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Atmospheric fate of small alkoxy radicals: recent experimental and theoretical advances

Pascal Devolder*

Laboratoire de Cinétique et Chimie de la Combustion, UMR CNRS 8522, Physicochimie des Processus de Combustion et de l'Atmosphère, FR CNRS 2416, Centre d'Etudes et Recherches Lasers et Applications (CERLA), Université des Sciences et Technologies de Lille, 59655 Villeneuve, D'ascq Cedex, France

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Abstract

New results concerning the kinetics and the atmospheric fate of small alkoxy radicals (ethoxy, 1-propoxy, 2-propoxy, 2-butoxy, *t*-butoxy, and 3-pentoxy) are reviewed here. The three main reactions of atmospheric relevance are considered to be: the bimolecular reaction with O_2, the unimolecular isomerization, and the unimolecular decomposition. Concerning the latter, significant advances have been achieved thanks to the combination of direct time resolved techniques and theoretical (ab initio and statistical) calculations. Based on a reasonable accord between theory and experiment, a few simple structure activity relationships (SAR), proposed recently by different authors, are compared and should allow a reliable prediction of the unimolecular decomposition rate constant of many alkoxys. On the other hand, new measurements concerning the reaction of a few alkoxys with O_2 confirm that the generic value of $k_{O_2} = (8\pm2)\times10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$ at 298 K is indeed applicable for all alkoxy radicals. Concerning the unimolecular isomerization, all recent experimental data (from indirect experiments) confirm the order of magnitude estimates proposed by Atkinson [Int. J. Chem. Kinet. 29 (1997) 99] for the isomerization rate constants but only direct absolute measurements, still lacking, will allow a reliable SAR to be developed.

Keywords: Structure activity relationships; Unimolecular decomposition rate constant; Tropospheric oxidation

1. Introduction

As clearly pointed out by Atkinson et al. [1,2] in two critical reviews, alkoxy radicals are important intermediates in the chemical mechanism of tropospheric oxidation of many classes of VOC. A few data relevant to alkoxy radicals (reactions with O_2 and NO) can also be found in IUPAC [3] and NASA [4] evaluations (the next update of IUPAC [3] will also include recommendations for decomposition and (or) isomerization of butoxy radicals). In the atmosphere, they are formed either by the reaction of small peroxy radicals with NO: $RO_2 + NO \rightarrow RO + NO_2$ (at high NO_x levels) or by the self reaction of peroxy radicals: $2\,RO_2 \rightarrow 2\,RO + O_2$ (at low NO_x levels). These two main formation channels are rather well characterized (rate constants and product yields) for a number of small peroxy radicals [5,6]. In recent years, the formation of nascent excited ("energized") alkoxy radicals—initially proposed by Wallington et al. [7]—in the exothermic reaction $RO_2 + NO \rightarrow RO^* + NO_2$, permitting a prompt decomposition of RO^*, has been invoked to account for variable yields of decomposition products according to the source reaction; this suggestion has been substantiated by a series of experimental and theoretical studies [7,8].

In contrast to peroxy radicals, the fate of most alkoxy radicals needs further investigations, except for the few small ones like methoxy (CH_3O), ethoxy (C_2H_5O), 1-propoxy and 2-propoxy (C_3H_7O) and 1-butoxy (C_4H_9O), for which the dominant sink reaction in the atmosphere—near 298 K and over 1000 mbar of air—(reaction with O_2, except isomerization for 1-butoxy) is well established.

In atmospheric conditions three different competing reactions have to be considered:

1. *Channel a*: Unimolecular decomposition, yielding an alkyl radical and a carbonyl. The rate constant of this reaction is denoted by k_d.
2. *Channel b*: Isomerization by intramolecular H atom transfer (only effective for alkoxys having at least four carbons). The corresponding rate constant is denoted by k_{isom}.
3. *Channel c*: Reaction with O_2, yielding a carbonyl molecule (aldehyde or ketone) and an HO_2 radical. The rate constant of this reaction is denoted by k_{O_2}.

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[*] Tel.: +33-3-20-43-4485; fax: +33-3-20-43-6977.
E-mail address: pascal.devolder@univ-lille1.fr (P. Devolder).

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The distribution of oxidized products depends on the relative importance of the available alkoxy radical sink reactions (a, b or c); this in turn may influence the propensity of the parent organic compound to generate ozone.

Regarding the decomposition (channel a), the absolute rate constant k_d had been derived for a few radicals by indirect or relative experimental methods—mostly above room temperature—providing, for example, the values of the ratios k_d/k_{NO} (k_{NO} is the bimolecular rate constant for reaction of the relevant alkoxy with NO) or k_d/k_{O_2}. Only recently those rate constants (k_d) have been measured directly over large temperature and pressure ranges (Section 2.3).

As for the channel b, various recent experiments have confirmed, on the basis of product analysis, the occurrence of fast alkoxy isomerizations already at room temperature [9–15], confirming earlier measurements of Carter et al. [16], Niki et al. [17] and Cox et al. [18].

Concerning channel c, it is agreed that the rate constant for the reaction of alkoxy radicals with O_2 should be rather small. The generic value of $k_{O_2,298\,K} = 8 \times 10^{-15}\,cm^3\,molecule^{-1}\,s^{-1}$, based on the data for ethoxy and 2-propoxy, was often the basis for estimates of k_d or k_{isom} from the measured ratios k/k_{O_2} [1,2].

However, in spite of various but dispersed data, an unified and coherent model for predicting the rate constants k_d or k_{isom} was clearly lacking. This probably explains the wealth of investigations related to alkoxys in the recent period. In particular, significant advances have been made concerning the unimolecular decomposition thanks to the combination of absolute time resolved techniques (direct measurement of k_d) and theoretical methods (quantum ab initio and statistical calculations). Also, part of the previous contradictions in literature were probably linked with the fact that both the decomposition and the isomerization are unimolecular reactions and thus may be pressure and bath gas-dependent.

This review is organized as follows:

- In the first part (Section 2), the recent advances concerning the unimolecular decomposition of a few alkoxys will be presented, resulting from both experimental and theoretical efforts.
- In the second part (Section 3), the data concerning the isomerization (indirect experiments and theoretical calculations), will be reviewed.
- In the third part (Section 4), all recently published absolute measurements of the rate constants with O_2, an important sink for many alkoxys, will be reviewed. This is an interesting parameter for two reasons: (i) the rate constant for ethoxy at 298 K is often taken as the reference for all alkoxys and it is worth checking this assumption; (ii) the low pre-exponential factor for k_{O_2} points to a complex reaction mechanism (i.e. not a simple abstraction).

This manuscript deals with alkoxy radicals containing up to five carbons for which (i) sufficient experimental data are available and (ii) sophisticated theoretical treatments from different groups have appeared recently in the literature.

2. Unimolecular decomposition of alkoxy radicals

The six following unimolecular decomposition reactions (R1), ... , (R6) will be considered. Where more than one decomposition pathway is possible, only the fastest decomposition channel, which happens to be the dominant one for the six radicals (as predicted by theory at 298 K and 1 bar or known from product analysis) is considered:

$$CH_3CH_2O^{\circ} \xrightarrow{M} CH_3 + HCH(O) \quad \text{(ethoxy)} \tag{R1}$$

$$CH_3CH_2CH_2O^{\circ} \xrightarrow{M} C_2H_5 + HCH(O) \quad \text{(1-propoxy)} \tag{R2}$$

$$(CH_3)_2CHO^{\circ} \xrightarrow{M} CH_3 + CH_3CH(O) \quad \text{(2-ropoxy)} \tag{R3}$$

$$C_2H_5CHO^{\circ}CH_3 \xrightarrow{M} + C_2H_5 + CH_3CH(O) \quad \text{(2-butoxy)} \tag{R4}$$

$$(CH_3)_3\,CO^{\circ} \xrightarrow{M} (CH_3)_2\,C(O) + CH_3 \quad (t\text{-butoxy}) \tag{R5}$$

$$(C_2H_5)_2CHO^{\circ} \xrightarrow{M} C_2H_5CH(O) + C_2H_5 \quad \text{(3-pentoxy)} \tag{R6}$$

The high and low pressure limiting values as well as their value in tropospheric conditions (298 K, 1000 mbar of air) will be, respectively, denoted $k_{d,0}$, $k_{d,\infty}$ and $k_{d,atm}$.

2.1. Earlier determinations of k_d

Before the 1980s, a few indirect experimental data relative to decomposition were available from detailed systematic product studies performed mainly by Batt [19], Heicklen [20], and Waddington and co-workers [21]. From variable temperature product analysis of the thermolysis (or photolysis) of alkylnitrites ($RONO \xrightarrow{\Delta} RO + NO$), they were able to derive the Arrhenius parameters of the ratios k_{NO}/k_{O_2} for a few alkoxy radicals (from C_2 to C_5); nevertheless, pressure effects (fall-off behavior) could not be properly accounted for in detail in these complex systems (also, both RONO and RO might exhibit fall-off behavior). The data of Batt [19], accepted in the reviews of Atkinson et al. [1,2] and Heicklen [20], were also in overall agreement with early theoretical estimations (with empirical Benson thermochemical rules) of Choo and Benson [22] and Baldwin et al. [23]; two sets of these earlier data are gathered in Table 1.

2.2. Indirect or relative determinations of k_d at room temperature

Initial measurements concerning the decomposition of 2-butoxy at 298 K, relative to its reaction with O_2, have been performed by Cox et al. [18], Carter et al. [24] and Atkinson et al. [2] using GC techniques. Using the FTIR technique in a photoreactor, Zabel and co-workers [25–28] and Carlier and co-workers [29,30] have also recently measured the

Table 1
Comparison of various estimations for the Arrhenius parameters of the decomposition rate constant of five alkoxy radicals (high pressure limits)

	Estimation (thermochemical rules) [22]		Review [1]	
	$A_{d,\infty}$	$E_{d,\infty}$	$A_{d,\infty}$	$E_{d,\infty}$
Ethoxy	4×10^{13}	83.6	2×10^{14}	84.5
1-Propoxy	5×10^{13}	65.2	–	–
2-Propoxy	6.3×10^{13}	70.2	4×10^{14}	73.6
2-Butoxy	4×10^{13}	56.4	2×10^{14}	59.8
t-Butoxy	1.3×10^{14}	64	6×10^{14}	67.7

ratios: decomposition or isomerization products/products of reaction with O_2 versus the mole fraction of O_2 in air; using a generic value for k_{O_2} at 298 K, all these authors determined the value of k_d at 298 K and atmospheric pressure; concerning the variation of $k_{d,atm}$ with T, Zabel and co-workers [28] very recently published a few measurements concerning 2-butoxy in a small range of temperatures.

Also in the recent period, Zellner and co-workers [31–33] have used a different approach: they monitored the time resolved kinetics of both OH and NO_2 in laser pulse initiated oxidation of alkanes in NO_x/air/alkane mixtures (at 298 K); from a modeling of the OH and NO_2 concentration/time profiles, sensitivity analysis and statistical calculations, (for extrapolation at 1 bar), they were able to derive the absolute value for k_d at room temperature.

The results of these relative or indirect determinations around room temperature are gathered in Table 2; for 2-butoxy, an average value of $k_{d,atm}/k_{O_2} = 2.8 \times 10^{18}$ molecule cm^{-3} (at 298 ± 4 K) is obtained, which translates into a value of $k_{d,atm} = 2.2 \times 10^4\ s^{-1}$ at room temperature, which is larger, as expected, than the absolute value determined by Hein et al. [31] at 50 mbar: $(3.5 \pm 2) \times 10^3\ s^{-1}$. The data for 1-propoxy and 2-propoxy are scattered but in overall agreement with theoretical predictions (Table 4, central columns) indicating that the values of $k_{d,atm}$ are in the range 10^2–$10^3\ s^{-1}$.

On the other hand, these relative or absolute data suggest, in agreement with recent statistical calculations [34], that even for 3-pentoxy radicals, the rate constants k_d are not yet close to their high pressure limits at 1 bar.

2.3. Absolute time resolved determinations of k_d at variable p and T

For alkoxys including three carbons or less, indications from a few early experiments [19,21] suggested that k_d is clearly in the fall-off range at atmospheric pressure. On the other hand, it is already well established from product yield analysis that the reaction with O_2 is the dominant pathway for these small radicals in atmospheric conditions. As a consequence, an accurate determination of k_d versus pressure and temperature is not of strict atmospheric relevance for these small alkoxys.

Table 2
Results of indirect determinations of a few alkoxy decomposition rate constants

	$k_{d,atm}/k_{O_2}$ (molecule cm^{-3})	T (K)	$k_{d,atm}$ (room temperature) (s^{-1})	Reference
2-Butoxy	$(2.6 \pm 0.35) \times 10^{18}$	296	$(3.9 \times 10^{12}) \exp(-47.1\ kJ\ mol^{-1}/RT)$[a]	[18]
	3.15×10^{18}	–		[24]
	$(3 \pm 0.6) \times 10^{18}$	298		[25]
	$(2.3 \pm 0.5) \times 10^{18}$	298.2		[28]
	$(2.9 \pm 0.3) \times 10^{18}$	–		[30]
Averaged data	2.8×10^{18}		2.2×10^{4}[b]	
		293	$(3.5 \pm 2) \times 10^{3}$ (at 50 mbar)[c]	[31]
3-Pentoxy		293	$(5 \pm 2.5) \times 10^{3}$ (at 50 mbar)[c]	
		293	3.3×10^{4} (at 1000 mbar)[c]	[33]
	$(3.6 \pm 0.6) \times 10^{18}$	298	2.9×10^{4}	[26]
	$(3.8 \pm 0.7) \times 10^{18}$	–	3×10^{4}	[30]
	3.3×10^{18}	296	2.6×10^{4}	[2]
Averaged data			3×10^{4}[b]	
i-Butoxy(2-methyl 1-propoxy)	$(6.2 \pm 1.2) \times 10^{18}$	298		[26]
	$(4 \pm 0.6) \times 10^{18}$	–		[30]
Averaged data			4×10^{4}[b]	
1-Propoxy	$(3.8 \pm 0.41) \times 10^{16}$	–	300	[30]
2-Propoxy	$(2.9 \pm 0.3) \times 10^{16}$	–	230	[30]
Ethoxy		–	0.8	[29]

$k_{d,atm}$ at the specified temperature or at room temperature (–) and (unless indicated) in 1 bar of air. The same value of $k_{O_2} = 8 \times 10^{-15}\ cm^3$ molecule^{-1} s^{-1} is adopted for all alkoxys to derive $k_{d,atm}$ from relative measurements.

[a] Variable temperature experiments (280–313 K) at 1 bar.

[b] Average of data at room temperature and 1 bar.

[c] Indirect absolute values (extrapolation from a fit of a complex mechanism) from time resolved experiments.

However, the main interest of a systematic experimental determination of k_d over wide range of pressure and temperature (and thus deriving an accurate construction of the whole fall-off curve) is to compare the experimentally derived results with computed values obtained by different theoretical methods and in this way to find the “best” adapted theory. This procedure is an essential step to elaborate and validate structure activity relationships (SAR) applicable to every alkoxy. To fill this gap, Devolder and co-workers have determined the complete fall-off curves for decomposition of three representative radicals: ethoxy [35], 2-propoxy [36] and *t*-butoxy [37] using the following procedures:

- The decay kinetics of the alkoxy radicals have been followed by time resolved LIF using two absolute complementary techniques: the discharge flow technique (in the mbar bath gas pressure range) and the pulsed laser photolysis technique (from ≈0.13 to 50 bar). For each radical, the temperature range of the experiments (always above 298 K) was chosen to obtain decay rates well adapted to the selected technique.
- The analysis of the fall-off curves have been performed combining the Troe fitting procedure with ab initio and statistical (RRKM) calculations.

Final results from analysis of these fall-off curves are gathered in Table 3 which includes the values of the Troe parameters: (i) low pressure limiting rate constant $k_{d,0}$ (in helium bath gas); (ii) high pressure limiting rate constant $k_{d,\infty}$ and (iii) broadening factor F_c and, from the latter parameters, the derived value of k_d in atmospheric conditions (298 K, 1 bar of air). Measurements using the discharge flow technique (low pressure range) have only been performed for reaction (R1) [35]. As a consequence, the limiting low pressure rate constants ($k_{d,0}$) are more reliable for this alkoxy; in contrast, examination of the fall-off curves has given confidence that the measurements at the highest pressures (a few tens of bars) allow a small extrapolation to derive accurately the limiting high pressure values (k_{∞}). The knowledge of these latter parameters ($A_{d,\infty}$ and $E_{d,\infty}$) represents an excellent benchmark for a meaningful comparison with theory since $E_{d,\infty}$ and $A_{d,\infty}$ are direct outcomes of combined ab initio and statistical calculations with almost no empirical or adjusted parameters.

2.4. Theoretical (quantum chemistry) determinations of k_d at variable temperature and pressure

In recent years, many quantum chemistry based calculations of the various parameters needed to completely calculate the fall-off curves of many simple alkoxy decompositions have appeared [34,38–41]: $E_{0\,\mathrm{K}}$ (barrier at 0 K), enthalpies of reaction, limiting low and high pressure rate constants (pre-exponential factor, activation energies), broadening factor, etc. Since all decomposition reactions (R1)–(R6) have significant barriers ($E_{0\,\mathrm{K}}$: at least 50 kJ mol^{-1}), and since the corresponding transition states are tight, their structural parameters can be accurately characterized by high level ab initio techniques. This in turn provides a sound basis for subsequent statistical calculations (“standard” RRKM or master equation based). As a consequence and not unexpected, various theoretical groups derived very close set of parameters, for example, for the value of $E_{d,\infty}$ (activation energy in the limiting high pressure range), even using rather different methodologies.

However, in this review, we have chosen to restrict the comparison of experiment to theory to those groups having performed systematic calculations on a complete set of reactions (R1)–(R5): (i) Caralp and co-workers [38,42], (ii) Somnitz and Zellner [34,39], and (iii) the group of Viskolcz and co-workers [37,40]. Their results are gathered in the columns subtitled “theory” of Table 4 together with the data from Atkinson et al. [1,2] and, where available, a few recent experimental determinations.

For each alkoxy decomposition, three parameters have been retained for a comparison of experimental data with results from various ab initio calculations: $A_{d,\infty}$, $E_{d,\infty}$ and $k_{d,\mathrm{atm}}$; for such a comparison, the two former ones (limiting high pressure values) have been preferred to the corresponding ones in standard conditions (298 K, 1 bar of air) because there is no need to take into account the bath gas collision efficiency; in contrast, for the decomposition rate constant $k_{d,\mathrm{atm}}$, we have reported in the tables, the experimental

Table 3
Results of direct absolute measurements of k_d (fall-off parameters $k_{d,0}$ and $k_{d,\infty}$, $E_{d,0}$ and $E_{d,\infty}$) for three alkoxys

	$k_{d,0}$		$k_{d,\infty}$ (s^{-1})		F_c	$k_{d,\mathrm{atm}}$ (s^{-1})	Reference
	$A_{d,0}$/[He] cm^3 molecule^{-1} s^{-1}	$E_{d,0}$ (kJ mol^{-1})	$A_{d,\infty}$ (s^{-1})	$E_{d,\infty}$ (kJ mol^{-1})			
Ethoxy	3.3×10^{-8}	58.5	1.1×10^{13}	70.3	$0.76 - T/2060$	5	[35][a]
			1×10^{14}	78.2			[37][b]
2-Propoxy	1×10^{-8}	43.8	1.2×10^{14}	63.7	$0.89 - T/935$	400	[36,58][a]
			1×10^{14}	63.1			[37][b]
t-Butoxy	1.5×10^{-8}	38.5	1×10^{14}	60.5	$0.87 - T/870$	2500	[37][b]

Troe formula: $\log(k_d/k_\infty) = \log(x/(1+x)) + \log F_c/[1+(\log x/(0.75 - (1.27 \times \log F_c)))^2]$ with $x = k_{d,0}/k_{d,\infty}$.

[a] Best experimental set of parameters.

[b] Idem but with $A_{d,\infty}$ fixed at 10^{14} s^{-1}.

Table 4
Decomposition of ethoxy, 1-propoxy and 2-propoxy, 2-butoxy and *t*-butoxy

	Reevaluation of Batt data [19] in [1,2]	Theory (ab initio and statistical calculations)				Experiments	
		[34,39]	[38][a]	[37]	[60]		
Ethoxy							
$A_{d,\infty}$ (s^{-1})	2×10^{14}	2.9×10^{13}	8×10^{13}	10^{14}	3.2×10^{13}	(1–2) $\times 10^{13}$ [35]	
$E_{d,\infty}$ (kJ mol^{-1})	84.4	75	75.7	75.6	79	72 ± 2 [35]	
$k_{d,atm}$ (s^{-1})	0.3	1.5	3.2	6		5 [35]	
1-Propoxy							
$A_{d,\infty}$		4.2×10^{13}	1.06×10^{14}	1.3×10^{14}			
$E_{d,\infty}$		63.6	66.3	67.6			
$k_{d,atm}$		2.4×10^{2}	4.5×10^{3}	1.9×10^{2}			
2-Propoxy							
$A_{d,\infty}$	4×10^{14}	7.1×10^{13}	1.85×10^{14}	1×10^{14}	4.4×10^{13}	1.2×10^{14} [36]	
$E_{d,\infty}$	73.6	63.7	68.8	66.5	63.5	63.7 [36]	
$k_{d,atm}$	49	3.5×10^{2}	2.2×10^{2}	2.2×10^{2}		∼400 [36]	
2-Butoxy							
$A_{d,\infty}$	2×10^{14}	4.5×10^{13}	1×10^{14}	1.6×10^{14}			(5 ± 4) $\times 10^{11}$ [56]
$E_{d,\infty}$	59.8	51.8	54.8	63.1			41.8 [56]
$k_{d,atm}$	6.5×10^{3}	2.7×10^{4}	1.6×10^{5}	1.4×10^{3}		0.35–2.4 $\times 10^{4}$ [25,31]	2×10^{4} [56]
t-Butoxy							
$A_{d,\infty}$	6×10^{14}		2.7×10^{14}	1×10^{14}		1×10^{14} [37]	1.4×10^{13} [59]
$E_{d,\infty}$	67.8		63.7	61.2		60.5 [37]	57 [59]
$k_{d,atm}$	790		1.2×10^{3}	1.9×10^{3}		2.5×10^{3} [37]	565 [59]

Comparison of the Arrhenius parameters (high pressure limits) and of $k_{d,atm}$ (estimated, experimental or theoretical data). $A_{d,\infty}$ and $k_{d,atm}$ in s^{-1}; $E_{d,\infty}$ in kJ mol^{-1}; in the right columns, the experimental data are referred to their specific reference.

[a] Average of BAC-MP4 and DFT results.

values (where computed by the quoted authors, either from indirect measurements or from extrapolated absolute measurements) together with the theoretical ones.

Comparing the various ab initio derived values of $E_{d,\infty}$ (Table 4), it is rewarding to notice that all recent experimental data are well reproduced by most different theoretical methodologies; also, these energy barriers ($E_{d,\infty}$, at the center of the lines) are between 6 and 10 kJ mol^{-1} below previous recommendations (left columns). Even if the corresponding pre-exponential factors are usually also below those recommended by Atkinson, these changes translate into rate constants in atmospheric conditions ($k_{d,atm}$) which are one or two orders of magnitude larger than previously estimated. As already explained above, this increase has no atmospheric implication for reactions (R1)–(R5) considered in Table 4 since the reaction with O_2, assumed to have a pseudo-first-order rate of $\approx 4 \times 10^4\ s^{-1}$ (in 1 bar of air at 298 K), remains by far the dominant sink in lower troposphere.

Nevertheless, the remarkable agreement between accurate experimental data and various theoretical predictions gives confidence to any structure activity relationship (for prediction of $k_{d,atm}$) based only on theoretical (ab initio and statistical) grounds as far as it has been validated for a few structurally different species. Obviously, it would be interesting to perform such a similar thorough comparison experiment/theory for a series of other types of alkoxys: β-hydroxyalkoxys, halogenated alkoxys, etc.

2.5. *Structure activity relationships for alkoxy decompositions*

In view of its obvious practical interest, it is highly desirable to rely upon a simple structure activity relationship between the alkoxy structure and its Arrhenius decomposition parameters: high pressure limits ($E_{d,\infty}$ and $A_{d,\infty}$) or values at 1 bar of N_2 or air.

In his latest review, Atkinson [1] has proposed the following SAR, considered to be accurate at ±4 kJ mol^{-1}:

$$E_d \text{ (cosidered close to } E_\infty) = (10.0\text{IP (eV)} - 33.9) + 1.50\, \Delta_r H \qquad \text{(a1)}$$

where IP is the ionization potential of the leaving alkyl group (in eV) and $\Delta_r H$ (kJ mol^{-1}) the reaction enthalpy of the decomposition reaction; the latter enthalpy was deduced from measured or estimated (with Benson rules) enthalpies of formation of the alkoxy radical and of its decomposition products. Except for ethoxy (which is apparently a specific case), the SAR (a1) fitted nicely existing data (but disagrees with recent determinations). After a detailed study focussed on a specific class of alkoxy radicals ($ROCO^{\bullet}R_1R_2$ radicals), Aschmann and Atkinson [43] have revised the SAR (a1) for the particular case corresponding to the methyl radical as the alkyl leaving group; their improved SAR (for all alkoxy radicals leaving a $-CH_3$ group) (a2) is as follows:

$$E_d = 58.5 + 2.05\, \Delta_r H \qquad \text{(a2)}$$

Table 5
Comparison of the predictions of a few recent different structure activity relationships (SAR)

	Reevaluation of Batt data [19] in [1]	Theory		SAR [34]	SAR (b) [38]	SAR (d) [38]
		[37]	[39]			
Ethoxy	84.5	75.6	75	73.5	75.4	76.9
1-Propoxy	–	67.6	63.6	61	65.6	58.9
2-Propoxy	73.6	66.5	63.7	61	68.1	68.1
2-Butoxy	59.9	63.1	51.8	51	50.2	50.2
t-Butoxy	67.7	61.2		61	61.9	59.3

Values of high pressure limiting barriers for decomposition at 298 K (in $\mathrm{kJ\,mol^{-1}}$). In columns 3, 6 and 7 the pre-exponential factors $A_{\mathrm{d},\infty}$ are close to $10^{14}\,\mathrm{s^{-1}}$.

(instead of (a1): $E_\mathrm{d} = 64.8 + 1.50\,\Delta_\mathrm{r}H$) To reproduce recent data, a few groups have proposed new SAR (Table 5); Méreau et al. [38] have developed SAR based on ab initio and DFT calculations (of E_∞ and $\Delta_\mathrm{r}H$) which support the basic principle of SAR (a); they propose the two following SAR (b) and (c), from DFT or BAC-MP4 based calculations, respectively,

$$E_{\mathrm{d},\infty}\,(\mathrm{kJ\,mol^{-1}}) = 7.5\mathrm{IP} - 18.2 + 1.42\,\Delta_\mathrm{r}H \quad (\mathrm{DFT}) \qquad \text{(b)}$$

$$E_{\mathrm{d},\infty}\,(\mathrm{kJ\,mol^{-1}}) = 7.5\mathrm{IP} - 12.5 + 1.46\,\Delta_\mathrm{r}H \quad (\mathrm{BAC\text{-}MP4}) \qquad \text{(c)}$$

Their SAR (b) (column 6 of Table 5) is in reasonable agreement with recent experimental data for $E_{\mathrm{d},\infty}$ (where available: right columns of Table 4 for reactions (R3) and (R5)); it is worth emphasizing that almost the same coefficient multiplying $\Delta_\mathrm{r}H$ is derived for SAR (a), (b) and (c), which is a hint that the transition states barriers are indeed highly correlated with reaction enthalpies.

However, these Evans–Polanyi type Eqs. (a)–(c) have been criticized by Somnitz and Zellner [34,39] for both practical (uncertainties of $\Delta_\mathrm{r}H$) and more fundamental reasons (the presence of multiple reaction channels for most alkoxys should affect the fastest canonical rate constant). After a detailed discussion and noting that the reactive center C–O° only "sees" adjacent neighbors, these authors [34] propose values of threshold barriers ($E_{0\,\mathrm{K}}$) depending only on the structure of resulting molecular fragments (products). They suggest the existence of only three different values, depending only on the number of carbon atoms of each of the two fragments (at right sides of (R1)–(R6)). Translated into activation energies they obtain: (i) for two $\mathrm{C_1}$ fragments: $E_{\mathrm{d,,atm}} = 73.6\,\mathrm{kJ\,mol^{-1}}$, (ii) for one $\mathrm{C_1}$ fragment, one $\geq\mathrm{C_2}$ fragment: $E_{\mathrm{d,atm}} = 61.0\,\mathrm{kJ\,mol^{-1}}$, (iii) for two $\geq\mathrm{C_2}$ fragments: $E_{\mathrm{d,atm}} = 51.0\,\mathrm{kJ\,mol^{-1}}$ (for a convenient comparison with other authors, the values of $E_{0\,\mathrm{K}}$ from [34] have been reported in the fourth column of Table 5; [39] shows that, according to the radical, the values of $E_{\mathrm{d,atm}}$ are between –1.7 and $1.2\,\mathrm{kJ\,mol^{-1}}$ of $E_{0\,\mathrm{K}}$). This very simple SAR does not require any thermochemical data and is in excellent agreement with experimental data; the authors also remark that all their theoretical values of $\log A_{\mathrm{d,atm}}$ are in the range 13–13.3; in its principle, this latter result supports the suggestion of Fittschen et al. [37] to adopt a generic value $\log A_{\mathrm{d,atm}} = 14$ for all alkoxys (of course, the barriers computed in [37] are systematically larger than those of [39]).

And finally, another simple SAR has also been proposed by Méreau et al. [38]:

$$E_{\mathrm{d},\infty}\,(\mathrm{kJ\,mol^{-1}}) = 10.45\mathrm{IP} + 8.8n_\mathrm{H} - 43.5 \qquad \text{(d)}$$

where n_H is the number of hydrogen atoms on the carbon atom bearing the reactive center C–O° (e.g. $n_\mathrm{H} = 1$ for 2-butoxy); the predictions of this last SAR are also presented in Table 5 (last column).

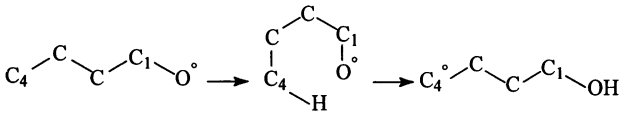
All the above SAR concerning $E_{\mathrm{d},\infty}$ are claimed to be accurate at $\pm 4\,\mathrm{kJ\,mol^{-1}}$; on the other hand, the associated pre-exponential factors are in the range 10^{13} to a few 10^{14}; altogether, in the worst case, this translates into a variation of rate constant of ≈ 50 at room temperature. For atmospheric purposes, this uncertainty is acceptable for alkoxys exhibiting an overwhelming sink reaction channel but not where a competition between two channels is anticipated. Also, taking into account the well established weak temperature dependence of $k_{\mathrm{O_2}}$, in contrast with the strong temperature dependence of k_d, a valid conclusion at ground level might be in error in the upper troposphere at lower pressure and temperature.

Inspection of Table 5 shows that there is satisfying agreement between all recent theoretically predicted values of $E_{\mathrm{d},\infty}$, either directly based on ab initio and statistical calculations or derived from SAR. The high value of $E_{\mathrm{d},\infty} = 63.1\,\mathrm{kJ\,mol^{-1}}$ predicted for 2-butoxy in [37] is probably in error. Most values for $E_{\mathrm{d},\infty}$ in the columns 2–6 are within $\pm 2\,\mathrm{kJ\,mol^{-1}}$, which corresponds to less than a factor of 5 on the rate constant in atmospheric conditions. This is probably well enough for most modeling purposes both in the atmosphere or in photoreactors.

To conclude, on the basis of these many various data, we recommend the following Arrhenius parameters for decomposition of small alkoxys in the troposphere: $k_{\mathrm{d,atm}}\,(\mathrm{s^{-1}}) = 5 \times 10^{13} \exp(-E_\mathrm{a}/RT)$, with the following E_a (in $\mathrm{kJ\,mol^{-1}}$ at $\pm 3\,\mathrm{kJ\,mol^{-1}}$): $75\,\mathrm{kJ\,mol^{-1}}$ (ethoxy), $65\,\mathrm{kJ\,mol^{-1}}$ (1-propoxy and 2-propoxy), $51\,\mathrm{kJ\,mol^{-1}}$ (2-butoxy), 61 (*t*-butoxy). For simplicity, fall-off effects have been purposely neglected in the latter recommendations, which are thus only appropriate at (or near) 1 bar of air; it is worth recalling that Somnitz and Zellner [39] have performed systematic calculations of the complete fall-off curves for reactions (R1)–(R6) between 220 and 300 K; from their figures and tables we note that, at 300 K, the reduction of k_d is modest between 1000 mbar and 267 mbar: $k_{d,1000\ \text{mbar}}/k_{d,267\ \text{mbar}} \approx 1.5$ while at 1 bar or below, the temperature coefficient is large: $k_{d,300\ \text{K}}/k_{d,220\ \text{K}} \approx 10^3–10^4$; as a consequence, over quite different experimental conditions—for example, below 10–100 mbar—and (or) over temperatures far from 298 K, fall-off behavior should be taken into account.

3. Isomerization reactions

Alkoxy isomerizations are intramolecular H atom transfer which are assumed to proceed via a six-membered transition state [1]:



The 1-butoxy is the smallest alkoxy for which there is experimental evidence of such an isomerization reaction. Like for decomposition, the data before 1997 concerning the isomerization rate constants k_{isom} at room temperature have been reviewed by Atkinson et al. [1,2]. Most experimental data were derived from the measurement of the ratios k_{isom}/k_{O_2}, based on product yields analysis, again assuming a generic value of k_{O_2} common to all alkoxys. Together with the recommendations of Atkinson et al. [1,2], Table 6 includes older and recent relative measurements at room temperature and theoretical predictions for 1-butoxy and 2-pentoxy (transfer of a primary H) and for 1-pentoxy (transfer of a secondary H). To our knowledge, there is no direct absolute measurement of k_{isom} and very few data outside room temperature [13].

Atkinson et al. [1,2] has proposed simple empirical formulas for predicting the rate constants for isomerization, based on the two following basic assumptions:

- The barrier for isomerization is the sum of two contributions: the ring strain energy for formation of the intermediate transition state (first step) and the activation energy for abstraction of an hydrogen atom (second step), the latter energy is supposed to exceed largely the former. This procedure has been originally suggested by Baldwin et al. [23].
- The activation energy of this second step—the hydrogen atom abstraction—is estimated by analogy with well known barriers for H atom abstractions by the hydroxyl radical in bimolecular reactions, with H-bonded either to a primary (–CH_3), secondary (–CH_2–) or tertiary (>CH–) carbon atom.

The isomerization barriers proposed by Atkinson on the previous basis are included in Table 7 (left column). In an attempt to validate this approach, Viskolcz et al. [44] performed quantum chemistry (ab initio) calculations to show that this additive rule holds for intramolecular H atom transfer in alkyl radicals. In addition, Lendvay and Viskolcz [40] reached the same conclusion by comparing the calculated barriers for the isomerization of 1-butoxy to the barriers for hydrogen atom abstraction in propane initiated by the methoxy radical, both attacking an H atom bonded to a primary C. The various theoretically predicted barriers for isomerization are gathered in Table 7 (column 3–5).

Inspection of Table 6 shows that there is a reasonable agreement between the estimations for k_{isom} provided by

Table 6
Comparison of the results for isomerization rate constants k_{isom} (s^{-1}) of three alkoxys at (297 ± 2) K and in 1 bar: experimental data and critical reviews, theoretical predictions

Experiments (relative data at 298 K)			Exp. [13]	Exp. and review		Exp.[a] [69]	Theory	
$(k_{\text{isom}}/k_{O_2}) \times 10^{-19}$	Reference			[1,2]	[5]		[34]	[42]
1-Butoxy								
1.5	[18]	1.3×10^5	10^5	$\sim 2 \times 10^5$	1.6×10^5 (2.4×10^{11} $\exp(-35\ \text{kJ mol}^{-1}/RT)$)	3.5×10^4	11×10^5	$10^5–10^6$
2.0	[17]							
1.6	[24]							
1.1	[30]							
1.8	[27]							
1.6 (average)								
2-Pentoxy								
				2×10^5	–	$>10^5$	2×10^6	1.8×10^5
1-Pentoxy								
					–	$>10^5$	2×10^6	1.8×10^6

$(k_{\text{isom}}/k_{O_2}) \times 10^{-19}$ in molecule cm^{-3}.

[a] At 50 mbar.

Table 7
Comparison of the energy barriers (kJ mol^{-1}) for abstraction of the three kinds of H atoms (bonded to a primary, secondary or tertiary carbon atom) either in alkoxy isomerizations or in CH_3O reactions

	Isomerizations				CH_3O abstractions	
	SAR [1,2,43]	Theory			Exp. [45,46]	Theory [46,48]
		[39,41]	[40]	[42]		
– CH_3 (primary)	40	37/41	29.3	35.5/41.4		
– CH_2 – (secondary)	28	32	18.9		24.5	18
> CH– (tertiary)	23				8/15 (allylic)	≈5
					5/10 (aldehydic)	

different authors, either from experiment or theory. Furthermore, very recent data are also in essential accord with the numbers recommended by Atkinson [1], i.e. abstraction of an H atom bonded to a primary C: $k_{isom} \cong 10^5\,s^{-1}$; abstraction of an H atom bonded to a secondary C: $k_{isom} \cong 10^6\,s^{-1}$. It is worth reminding that these numbers are within the range of the pseudo-first-order rate constant (generic value) for alkoxy reaction with O_2: $4\times10^4\,s^{-1}$ at 298 K and 1 bar of air. Concerning the pressure dependence, statistical calculations [39,42] show that already for 1-butoxy the unimolecular reaction of isomerization is close to its high pressure limit at 1 bar and thus it is expected to be so for all larger alkoxys. On the other hand, the temperature dependence of k_{isom} is certainly important to predict the fate of alkoxys exhibiting $k_{isom} \cong 10^5\,s^{-1}$ at 298 K: for a typical barrier of 30 kJ mol^{-1}, an increase of 20 K would double k_{isom}.

To provide a new insight into these empirical correlations, Devolder and co-workers have measured the rate constants for the reactions (hydrogen abstractions) of CH_3O with a series of hydrocarbons [45–47]; experiments at variable temperatures have provided the corresponding barriers. In parallel with our experiments, ab initio calculations on model systems have been performed by Bohr and co-workers [46–48]. Though the rate constant for the reaction with ethane (six H atoms bonded to primary C atoms) happened to be too small at our accessible oven temperature, we have been able to measure the rate constants for CH_3O reactions with cyclohexane, formaldehyde, acetaldehyde, cyclohexene and 1–4 cyclohexadiene. The decreasing C–H bond energies [49] in this series of hydrocarbons: secondary (≈397 kJ mol^{-1}), aldehydic (≈364 kJ mol^{-1}), allylic (≈305 kJ mol^{-1}) is in line with the increase of the rate constant. However, for the two alkenes, detailed ab initio calculations [46] show that a contribution of the addition channel cannot be totally excluded. The experimental barriers for CH_3O abstractions (either experimental or theoretical) are gathered in Table 7 (columns 7 and 8).

Table 7 shows that recent theoretical data confirm both the trends and the order of magnitude of the isomerization barriers heights of Atkinson [1]; however, in contrast to decomposition barriers, theoretically predicted isomerization barriers are more scattered, according to the selected theoretical method (difference up to 10 kJ mol^{-1}). Also, when the comparison is possible, for example, for abstraction of a secondary H, the barriers for H atom abstractions by the CH_3O radical are within the range of isomerization barriers and further, these barriers undergo a similar trend in function of the C–H bond energy. However, more measurements of such H abstraction reaction rates by the methoxy radical (which are less demanding than direct absolute measurements of isomerization rates) should be performed before presenting a significant structure activity relationship.

4. Reaction rates with O_2

Available data concerning absolute measurements of the reaction rates with O_2 of seven alkoxy radicals (all of them using the laser photolysis/laser induced fluorescence (LIF) technique) are gathered in Table 8; most of the more recent absolute determinations have benefited from recent findings concerning the excitation and fluorescence spectra of a series of alkoxys [50–53]. Using the classical discharge flow/LIF technique, we have recently performed measurements of the reaction rate of (ethoxy + O_2 → products) [61]. We have displayed on Figs. 1 and 2 the Arrhenius plots of the various measurements for, respectively, ethoxy + O_2 and 1-propoxy or 2-propoxy + O_2; signs at the extremities of the plots indicate the two limits of the range of temperatures achieved by the authors. Fig. 1 (dotted line) shows that the recommendation of IUPAC [3] for the rate constant of ethoxy + O_2: k_{O_2} (cm^3 molecule^{-1} s^{-1}) $= 6 \times 10^{-14} \exp(-4.6\,\text{kJ mol}^{-1}/RT)$ is indeed a good compromise. The data for 1-propoxy and 2-propoxy are also in good shape; our recommendations (dotted lines of Fig. 2) are: $k_{O_2}(\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}) = 2.4 \times 10^{-14} \exp(-1.9\,\text{kJ mol}^{-1}/\text{RT})$ and $k_{O_2}(\text{cm}^3\ \text{molecule}^{-1}\,\text{s}^{-1}) = 1.6 \times 10^{-14} \exp(-2.1\,\text{kJ mol}^{-1}/\text{RT})$ for, respectively, 1-propoxy and 2-propoxy. For 2-butoxy and 3-pentoxy, Table 8 shows that new measurements are needed. The data gathered in Table 8 support the generic value of $k_{O_2} = 8 \times 10^{-15}\,\text{cm}^3$ molecule^{-1} s^{-1} at 298 K for all alkoxys (excluding CH_3O). Also, all temperature coefficients of k_{O_2} are rather small, corresponding to activation

Table 8
Rate constants with O_2 of a few alkoxys, experimental data in Arrhenius form $k_{O_2} = A\exp(-E/RT)$

	A (cm^3 molecule^{-1} s^{-1})	E (kJ mol^{-1})	k_{O_2} at 298 K (cm^3 molecule^{-1} s^{-1})	References
Methoxy	3.9×10^{-14}	7.5 ± 2.5	1.9×10^{-15}	[6][a]
Ethoxy	$(2.4 \pm 0.9) \times 10^{-14}$	2.7 ± 1	8.1×10^{-15}	[65]
	6×10^{-14}	4.6	9.4×10^{-15}	[3]
	2.9×10^{-14}	1.1 ± 0.1	8×10^{-15}	[62]
	$(7.1 \pm 0.7) \times 10^{-14}$	4.5	11×10^{-15}	[66]
	4.85×10^{-14}	4.4	8.2×10^{-15}	[61][b]
1-Propoxy	$(2.5 \pm 0.5) \times 10^{-14}$	2 ± 0.5	1.1×10^{-14}	[65]
	$(1.4 \pm 0.3) \times 10^{-14}$	0.9 ± 0.5	8×10^{-15}	[1,2]
			9.8×10^{-15}	[52]
2-Propoxy	$(1.6 \pm 0.2) \times 10^{-14}$	2.2 ± 0.2	6.6×10^{-15}	[65]
	1.5×10^{-14}	1.6	7.9×10^{-15}	[67]
	1.4×10^{-14}	1.8 ± 0.5	6.8×10^{-15}	[52]
2-Butoxy	$(1.33 \pm 0.43) \times 10^{-15}$	$-(5.48 \pm 0.69)$	$(1.2 \pm 0.4) \times 10^{-14}$	[68][c]
			$(6.5 \pm 2) \times 10^{-15}$	[53]
	1.2×10^{-15}	-4.6	7.7×10^{-15}	[70][c]
1-Butoxy			$(1.4 \pm 0.7) \times 10^{-14}$	[69]
3-Pentoxy	$(4.1 \pm 1.2) \times 10^{-15}$	$-(2.6 \pm 0.6)$	$(1.2 \pm 0.6) \times 10^{-14}$	[70][c]
			$(7.2 \pm 3.5) \times 10^{-15}$	[33]
1-Pentoxy	–	–	$<10^{-13}$	[69]

[a] This recommendation is based on the data of Gutman et al. [62], Lorenz et al. [63] and Wantuck et al. [64].

[b] Recent measurements from our group, using the discharge flow/LIF technique [61].

[c] Negative temperature coefficient.

energies of $\cong 2$ kJ mol^{-1}, and the pre-exponential factors are usually much smaller ($\cong 10^{-14}$ s^{-1}) than expected for a classical H abstraction [54]. This latter feature has been tentatively explained by Jungkamp and Seinfeld [54] by ab initio calculations on the basis of an addition–elimination mechanism:

$$CH_2O + O_2 \Leftrightarrow RCH_2OOO \rightarrow RCH(O) + HO_2$$

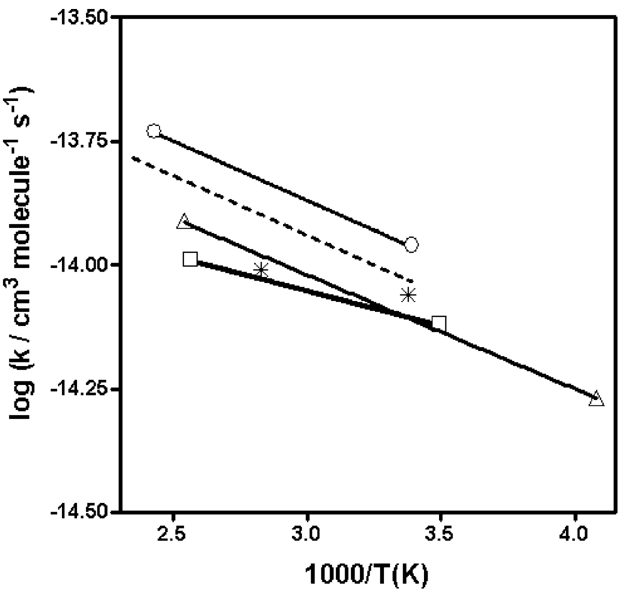


Fig. 1. Arrhenius plots for the rate constant of (ethoxy + O_2 → products); the signs at the extremities of the lines indicate the upper and lower temperatures of the relevant measurements: (△) [61]; (□) [65]; (○) [66]; (✳) [62]; dotted line: IUPAC recommendation [3]. The IUPAC recommendation for 1-butoxy + O_2 is identical to that for ethoxy + O_2.

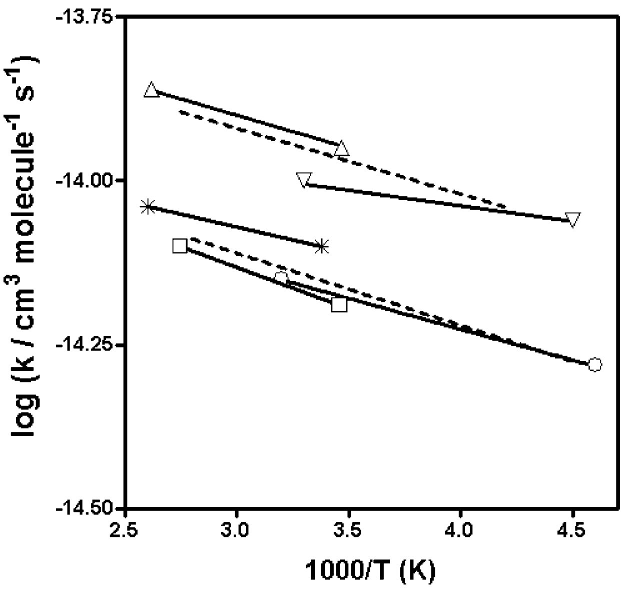


Fig. 2. Arrhenius plots for the rate constants of (1-propoxy and 2-propoxy + O_2 → products); upper curves: 1-propoxy; lower curves: 2-propoxy; the signs at the extremities of the lines indicate the upper and lower temperatures of the relevant measurement; (△) and (□) [65]; (▽) and (○) [52]; (✳) [67]. Dotted lines: our recommendations.

However, other recent theoretical data [55] seem to exclude such addition elimination mechanism because of a too large energy barrier of the first step.

5. Conclusion

In the recent period, significant advances concerning one of the three main sink reactions of alkoxy radicals—the unimolecular decomposition—have been achieved, especially thanks to a combined effort of various groups coordinated within the SARBVOC project of the CEC [56]. Particularly fruitful has been the close comparison of results from absolute time-resolved experiments and theoretical calculations (quantum chemistry based and statistical methods). The good predictive value of ab initio computations is particularly remarkable for small alkoxys and gives confidence to predictions for other larger alkoxys. It is tempting to extend these conclusions to other classes of alkoxy radicals such as, the halogenated ones, which may exhibit quite different decomposition behaviors (for example, expulsion of HCl in chloroalkoxys [57]). However, direct absolute measurements, preferably over large ranges of pressure and temperature, on a few representative haloalkoxys should be useful to check again the validity of theoretical predictions. The same remark should be true for other classes of atmospherically important radicals such as the β-hydroxyalkoxys or the β-nitrooxyalkoxys. As already mentioned in Section 2.5, in a recent article dealing with ether derived alkoxys having an oxygen atom bonded to the reactive site (i.e. of structure $R_1R_2C(O^{\circ})OR$), Aschmann and Atkinson [43] have proposed a revised SAR relevant to the decomposition together with twice as large reaction rates with O_2; wisely, they further add that “clearly, additional experimental and theoretical studies of alkoxy radical decomposition reactions are needed.”

On the other hand, the unimolecular isomerization reaction is still a critical issue, since available data are only theoretical estimations or relative measurements; it is also apparent from this review that fall-off effects should be accounted for in isomerization reactions and thus—like for decomposition reactions—direct absolute measurements—including room temperature and atmospheric pressure—are needed. The recent detection of LIF spectra of a few alkoxys known to exhibit fast isomerizations should open the way to more systematic and direct measurements of isomerization rate constants. The rate constant for the reaction of most alkoxy radicals with O_2 seems to be well known, but a low pre-exponential factor in combination with a small temperature dependence is probably a hint to a complex mechanism not yet completely understood.

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