl 2-methylprop-2-enoate	*n*-Butyl methacrylate	97-88-1	Prop-1-ene	9.9	11	1.09	10	1.03
Butyl (*E*)-but-2-enoate	*n*-Butyl crotonate	591-63-9	Prop-1-ene		11		10	
Pentyl 2-methylprop-2-enoate	*n*-Amyl methacrylate	2849-98-1	Prop-1-ene		12		11	
Hexyl prop-2-enoate	*n*-Hexyl acrylate	2499-95-8	Ethene		2.2		2.9	
Hexyl 2-methylprop-2-enoate	*n*-Hexyl methacrylate	142-09-6	Prop-1-ene	14	14	1.02	13	1.07
Hexyl (*E*)-but-2-enoate	*n*-Hexyl crotonate	1617-25-0	Prop-1-ene		14		13	

[a] Based on eqn (7) and (8). [b] Based on Jenkin *et al.*[28] [c] An average value of 1.0×10^{-17} cm^3 molecule^{-1} s^{-1} has been used for the C_4–C_8 alk-1-enes. [d] Grosjean *et al.*[8] [e] Average of the rate coefficients determined by Sato *et al.*[12] and Kalalian *et al.*[24] [f] *trans*-Substitution has been assumed for the calculation. [g] The rate coefficient of Avzianova and Ariya[53] has been used for the calculation. [h] Kalalian *et al.*[24] [i] Gaona Colmán *et al.*[23] [j] Average of the rate coefficients determined by Atkinson *et al.*,[25] Grosjean *et al.*[26] and Kalalian *et al.*[24] [k] Gaona Colmán *et al.*[27] [l] Neeb *et al.*[20] [m] McGillen *et al.*[38]

Jenkin[28] approach. Huge discrepancies are found for substances where *Z*2-butene is the analogue structure according to method (a) as for ''vinylic esters and acids'' Jenkin and co-workers[28] only differentiate between two categories of substitution patterns, namely ethene and higher substituted alkenes. More experimental data are thus required. However, for the same reason the recent SAR method underestimates the experimentally determined rate coefficient of methyl tiglate by a factor of 10.

According to a similar rationale α,β-unsaturated aldehydes could be classified as C_0, 3-alken-2-ones as C_1, 4-alken-3-ones as C_2, and so on. However, an attempt to apply this treatment for aldehydes and ketones proved difficult first due to lack of reference data. For longer alkyl chains ($n > 2$) kinetic information are missing for target carbonyls. Even so the reactivity factors x_r for ethyl vinyl ketone and 4-hexen-3-one should be much lower than the values one obtains using method (a) directly, *i.e.* 3.77 and 6.34, respectively. The cause of the significant enhancement of the reactivity towards ozone observed for ketones comparative to other α,β-unsaturated carbonyls cannot be satisfactorily explained yet.

Nevertheless, the x_r – value determined for the aldehydes can also be applied to predict longer chain or higher substituted α,β-unsaturated aldehydes according to eqn (8) when using $f(\text{–CHO}) = 0.130$ instead of $f(\text{–C(O)OC}_n\text{H}_{2n+1})$. In doing so the *r*-values are <1.25 for methacrolein, crotonaldehyde, 3-methyl-2-butenal, 2-ethyl acrolein, *E*2-pentenal and *E*2-hexenal (Table 5). Exceptions are, as previously mentioned, tiglic aldehyde ($r = 3.05$) and 2-methyl-2-pentenal. For the latter compound two determinations of the rate coefficient (in 10^{-18} cm^3 molecule^{-1} s^{-1}) are found in the literature: 7.1 ± 1.6[23] ($r = 3.83$) and 1.58 ± 0.20[24] ($r = 17.21$). Kalalian *et al.*[24] argued that the difference of a factor of 5 can be attributed to an OH interference in the other study. On the contrary, Gaona Colmán *et al.*[23] argued that any influence of OH cannot be very significant based on similar results when determining the rate coefficient relative to the ozonolysis reaction of either 2-methylpropene or 1,3-butadiene. Thus, before rating the predictability of this species a re-determination of the rate coefficient is needed. On the other hand the predictive capacity of eqn (8) applied for aldehydes seems to be less accurate for longer *E*2-alkenals. But given that rate coefficients for C_7–C_9 *E*2-alkenals have only been determined once in the absence of an OH scavenger[27] it could also be worth re-investigating these compounds.

Conclusions

Room-temperature rate coefficients for the gas-phase ozonolysis of a series of acyclic α,β-unsaturated carbonyls have been determined using the relative rate technique. The discussion of reactivity in terms of a relative ratio between the target compound and a core structure has already been quite common. However, we have shown here that only the replacement of the carbonyl containing substituent by a hydrogen atom provides a useful tool for the quantification of the deactivating effect of the carbonyl moiety upon the olefinic bond in the case of ozonolysis reactions. This concept is validated by the consistency of the x_r – values of the α,β-unsaturated acids, esters with different *n*-alkyl chain length and aldehydes. The linearity between x_r and the number of carbon atoms up to C_6 further indicates a cumulative nature of the positive inductive effect of the alkyl group in the case of the esters. This is in contradiction to the intuitive notion that the influence of a substituent on a reactive centre is smaller the more remote it is located. This effect needs to be further investigated for a larger pool of substances to prove if the presented correlation is able to well predict rate coefficients for ozonolysis reactions. On the other hand, this concept points out that the reactivity of most of the ketones differs from other α,β-unsaturated carbonyls as shown by the large x_r – values. This effect solely becomes visible using method (a). In order to explain the complex reactivity of the ketones detailed quantum mechanical calculations are needed.

Conflicts of interest

There are no conflicts to declare.

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References

1 W. Bauer, Jr., *Ullmann's Encyclopedia of Industrial Chemistry*, 2011, DOI: 10.1002/14356007.a16_441.pub2.
2 C. Chapuis and D. Jacoby, *Appl. Catal., A*, 2001, **221**, 93.
3 D. R. Bickers, P. Calow, H. A. Greim, J. M. Hanifin, A. E. Rogers, J.-H. Saurat, I. G. Sipes, R. L. Smith and H. Tagami, *Regul. Toxicol. Pharmacol.*, 2003, **37**, 218.
4 S. Sifniades, A. B. Levy and H. Bahl, *Ullmann's Encyclopedia of Industrial Chemistry*, 2011, DOI: 10.1002/14356007.a01_079.pub3.
5 J. G. Calvert, A. Mellouki, J. J. Orlando, M. J. Pilling and T. J. Wallington, *The Mechanisms of Atmospheric Oxidation of the Oxygenates*, Oxford University Press, New York, 2011.
6 M. B. Blanco, I. Barnes and P. Wiesen, *J. Phys. Chem. A*, 2012, **116**, 6033.
7 J. P. Colomer, M. B. Blanco, A. B. Peñéñory, I. Barnes, P. Wiesen and M. A. Teruel, *Atmos. Environ.*, 2013, **79**, 546.
8 D. Grosjean, E. Grosjean and E. L. Williams, II, *Int. J. Chem. Kinet.*, 1993, **25**, 783.
9 F. Bernard, G. Eyglunent, V. Daële and A. Mellouki, *J. Phys. Chem. A*, 2010, **114**, 8376.
10 Y. Ren, M. Cai, V. Daële and A. Mellouki, *Atmos. Environ.*, 2019, **200**, 243.

11 C. R. Greene and R. Atkinson, *Int. J. Chem. Kinet.*, 1994, **26**, 37.
12 K. Sato, B. Klotz, T. Taketsuga and T. Takayanagi, *Phys. Chem. Chem. Phys.*, 2004, **6**, 3969.
13 R. Atkinson, S. M. Aschmann, A. M. Winer and J. N. Pitts, Jr., *Int. J. Chem. Kinet.*, 1981, **13**, 1133.
14 X. Wang, J. Sun, L. Bao, Q. Mei, B. Wie, Z. An, J. Xie and M. He, *J. Phys. Chem. A*, 2019, **123**, 2745.
15 J. Wang, L. Zhou, W. Wang and M. Ge, *Phys. Chem. Chem. Phys.*, 2015, **17**, 12000.
16 Y. Gai, M. Ge and W. Wang, *Chem. Phys. Lett.*, 2009, **473**, 57.
17 E. Grosjean and D. Grosjean, *Int. J. Chem. Kinet.*, 1998, **30**, 21.
18 I. Al Mulla, L. Viera, R. Morris, H. Sidebottom, J. Treacy and A. Mellouki, *ChemPhysChem*, 2010, **11**, 4069.
19 J. Treacy, M. E. Hag, D. O'Farrell and H. Sidebottom, *Ber. Bunsenges. Phys. Chem.*, 1992, **96**, 422.
20 P. Neeb, A. Kolloff, S. Koch and G. K. Moortgat, *Int. J. Chem. Kinet.*, 1998, **30**, 769.
21 E. Grosjean and D. Grosjean, *J. Atmos. Chem.*, 1999, **32**, 205.
22 E. Gaona Colmán, M. B. Blanco, I. Barnes and M. A. Teruel, *Chem. Phys. Lett.*, 2013, **579**, 11.
23 E. Gaona Colmán, M. B. Blanco, I. Barnes and M. A. Teruel, *Atmos. Environ.*, 2015, **109**, 272.
24 C. Kalalian, E. Roth and A. Chakir, *Int. J. Chem. Kinet.*, 2018, **50**, 47.
25 R. Atkinson, J. Arey, S. M. Aschmann, S. B. Corchnoy and Y. Shu, *Int. J. Chem. Kinet.*, 1995, **27**, 941.
26 E. Grosjean, D. Grosjean and J. S. Seinfeld, *Int. J. Chem. Kinet.*, 1996, **28**, 373.
27 E. Gaona Colmán, M. B. Blanco, I. Barnes and M. A. Teruel, *RSC Adv.*, 2015, **5**, 30500.
28 M. E. Jenkin, R. Valorso, B. Aumont, M. J. Newland and A. R. Rickard, *Atmos. Chem. Phys.*, 2020, **20**, 12921.
29 I. Barnes, K. H. Becker and N. Mihalopoulos, *J. Atmos. Chem.*, 1994, **18**, 267.
30 J. G. Calvert, R. Atkinson, J. A. Kerr, S. Maldronich, G. K. Moortgat, T. J. Wallington and G. Yarwood, *The Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford University Press, New York, 2000.
31 D. J. Stewart, S. H. Almabrok, J. P. Lockhart, O. M. Mohamed, D. R. Nutt, C. Pfrang and G. Marston, *Atmos. Environ.*, 2013, **70**, 227.
32 A. W. Turnipseed, P. C. Andersen, C. J. Williford, C. A. Ennis and J. W. Birks, *Atmos. Meas. Tech.*, 2017, **10**, 2253.
33 E. J. Dunlea, S. C. Herndon, D. D. Nelson, R. M. Volkamer, B. K. Lamb, E. J. Allwine, M. Grutter, C. R. Ramos Villegas, C. Marquez, S. Blanco, B. Cardenas, C. E. Kolb, L. T. Molina and M. J. Molina, *Atmos. Chem. Phys.*, 2006, **6**, 3163.
34 E. J. Williams, F. C. Fehsenfeld, B. T. Jobson, W. C. Kuster, P. D. Goldan, J. Stutz and W. A. McClenny, *Environ. Sci. Technol.*, 2006, **40**, 5755.
35 M. Fiedrich, R. Kurtenbach, P. Wiesen and J. Kleffmann, *Atmos. Environ.*, 2017, **165**, 57.
36 M. P. Gallego-Iniesta, B. Cabañas, S. Salgado, E. Martínez and P. Martín, *Atmos. Environ.*, 2014, **90**, 133.
37 C. Pfrang, M. D. King, C. E. Canosa-Mas, M. Flugge and R. P. Wayne, *Atmos. Environ.*, 2007, **41**, 1792.
38 M. R. McGillen, A. T. Archibald, T. Carey, K. E. Leather, D. E. Shallcross, J. C. Wenger and C. J. Percival, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2842.
39 I. W. M. Smith and A. R. Ravishankara, *J. Phys. Chem. A*, 2002, **106**, 4798.
40 A. Mellouki, G. Le Bras and H. Sidebottom, *Chem. Rev.*, 2003, **103**, 5077.
41 M. D. King, C. E. Canosa-Mas and R. P. Wayne, *Phys. Chem. Chem. Phys.*, 1999, **1**, 2231.
42 C. Pfrang, M. D. King, C. E. Canosa-Mas and R. P. Wayne, *Atmos. Environ.*, 2006, **40**, 1170.
43 C. Pfrang, M. D. King, C. E. Canosa-Mas and R. P. Wayne, *Atmos. Environ.*, 2006, **40**, 1180.
44 C. Pfrang, M. D. King, M. Braeckevelt, C. E. Canosa-Mas and R. P. Wayne, *Atmos. Environ.*, 2008, **42**, 3018.
45 B. E. Rossiter and N. M. Swingle, *Chem. Rev.*, 1992, **92**, 771.
46 R. Criegee, *Angew. Chem.*, 1975, **87**, 765.
47 D. Grosjean, E. L. Williams, II and E. Grosjean, *Environ. Sci. Technol.*, 1993, **27**, 830.
48 Y. Ren, B. Grosselin, V. Daële and A. Mellouki, *Faraday Discuss.*, 2017, **200**, 289.
49 R. W. Taft, *J. Am. Chem. Soc.*, 1952, **74**, 3120.
50 S. Ehrenson, R. T. C. Brownlee and R. W. Taft, *Prog. Phys. Org. Chem.*, 1973, **10**, 1.
51 O. Exner, *J. Phys. Org. Chem.*, 1999, **12**, 265.
52 M. R. McGillen, M. Ghalaieny and C. J. Percival, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10965.
53 E. V. Avzianova and P. A. Ariya, *Int. J. Chem. Kinet.*, 2002, **34**, 678.

