RESEARCH PAPER

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The kinetics of the gas-phase decomposition of the 2-methyl-2-butoxyl and 2-methyl-2-pentoxyl radicals

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Received 27th January 2005, Accepted 31st March 2005 First published as an Advance Article on the web 15th April 2005

The kinetics of the title reactions have been studied by relative-rate methods as a function of temperature. Relative-rate coefficients for the two decomposition channels of 2-methyl-2-butoxyl have been measured at five different temperatures between 283 and 345 K and the observed temperature dependence is consistent with the results of some previous experimental studies. The kinetics of the two decomposition channels of 2-methyl-2pentoxyl have also been investigated, as a function of temperature, relative to the estimated rate of isomerisation of this radical. Room-temperature rate coefficient data for the two decomposition channels of both 2-methyl-2pentoxyl and 2-methyl-2-butxoyl (after combining the relative rate coefficient for this latter with a value for the rate coefficient of the major channel, extrapolated from the data presented by Batt et al., Int. J. Chem. Kinet., 1978, 10, 931) are shown to be consistent with a non-linear kinetic correlation, for alkoxyl radical decomposition rate data, previously presented by this laboratory (Johnson et al., Atmos. Environ., 2004, 38, 1755–1765).

Introduction

Products of the atmospheric oxidation of volatile organic compounds (VOCs)-which are released into the atmosphere from biogenic and anthropogenic sources-affect not only the chemistry at the Earth's surface (e.g. see refs. 1 and 2), but also it has recently been shown,³ that occurring in the upper troposphere. For example, the photooxidant ozone constitutes a secondary pollutant when it is produced following the interaction of organic radicals, derived from VOC pollutants, with oxides of nitrogen, NO_x ($NO_x = NO + NO_2$).^{1,2,4} At ground level, ozone formation contributes to urban "smog" and reduced air quality in general—for example, ozone is a respiratory irritant.⁴ In the upper troposphere/lower stratosphere (UTLS) region of the atmosphere ozone is an important greenhouse gas.⁵ The general mechanisms of the atmospheric degradation of VOCs are fairly well established.⁶ In the majority of cases, the oxidative degradation is initiated by reaction with the hydroxyl radical, OH, and proceeds to the production of a first generation carbonyl product through a chain of reactions mediated by alkyl (R[•]), peroxyl (RO₂•) and alkoxyl (RO•) radicals. Under polluted urban atmospheric conditions (with 20% O₂ and significant levels of NO_x from, primarily, combustion sources) R^{\bullet} are largely converted to RO• radicals.^{1,2,6} The atmospheric impact of the oxidation chemistry of a given VOC is determined by the nature of the first generation products and this is determined by the chemistry of RO[•]. In the atmosphere, RO[•] exhibits three modes of reaction: $^{6-9}$ (i) bimolecular reaction with O₂ (yielding a carbonyl product, of the same carbon chain length as the parent VOC, and a hydroperoxy radical, HO_2^{\bullet} ; (ii) decomposition (yielding carbonyl and alkyl radical fragments, of smaller carbon chain length than the parent VOC) and (iii) isomerisation (a 1,5 H shift occurring through a six-membered cyclic transition state). The energetic demands, and hence temperature-dependencies, of these three processes are different (generally, the activation barriers for the processes are in the order (ii) > (iii) >

ö Ascot, Berkshire, UK SL5 7PY. (i)) and hence the relative-rates of these reactions are expected to be temperature dependent.^{6–10} Relative-rate coefficients have been reported for the unimolecular reactions (i.e. decomposition and isomerisation) of a number of simple alkoxyl radicals but in the majority of cases the data were obtained from measurements made at room temperature (e.g. see refs. 10-13) or, in some cases, at temperatures not representative of the Earth's atmosphere (e.g. see refs. 14-16). A number of absolute kinetic studies have also been made of the decomposition of selected RO• and of their bimolecular reaction with O_2 .^{17–27} Recent atmospheric measurements have revealed higher than expected concentrations of partially oxidised hydrocarbons in the free and upper troposphere³ which is suggestive of the occurrence of VOC oxidation at higher altitudes where temperatures and pressures are lower than at the Earth's surface. It has thus become clear that it is important to understand the relative-rates of processes (i)-(iii) as a function of temperature-in a range pertinent to the Earth's atmosphere-for a variety of alkoxyl radicals, derived not only from small but also larger VOCs, to assess the atmospheric impact of the photooxidation of VOCs throughout the troposphere. Further to this, the importance of identifying patterns and trends in the reactivity of alkoxyl radicals of various size and structure is becoming clear.

Recent work in this laboratory was aimed at determining the temperature-dependence of the relative-rates (relative to bimolecular reaction with O_2) of isomerisation reactions of various model RO[•] species.²⁸ These relative-rate data were then used to estimate absolute rate parameters and the effect of the structure of RO[•] upon Arrhenius activation barriers and A factors was investigated. Derived Arrhenius activation barriers were shown to correlate linearly with the strength of the C-H bond cleaved in the isomerisation process and the A factors were found to scale linearly with the number of abstractable H atoms in the γ -position to the alkoxyl functionality. The kinetics of the decomposition of the 2-butoxyl radical have also been investigated in this laboratory using the same experimental technique.²⁹ The effect of the structure of RO[•] upon the decomposition kinetics of various alkoxyl radicals was also investigated and a non-linear correlation between the logarithm of the unimolecular rate coefficient and the average

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ionisation potential (IP_{mean}) of the product fragments was found for data obtained at 298 K.³⁰ Correlations between measured, estimated and theoretically calculated activation barriers were also presented. During the course of this latter investigation it was found that the kinetics of the decomposition of the 2-methyl-2-butoxyl (*t*-amyloxyl) radical to butanone and methyl radical products were anomalous in terms of the identified correlation. 2-Methyl-2-butoxyl can decompose by more than one pathway:

$$CH_3CH_2C(O^{\bullet})(CH_3)_2 \rightarrow CH_3C(O)CH_3 + C_2H_5^{\bullet} \quad (R1)$$

$$CH_3CH_2C(O^{\bullet})(CH_3)_2 \rightarrow CH_3C(O)CH_2CH_3 + CH_3^{\bullet} \quad (R2)$$

The room temperature rate coefficient data for (R1) and (R2) included in the correlation plot^{30} were those presented by Atkinson.⁷ These were values extrapolated (to 298 K) from the higher temperature measurements (120–190 °C; 393–463 K) of Batt *et al.*³¹—rate coefficients, at four different temperatures between 433 and 463 K, were determined relative to the reaction of 2-methyl-2-butoxyl with NO.

 $CH_3CH_2C(O^{\bullet})(CH_3)_2 + NO \rightarrow CH_3CH_2C(ONO)(CH_3)_2(R3)$

The source of alkoxyl radicals in this study was the thermal decomposition of 2-methyl-2-butylnitrite:

$CH_3CH_2C(ONO)(CH_3)_2 \rightarrow CH_3CH_2C(O^{\bullet})(CH_3)_2 + NO (R4)$

The rate of reaction (R1) was found to dominate over that of (R2) with a rate coefficient ratio (k_1/k_2) of 80 at 433 K, and an Arrhenius expression for (R1) was reported: $k_1 = 5.0 \times 10^{14}$ exp(-59.8 kJ mol⁻¹/*RT*).³¹ These data were extrapolated to 298 K following the method described by Atkinson.⁷ A value for k_1 was calculated using the above Arrhenius expression of Batt *et al.*³¹ for T = 448.2 K (the mid-point of the temperature range employed in their experimental study) and then corrected to reflect the recommendation of Atkinson³² for rate coefficients for the combination reactions of alkoxyl radicals with NO (this was the reference reaction in the study). An Arrhenius A factor of 1×10^{13} s⁻¹ was then assumed for reaction (R1)—A factors close to this value have been obtained in a number of recent relative- and direct-kinetic studies of the decomposition of alkoxyl radicals, as discussed by Johnson et al.³⁰-and an activation barrier for (R1) was calculated to match the value of $k_1^{448.2K}$. This new Arrhenius expression was then used to calculate $k_1^{298K} = 3.4 \times 10^4 \text{ s}^{-1}$. A similar extrapolation employing the Batt *et al.* determination of k_1^{433K}/k_2^{433K} yields $k_2^{298K} = 36 \text{ s}^{-1}$ and hence $k_1^{298K}/k_2^{298K} \approx 950$. These experimentally derived values for k_1 and k_2 (and, of course, k_1/k_2) can be compared with the recent theoretical calculations of Méreau *et al.*³³ and Peeters *et al.*³⁴ (with values of $k_1^{298K} = 9.4 \times 10^5$ and 1.6×10^6 s⁻¹; and $k_2^{298K} = 1.1 \times 10^4$ and 1.3×10^4 s⁻¹,

Table 1 Summary of previous experimental determinations of k_1/k_2

respectively; giving $k_1^{298\text{K}}/k_2^{298\text{K}} = 85$ and 123, respectively). Other experimental determinations of k_1/k_2 have been made by measuring the relative yields of acetone and butanone.^{35–37} In these studies, which are summarised in Table 1, 2-methyl-2-butoxyl radicals were produced from both the thermolysis and photolysis of various precursor compounds (alkyl nitrites and dialkyl peroxides) under a variety of different conditions of temperature, reactant concentration and in the presence and absence of added NO. What is clear from the data presented in Table 1 is that there is no clear consensus between the various determinations of the ratio of decomposition rate coefficients for 2-methyl-2-butoxyl. Similarly, the theoretically determined rate coefficients for the major decomposition process (R1) are significantly greater than the experimental determination of Batt *et al.*³¹ and yet this latter value is consistent with the kinetic correlation identified previously in this laboratory.

The first aim of the present investigation, therefore, was to reassess the relative kinetics of the decomposition channels of 2-methyl-2-butoxyl using the same methodology employed in this laboratory to study the isomerisation²⁸ of simple alkoxyl radicals and the chemistry of the 1- and 2-butoxyl radicals.²⁹ This was achieved by measuring the relative-yields of acetone and butanone from the steady-state, near-UV photolysis of dilute mixtures of 2-methyl-2-butyl nitrite, as a function of temperature, in a flow-reactor. The second aim of the investigation was to attempt to place these relative-data onto a more absolute basis by studying the chemistry of the 2-methyl-2-pentoxyl radical. As discussed later, the decomposition kinetics (R5,6) of this radical are expected to be similar to those of 2-methyl-2-butoxyl. In addition to decomposing, 2-methyl-2-pentoxyl is able to isomerise (R7).

$$\begin{array}{c} CH_{3}CH_{2}CH_{2}C(O^{\bullet})(CH_{3})_{2} \rightarrow CH_{3}C(O)CH_{3} \\ + CH_{3}CH_{2}CH_{2}^{\bullet} \quad (R5) \end{array}$$

$$CH_{3}CH_{2}CH_{2}C(O^{\bullet})(CH_{3})_{2} \rightarrow CH_{3}CH_{2}CH_{2}C(O)CH_{3} + CH_{3}^{\bullet} \\ \quad (R6) \end{array}$$

$$CH_{3}CH_{2}CH_{2}C(O^{\bullet})(CH_{3})_{2} \rightarrow {}^{\bullet}CH_{2}CH_{2}CH_{2}C(OH)(CH_{3})_{2} \\ \quad (R7) \end{array}$$

The rate of the isomerisation process (R7) (involving the cleavage of primary C–H bond) can be estimated, as a function of temperature, using the structure activity relationship recently developed in this laboratory²⁸ and it is proposed that this may be used as an estimated kinetic reference for the decomposition reactions. Neither 2-methyl-2-butoxyl nor 2-methyl-2-pentoxyl possesses H atoms in a position α - to the alkoxyl functionality and hence reaction of the radicals with O₂ (which can yield useful diagnostic carbonyl products with fairly well established kinetics)^{7–9} does not occur and hence cannot be used as a kinetic reference.

RO• Precursor Experiment type CH ₃ -O-O-C(CH ₃) ₂ CH ₂ CH ₃ Thermolysis		Conditions	T/K 468	<i>k</i> ₁ / <i>k</i> ₂ 8.4	Ref.
		Peroxide : N_2 molar ratio 2 : 3			35
CH ₃ CH ₂ -O-O-C(CH ₃) ₂ CH ₂ CH ₃	Thermolysis	20 Torr peroxide	387	16	36
CH ₃ CH ₂ –O–O–C(CH ₃) ₂ CH ₂ CH ₃	Thermolysis	20 Torr peroxide	410	15	36
CH ₃ CH ₂ C(ONO)(CH ₃) ₂	Thermolysis	26 Torr nitrite	430-456	160	37
CH ₃ CH ₂ C(ONO)(CH ₃) ₂	Thermolysis	26 Torr nitrite, 14 Torr NO	427-455	104	37
CH ₃ CH ₂ -O-O-C(CH ₃) ₂ CH ₂ CH ₃	Thermolysis	a	387	16	37
CH ₃ CH ₂ C(ONO)(CH ₃) ₂	Thermolysis	2.3 Torr nitrite	433	80	31
CH ₃ CH ₂ -O-O-C(CH ₃) ₂ CH ₂ CH ₃	Photolysis	20 Torr peroxide, $\lambda = 313$ nm	299	16	36
CH ₃ CH ₂ -O-O-C(CH ₃) ₂ CH ₂ CH ₃	Photolysis	20 Torr peroxide, $\lambda = 313$ nm, 15 Torr NO	299	10	36
CH ₃ CH ₂ –O–O–C(CH ₃) ₂ CH ₂ CH ₃	Photolysis	20 Torr peroxide, $\lambda = 313$ nm, 15 Torr NO	346	8.3	36
CH ₃ CH ₂ C(ONO)(CH ₃) ₂	Photolysis	26 Torr nitrite, 26–105 Torr NO, $\lambda = 366$ nm	387	33-42	37
CH ₃ CH ₂ C(ONO)(CH ₃) ₂	Photolysis	26 Torr intrite, 20–85 Torr NO, $\lambda = 313$ nm	387	11.3	37
CH ₃ CH ₂ C(ONO)(CH ₃) ₂	Photolysis	26 Torr nitrite, 0–85 Torr NO, $\lambda = 253.7$ nm	387	6.8	37
a					

^{*a*} Details not given.



Fig. 1 Schematic diagram of the steady-state, slow-flow, photochemical apparatus.

Experimental

Experiments were performed in steady-state using a slow-flow photochemical reactor and dedicated gas chromatograph with flame ionisation detection (GC-FID). A schematic diagram of the experimental apparatus is shown in Fig. 1.

The flow-reactor comprised a double-jacketed, 1 m long, cylindrical quartz cell with an internal volume of 220 ± 10 cm³ The internal surfaces of the cell were coated with halocarbon wax to reduce their reactivity. The temperature of the cell was controlled, between 283 and 345 K, by flowing a thermostatted water/ethylene glycol mixture (equal concentrations by volume) from a circulating bath (Neslab RTE-140) through the middle jacket. The outer jacket was evacuated to provide thermal insulation. Surrounding the cell were four, metre-long, fluorescent black-lamps (F40-BLB-EX) which provided continuous near-UV radiation in the range 350 to 400 nm, with $\lambda_{\rm max} \approx 365$ nm. The lamps were mounted equidistantly around and parallel to the flow-cell, and the lamps and cell were housed in an aluminium box. The alkoxyl radicals studied were produced directly from the photodissociation of alkyl nitrite (RONO) precursors using the radiation from the blacklamps. Pure samples of RONO were synthesised from the parent alcohol (ROH) by reaction with nitrous acid (HONO), at 0 $^{\circ}$ C, and stored under vacuum at 4 $^{\circ}$ C.³⁸ The purity of each RONO sample was assessed by GC-FID and proton nuclear magnetic resonance spectroscopy, and was found to be $\geq 95\%$ in all cases. The major impurity in all samples was unreacted ROH. Measured UV/visible absorption spectra of 2-methyl-2butyl nitrite and 2-methyl-2-pentyl nitrite are shown in Fig. 2.

These spectra are typical of those for simple alkyl nitrites and compare well, in terms of general shape and maximal absorption cross-section, with spectra reported in the literature for other simple C_2 - C_4 alkyl nitrites.^{39,40}

A mixture of the RONO precursor (100-140 ppmv) and sufficient cyclohexane (2500 ppmv) to scavenge >95% of any OH formed during the experiments (from the reaction of any HO₂ formed with NO) was prepared in N₂ (Air Products, grade 5.0) and O_2 (Air Products, grade 5.0) in a 300 L collapsible Tedlar bag (Andersen Instruments, Nutech 219). The diluent gas mixture was 80% N_2 and 20% O_2 by volume. During the photochemical experiments, the contents of the Tedlar reactant reservoir were drawn first through a jacketed glass mixing-manifold (which was thermostatted using the same circulating water/ethylene glycol mixture as the flow-cell) before passing through the flow-cell. The flow of gases was achieved using a rotary vacuum pump and was regulated using two calibrated mass flow controllers (Tylan) which were connected before the pump (see Fig. 1). Connections between the reactant reservoir, the mixing manifold and the inlet of the flow-cell were made with 1/4'' Teflon tubing which was externally, thermally insulated with polyurethane foam. The

outlet of the flow-cell was connected to the first mass flow controller (calibration range 0-500 cm³ min⁻¹) with 1/4''Teflon tubing and the outlet of the mass flow controller was connected to a glass, gas-handling line, again with Teflon tubing, which in turn was connected to the rotary pump. The total flow-rate through the cell was controlled between 125 and 325 cm³ min⁻¹ giving a residence time in the flow-cell of between 108 and 42 s. This resulted in fractional photolytic consumption of the RONO precursors of between 75 and 25%. Also connected between the outlet of the flow-cell and the gashandling line (and hence the rotary pump) was a small sampling loop, which consisted of a broken short length of 1/4'' Teflon tubing with 1/4'' PFA compression fittings, and a by-pass loop, both of which were connected up-line of the second calibrated mass flow controller (see Fig. 1). The PFA compression fittings allowed an adsorbant tube (1/4" outside diameter, stainless steel tube containing Tenax TA) to be connected in-line with the photochemical flow-cell and the second mass flow controller (calibration range 0-100 cm³ \min^{-1}). A controlled flow, of 30 cm³ min⁻¹, from the outlet of the photochemical cell was maintained through the second flow controller throughout each experiment and this came either via the sample loop (with adsorbant tube in place) or the by-pass loop. The "route" of this 30 $\text{cm}^3 \text{ min}^{-1}$ flow was determined using three PFA valves (again, see Fig. 1). Gas-flow through the sample loop (with adsorbant tube in place) was used to immobilise, and hence concentrate, 150 cm³ gas samples after passage through the photochemical flow-cell. A



Fig. 2 UV/visible absorption spectra of 2-methyl-2-butyl nitrite (solid line) and 2-methyl-2-pentyl nitrite (dotted line).

clean adsorbant tube was connected in-line with the sample loop, the two sample-loop PFA valves were opened and the bypass loop PFA valve was closed for 5 min. After this time, the sample-loop was isolated, the by-pass PFA valve was reopened and the adsorbant tube was removed and placed into a thermal desorber (Markes International Ltd UNITY thermal desorber) which was connected to the GC (Agilent 6890N). The immobilised hydrocarbons were then flash desorbed and flushed into the capillary column (50 m, CP-Sil 5CB) of the GC for subsequent separation and detection. An example temperature programme, for experiments involving 2-methyl-pentyl nitrite, started with the column at a temperature of 10 °C for 5 min before being raised to 110 °C at a rate of 25 °C min⁻¹. A carrier gas pressure of 18 psi was used for these experiments which gave a carrier gas flow-rate of 2.8 $\text{cm}^3 \text{ min}^{-1}$ through the capillary column.

GC peak areas were converted to volume mixing ratios after calibration with pure standards. Standard mixtures were prepared by flushing a known pressure of pure vapour in a calibrated glass volume into an 80 L, collapsible Tedlar[™] bag with a known volume of GC grade nitrogen. The standard mixture was then drawn through the mixing manifold and flow-cell, and subsequently sampled and analysed in the same way as described above for photolysis experiment samples. Five or six separate mixtures for each reactant and product of interest, of varying volume mixing ratio, were prepared and analysed in this way to construct calibration curves. The linear regression statistics of these calibration curves gave an indication of the repeatability of the analyses, 5% (2σ). The total uncertainty in measured mixing ratios, accounting for systematic uncertainties in the preparation of calibration mixtures (i.e. uncertainty in pressure measurements and, in the case of alkyl nitrites, the purity of standards), was of the order of 7-10%. In this way, yields of diagnostic carbonyl reaction products were determined relative to the amount of alkyl nitrite precursor consumed. All experiments were carried out at atmospheric pressure (760 \pm 10 Torr). All condensed-phase reagents underwent two freeze-pump-thaw cycles before being used. UV/ visible absorption spectra of the synthesised alkyl nitrites were measured and recorded, with a spectral resolution of 0.5 nm, using a spectrograph (Acton Research Corporation), with broadband CCD detector, connected to a personal computer. The pyrex-filtered radiation from a deuterium discharge lamp was passed longitudinally through a second quartz cell (60 cm length) before being directed, with a fibre optic, into the entrance slit of the spectrograph. The absorption cell was connected to the glass gas-handling line and this allowed absorption spectra to be measured as a function of the partial pressure of the alkyl nitrite in the absorption cell, in the range 0.5-3 Torr. The absorption cross-sections indicated in Fig. 2 were determined in this way.

Results and discussion

2-Methyl-2-butoxyl

The results of experiments using the photolysis of 2-methyl-2butyl nitrite as a source of 2-methyl-2-butoxyl radicals are summarised in Table 2. The ratios of the measured yields of acetone and butanone are assumed to be equal to the relative rate coefficient k_1/k_2 . Implicit with this analysis is the assumption that no significant proportion of activated, or "hot", alkoxyl radicals is produced from the near-UV photolysis of the alkyl nitrite precursor. This assumption is consistent with the results of other experimental studies made in this laboratory‡ and the conclusion of Heicklen⁴⁰ that the propor-

 Table 2
 Measured relative-yields of acetone and butanone from the near-UV photolysis of 2-methyl-2-butyl nitrite

T/K	[2-Methyl-2- butyl nitrite] ₀ / ppmv	No. of determinations	Δ [acetone]/ Δ [butanone] ^a (k_1/k_2)
283.2	20.6	4	71.0 (±7.9)
298.2	9.6	4	48.7 (±6.9)
308.2	12.9	5	42.8 (±10.0)
323.2	11.8	5	35.0 (±6.9)
338.2	11.2	5	30.7 (±7.0)
$a^{a} \pm 2\sigma$ from	om replicate determina	ations.	

tion of "hot" RO \bullet produced from the 360 nm photolysis of alkyl nitrites is of the order of 5–10%.

The data in Table 2 are plotted in Fig. 3a in Arrhenius form—*i.e.* the natural logarithm of the relative rate coefficients *vs.* the reciprocal of the absolute temperature—although there does appear to be some curvature in these data. If the rate coefficients for reactions (R1) and (R2) are expressed by Arrhenius expressions—*i.e.* $k_1 = A_1 \exp(-E_1/RT)$ and $k_2 = A_2 \exp(-E_2/RT)$ —then the intercept of the plot corresponds to the logarithm of the ratio of the A factors of the two decomposition pathways (E1).

$$\ln(k_1/k_2) = \ln(A_1/A_2) + (E_2 - E_1)/RT$$
(E1)

It is expected that Arrhenius A factors for a single RO[•] decomposition channel are similar for any given alkoxyl radical-this is to say that the electronic rearrangements commensurate with a given decomposition processes (*i.e.* a β C–C scission giving rise to carbonyl and alkyl radical fragments) are similar. For the decomposition of 2-methyl-2-butoxyl, however, via reaction (R2) there are two possible carbon atoms that can be ejected as methyl radicals and hence, statistically, we expect A_2 to be twice the value of A_1 and thus the intercept of Fig. 3a to be ln(1/2) (-0.69, two decimal places). From a least squares linear regression analysis of the data in Fig. 3a, weighted by the uncertainties in the data, the intercept is -1.16 ± 2.24 (uncertainty = 2 × standard error) and thus the relative-rate data obtained in the present investigation are consistent with the expected relative degeneracies of pathways (R1) and (R2). That said, however, the data are also consistent with the values of A_1 and A_2 being equal and with the value of A_1 being twice that of A_2 —all that can really be inferred from the data is that the values of A_1 and A_2 are similar and that this is consistent with the measured carbonyls being produced by similar decomposition mechanisms.

Plotted in Fig. 3b are the various relative-rate coefficient determinations listed in Table 1. It is interesting to divide these additional data into four groups depending on the type of precursor used and the method of RO• production from that precursor, viz.: thermolysis of organic peroxide, thermolysis of organic nitrite, photolysis of organic peroxide and photolysis of organic nitrite. It can be seen in Fig. 3b that the relative-rate determinations from peroxide thermolysis studies are consistent with the results obtained in the present investigation and that the apparent curvature in Fig. 3a does not appear to be as significant over the extended temperature range of the combined two datasets. Relative-rate coefficients from peroxide photolysis studies lie, unsurprisingly, below the solid line in the figure and this can be explained in terms of the effects of chemical activation in the alkoxyl radicals resulting from the 313 nm photolysis of organic peroxide precursors. Relatively more butanone (and methyl) will result from the decomposition of "hot" 2-methyl-2-butoxyl radicals than from the decomposition of thermalised radicals and thus the value of

[‡] Unpublished experimental results of studies of the near-UV photolysis of 1- and 2-butyl nitrite are consistent with a production of *ca*. 10% "hot" alkoxyl radicals in both systems.



0.0036

0.004

Fig. 3 (a) Arrhenius plot of relative rate coefficients (k_1/k_2) for the decomposition of 2-methyl-2-butoxyl to acetone and ethyl (R1), and to butanone and methyl (R2). The indicated error bars (2σ) were calculated from replicate determinations of Δ [acetone]/ Δ [butanone] (see Table 2). The solid line represents the weighted least squares regression line for these data. (b) Arrhenius plot of relative rate coefficients for the decomposition of 2-methyl-2-butoxyl. The filled diamonds correspond to the data measured in the present investigation; also included are data from experiments in which RO[•] was produced from organic peroxide precursors (by thermolysis (open circles) and photolysis (open triangles) and photolysis (crosses)). The solid line is reproduced from Fig. 2a and is extrapolated to 1/T = 0. The short horizontal line indicates a value on the *y*-axis of hn(1/2).

 k_1/k_2 will be reduced—*i.e.* the decomposition of these RO[•], containing a significant excess of energy, will be more indiscriminate. The effect of activation is discussed by McMillan.³⁶ The relative rate coefficients obtained from experiments using 2-methyl-2-butyl nitrite are, however, more difficult to explain. Evidence for the production of "hot" radicals from the shorter wavelength ($\lambda = 253.7, 313$ nm) photolysis of 2-methyl-2-butyl-nitrite was presented by Durant and McMillan³⁷ who observed an increased randomisation in the bond breaking of 2-methyl-2-butyl-2-butyl at these shorter wavelengths—this is to say that the relative rate of the more endothermic decomposition process (R2) increased. The dependence of the (366 nm) photolysis quantum yield sum ($\Phi_{acetone} + \Phi_{butanone}$) upon the concentra-

tion of added NO was also investigated by these authors. An initial rapid decrease of the quantum yield sum with the amount of added NO (up to *ca.* 20 Torr NO) was attributed to the scavenging of thermalised alkoxyl radicals by NO and a subsequent slower decrease (35 Torr < NO < 100 Torr) was attributed either to the deactivation of excited RO[•] by NO or some other reaction of excited RO[•] with NO giving products other than ketones. These conclusions are not, however, consistent with the results of other studies in which alkoxyl radicals were produced from the near-UV photolysis of alkyl nitrites where evidence for very much smaller proportions of excited RO[•] were obtained.^{28,29,40}

The effect of added NO upon the ratio of the yields acetone and butanone in thermolysis and photolysis experiments was also investigated by Durant and McMillan³⁷ and in both experiment types Δ [acetone]/ Δ [butanone] decreased with added NO. In the experiments of Batt et al.³¹ around 1 atm of NO was added to around 2 Torr 2-methyl-2-butyl nitrite and no butanone could be observed at all. One of the major differences between the experiments carried out in the present investigation and the alkyl nitrite thermolysis and photolysis experiments indicated in Table 1 are the starting concentrations of the radical precursor. In the present investigation, mixing ratios of around 10 ppmv 2-methyl-2-butyl nitrite were employed which equate to partial pressures of around 1×10^{-2} Torr. This compares with pressures of 2.3 and 26 Torr of alkyl nitrite employed in the studies in Table 1. It may be possible that, under the conditions of these latter experiments, a large proportion of the ethyl (and methyl) radicals formed from the decomposition of alkoxyl radicals can react with the alkyl nitrite.

$C_2H_5^{\bullet} + CH_3CH_2C(ONO)(CH_3)_2 \rightarrow Products$ (R8)

If this reaction promotes the formation of acetone over that of butanone then this will result in an "artificially" high value of k_1/k_2 being determined from measurements of Δ [acetone]/ Δ [butanone]. The effect of adding NO to such systems can now, qualitatively, be explained in terms of a scavenging of the ethyl radicals. From our relative rate data we can estimate $k_1^{433\dot{K}}$ $k_2^{433K} = 11.5$ which compares with the ratio of 80 reported by Batt et al.³¹ If we consider the limiting case where every ethyl radical produced reacts with a molecule of 2-methyl-2butyl nitrite and leads to the formation of a molecule of acetone then, according to the relative-rate data obtained in the present investigation, Δ [acetone]/ Δ [butanone] = 23. This is still a factor of four smaller than the carbonyl yield (and hence rate coefficient) ratio reported by Batt et al. A possible explanation for this discrepancy may involve the oxidation of NO to NO_2 by nitrosoethane (which is formed in the reaction of ethyl radicals with NO) with the reproduction of ethyl radicals.

$$C_2H_5^{\bullet} + NO \rightarrow C_2H_5NO$$
 (R9)

$$C_{2}H_{5}NO+NO+NO(+NO) \rightarrow C_{2}H_{5}^{\bullet}+N_{2}+NO_{2}(+NO_{2})$$
(R10)

Christie *et al.*⁴¹ observed NO₂ quantum yields of up to 110 from the photolysis of *t*-butyl nitrite in the presence of high pressures of NO. If the product of reaction (R8) is a C-centred radical, resulting from the abstraction of a secondary-H atom, then it is possible that the reaction of this radical with NO₂ may produce an alkoxyl radical, the subsequent decomposition of which can yield acetone, acetaldehyde and NO:

$$CH_{3}^{\bullet}CHC(ONO)(CH_{3})_{2} + NO_{2} \rightarrow$$

$$CH_{3}CH(O^{\bullet})C(ONO)(CH_{3})_{2} + NO \qquad (R11)$$

$$CH_{3}CH(O^{\bullet})C(ONO)(CH_{3})_{2} \rightarrow CH_{3}CHO + CH_{3}C(O)CH_{3} + NO \qquad (R12)$$

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Table 3Rate data for the decomposition of 2-methyl-2-pentoxyl derived from measurements of the change in concentration of 2-methyl-2-pentylnitrite, acetone and pentanone (see text and eqn. (E3)). The initial mixing ratio of alkyl nitrite in each experiment was 100–140 ppmv. Between fiveand seven separate measurements of reactant and product concentrations were made at each different temperature

T/K	$(k_{\rm isom}/k_{\rm decomp})^{ab}$	$k_{ m decomp}{}^{cd}/{ m s}^{-1}$	k_{5}/k_{6}^{e}	k_5/s^{-1d}	k_6/s^{-1d}
283.2	24.2 (±9.4)	$9.53 (+17.0, -8.0) \times 10^3$	21.2 (±6.9)	9.1 (+16.6, -8.2) × 10 ³	$4.3 (+7.8, -3.9) \times 10^2$
298.2	19.3 (±2.6)	$2.30 (+4.0, -1.8) \times 10^4$	22.2 (±4.1)	$2.2(+3.9, -1.7) \times 10^4$	$9.9 (+17.5, -7.8) \times 10^{2}$
305.2	$18.1 (\pm 2.7)$	$3.25 (+5.7, -2.5) \times 10^4$	12.0 (±0.76)	$3.0 (+5.3, -2.3) \times 10^4$	$2.5 (4.4, -1.9) \times 10^3$
320.2	12.2 (±3.1)	$8.44 (+14.9, -6.7) \times 10^4$	18.2 (±3.8)	$8.0 (+14.2, -6.6) \times 10^4$	$4.4 (+7.8, -3.6) \times 10^3$
333.2	7.52 (±0.94)	$2.12 (+3.7, -1.6) \times 10^5$	16.7 (±2.6)	$2.0 (+3.5, -1.6) \times 10^5$	$1.2 (+2.1, -0.9) \times 10^4$
345.2	7.36 (±1.4)	$3.14 (+5.5, -2.4) \times 10^5$	12.1 (±2.2)	$2.9 (+5.1, -2.3) \times 10^5$	$2.4 (+4.2, -1.9) \times 10^4$
^{<i>a</i>} $k_{\rm isom}/k_{\rm o}$	$k_{\rm decomp} = k_7 / ((\Delta [\rm nitrite])/($	Δ [acetone] + Δ [pentanone]) - 1); ^b $\pm 2\sigma$ from replic	ate determinations; $^{c} k_{decomp}$ (=	$k_5 + k_6$) values derived by

 $k_{isom}/k_{decomp} = k_7/((\Delta [intrie]/(\Delta [acetone] + \Delta [pentanone]) - 1), \pm 26$ from replicate determinations, $k_{decomp} = k_5 + k_6$ values derived by estimating k_{isom} (*i.e.* k_7) using the following Arrhenius expression from Johnson *et al.*³⁰ - $k_{isom} = 9.0 \times 10^{10} \exp(-30.3 \text{ kJ mol}^{-1}/RT)$. The uncertainty ascribed to these estimated reference rate coefficients is +175%, -75% (see text); ^d Combined uncertainty from replicate determinations of carbonyl yields and estimated kinetics of reference reaction; ^e Values and uncertainties calculated from replicate measurements of Δ [acetone]/ Δ [pentanone].

A reaction such as (R11) was proposed to be occurring for the *n*-propyl radical by Jaffe and Wan⁴² in order to explain products observed in both thermal and photochemical reactions of NO₂ with butanal. For the purposes of the present discussion it was not attempted to numerically simulate the kinetics of the experiments of Batt *et al.* due to the catalytic nature of the chemistry and the unknown kinetics of the various potential chain-terminating reactions. What does seem clear, however, is that the presence of high concentrations of alkyl nitrite molecules and the potential catalytic oxidation of NO to NO₂ will add significant complexity to the reaction system studied, and to the kinetic interpretation of product yield data.

Using a value for k_1 (at 298 K) obtained by extrapolation of the data of Batt *et al.*³¹ (3.9 × 10⁴ s⁻¹) and the value of k_1^{298K}/k_2^{298K} determined in the present investigation we propose a 298 K value for k_2 of 800 s⁻¹. Both of these values are significantly smaller than the theoretical calculations of Méreau *et al.*³³ ($k_1^{298K} = 9.4 \times 10^5 \text{ s}^{-1}, k_2^{298K} = 1.1 \times 10^4 \text{ s}^{-1}$) and Peeters *et al.*²⁸ ($k_1^{298K} = 1.6 \times 10^6 \text{ s}^{-1}, k_2^{298K} = 1.3 \times 10^4 \text{ s}^{-1}$) and yet the relative-rate coefficient measured at 298 K in the present investigation is in reasonable agreement—within a factor of two—with the results of both theoretical studies. Certainly, this latter agreement is much better than with the values of k_1^{298K} and k_2^{298K} derived from the data of Batt *et al.*³¹

2-Methyl-2-pentoxyl

The results of the experiments using 2-methyl-2-pentyl nitrite are summarised in Table 3. As already mentioned, the kinetics of the isomerisation reaction (R7) were used as an estimated reference in order to estimate the kinetics of the two decomposition channels (R5,6). Rate coefficients for (R7) were estimated using the expression recently proposed by Johnson *et al.*²⁸ for the isomerisation of a simple alkoxyl radical involving the cleavage of a primary C–H bond.

$$k_{\rm isom}({\rm Primary}) = 9.0 \times 10^{10} \exp(-30.3 \text{ kJ mol}^{-1}/RT)$$
 (E2)

Expression (E2) itself was derived from a series of relative-rate experiments in which the reference reaction was that of a model alkoxyl radical (2-pentoxyl) with O₂. Thus, the combined uncertainty of rate coefficients estimated using expression (E2) (the uncertainty in the reference rate coefficient (*e.g.* see ref. 9) combined with the uncertainty in the relative rate coefficients measured in the study of Johnson *et al.*²⁸) is of the order of $\pm 175\%$, -75%. Thus by assuming that reactions (R5–R7) were the only ones available to 2-methyl-2-pentoxyl, and that the quantum efficiency for thermalised alkoxyl radical production from alkyl nitrite photolysis was unity, the total rate of decomposition of 2-methyl-2-pentoxyl could be determined. The relative-rates of (R5) and (R6) were measured directly (as Δ [acetone]/ Δ [2-pentanone]). It should be noted that the products of the isomerisation reaction (R7) (*i.e.* from the

further chemistry of the δ -hydroxyalkyl radical formed) were not measured and thus the proportions of RO[•] chemistry proceeding *via* this route were calculated from the difference between the change in nitrite concentration (*i.e.* assumed to be equal to the total concentration of alkoxyl radicals) and the sum of the carbonyl yields (*i.e.* the total proportion of reaction going *via* the decomposition channels). The total decomposition rate coefficient ($k_{decomp} = k_5 + k_6$) was then simply calculated from the following expression:

 Δ [nitrite]/(Δ [acetone]+ Δ [2-pentanone]) = 1+(k_7/k_{decomp}) (E3)

where nitrite corresponds to 2-methyl-2-pentyl nitrite. Average values of k_{decomp} , k_5/k_6 (and hence, k_5 and k_6) determined from (E3) are listed in Table 3. These temperature-dependent data for k_4 and k_5 are plotted in Arrhenius form in Fig. 4 where the solid lines correspond to the following expressions:

$$k_5 = 4.5 \times 10^{12} \exp(-47.4 \ (\pm 16.2) \text{ kJ mol}^{-1}/RT)$$

 $k_6 = 7.1 \times 10^{12} \exp(-53.0 \ (\pm 16.1) \text{ kJ mol}^{-1}/RT)$

which were obtained by a weighted least squares regression analysis. The uncertainty associated with the Arrhenius *A* factors for (R5) and (R6) are very large, with the following ranges of values: $A_5 = 1.7 \times 10^7$ to 1.2×10^{18} s⁻¹ and $A_6 = 9.6 \times$ 10^7 to 5.9×10^{17} s⁻¹ (these ranges are 2 × the standard error in the intercept from the regression analyses).



Fig. 4 Arrhenius plot of rate coefficients determined for the decomposition of 2-methyl-2-pentoxyl to acetone and *n*-propyl ((R5), open circles), and to pentanone and methyl ((R6), open diamonds). The indicated error bars were calculated from replicate measurements (see Table 3) and include the estimated uncertainty in the reference rate coefficient (see text).

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Correlation-type structure activity relationship (SAR)

As already stated, the first aim of the present investigation was to re-determine the relative rate coefficient k_1/k_2 and the motivation for this was the fact that a value for k_1^{298K} , extrapolated by Atkinson from the higher-temperature data of Batt *et al.*, was consistent with a kinetic correlation identified in this laboratory³⁰ and yet a similarly extrapolated value for k_2^{298K} was not.

In the SAR of Johnson et al.³⁰ the logarithm of 298 K decomposition rate coefficients are correlated with the average ionisation potential (IPmean) of the decomposition reaction products, for a variety of simple alkoxyl radicals for which rate data are available. The observed quadratic dependence was rationalised in terms of simple Marcus theory⁴³ in which the activation barrier for the endothermic decomposition reaction is non-linearly related to the enthalpy of the reaction. The enthalpy of reaction was simply related to the difference in IP of the reactant RO[•] and the average IP of the reaction products. If the former value is assumed to be constant (calculations suggest that the spin density is mostly centred on the O atom of the radical)⁴⁴ then the reaction enthalpy can simply be related to the average IP of the reaction products. Previously, Baldwin et al.45 proposed a dependence of Arrhenius decomposition energies (E_d) upon (estimated) reaction enthalpies (ΔH_d). This dependence was, however, subsequently amended to account for the fact that the correlation only worked for reactions with a common radical product and thus expression (E4) was proposed by Choo and Benson⁴⁶

$$E_{\rm d} = a + b\Delta H_{\rm d} \tag{E4}$$

where b is a constant and a is linearly dependent upon the ionisation potential of the alkyl radical fragment. The dependence of a upon ionisation potential was attributed to polarisation in the late, tight transition state with a partial positive charge residing on the carbon atom of the nascent alkyl radical and a partial negative charge on the O atom (which now resembles a carbonyl O atom).



If ionisation of the alkyl radical is relatively facile, the charge transfer required to produce the product-like transition state will be relatively easier and the reaction barrier relatively lower. Observation of a large solvent effect in the decomposition of t-butoxyl is consistent with a charge separation in the transition state.47 Expression (E4) was later updated by Atkinson⁷ who proposed the following values for the coefficients: $a = (2.4 \times \text{IP} - 8.1)$ and b = 0.36. Somnitz and Zellner,⁴⁸ however, observed of the development of expression (E4), as new and additional experimentally determined rate data became available, the importance of the reaction enthalpy in determining the Arrhenius activation energy had decreased on going from the original expression of Baldwin,⁴⁵ to the expression of Choo and Benson⁴⁶ (with b = 0.58) and to the updated version of expression (E4) of Atkinson⁷ (with b = 0.36). They further showed that the use of a constant value in place of the $\Delta H_{\rm d}$ term (*i.e.* independent of the alkoxyl radical reaction) did not degrade the accuracy of the predictions of activation energies and thus that E_d has a purely structural dependence on the decomposition fragments. This is consistent with the correlation-type SAR of Johnson *et al.*³⁰ which further takes into account the ionisation potential of the carbonyl product. In terms of the production of the polarised transition state from the combination of the products this will require a shift of electron density from the alkyl radical and the carbonyl and



Fig. 5 Correlation plot of $\ln(k/\theta/s^{-1})$ vs. the average ionisation potential of the reaction products (where k is the 298 K rate coefficient for a given decomposition channel and θ is the reaction path degeneracy for that channel) reproduced from Johnson *et al.*²⁴ Decomposition rate coefficient data are included for the following radicals (open circles): ethoxyl, *n*-propoxyl, *i*-propoxyl, 2-butoxyl (2 channels), *t*-butoxyl, 3-pentoxyl, *i*-butoxyl and 2-pentoxyl. Data are also included for 2-methyl-2-butoxyl corresponding to (R1) and (R2) extrapolated from the measurements of Batt *et al.*²⁵ (filled circle and open diamond, respectively), and (R2) calculated using the relative rate coefficient (k_1/k_2) determined in the present investigation (filled diamond). Data are also included for the decomposition of 2-methyl-2-pentoxyl, (R5,6), as determined in the present investigation (filled square and filled triangle, respectively). The indicated error bars correspond to a variation in each rate coefficient by a factor of three.

will hence be easier if the ionisation potentials of both products are relatively low. Thus the energy of the transition state will be lower with respect to the energy of the alkyl radical and carbonyl, regardless of whether it is accessed from the β -scission of an alkoxyl radical or from the addition of an alkyl radical to a carbonyl. The data used by Johnson *et al.*³⁰ to construct the original correlation are re-plotted in Fig. 5 along with values for k_1 and k_2 § derived from the studies of Batt *et al.*³¹ and a second value for k_2 obtained using the same value for k_1 and the rate coefficient ratio, k_1/k_2 , determined in the present investigation.

The new value for k_2 is clearly seen to be consistent with the quadratic line plotted through the data which provides some further support for an additional source of acetone, in experiments employing high concentrations of 2-methyl-2-butyl nitrite, other than the thermal decomposition of 2-methyl-2butoxyl radicals. Although this additional acetone source will significantly affect the value of k_2 derived from the carbonyl yield ratio measurements of Batt *et al.*³¹ the value of k_1 derived from their data is still valid as-according to the relative rate coefficients measured in the present investigation-the minor decomposition channel still only constitutes < 5%, at 298 K, of the total decomposition of the radical. The kinetic correlation reproduced in Fig. 5 suggests that the 298 K rate coefficient for the decomposition of 2-methyl-2-butoxyl and 2-methyl-2-pentoxyl to acetone and alkyl radicals (ethyl and propyl, respectively) should be very similar-this is to say that the reaction products are alike with very similar average product ionisation potentials (IP(acetone) = 9.70 eV; IP(ethyl) = 8.12 eV; IP $(\text{propyl}) = 8.10 \text{ eV})^{49}$ and this is seen to be the case. This also

 $[\]S$ In Fig. 5 the rate coefficient has been divided by the reaction path degeneracy, $\theta.$

 Table 4
 Measured and estimated rate coefficients for the decomposition of simple alkoxyl radicals

	$k_{\text{decomp } 298 \text{ K}}/\text{s}^{-1}$						
Alkoxyl radical ^a	Experimental ^b	Atkinson ^c	Méreau et al. ^d	Somnitz and Zellner ^e	Peeters et al. ^g	Johnson et al.	
Ethoxyl (CH ₃ O•)	4.8	0.31	3.4	1.2	2.6	6.5	
1-Propoxyl (CH ₃ O•)	1.0×10^{3}	3.5×10^{2}	2.5×10^{2}	3.5×10^{2}	4.9×10^{2}	1.9×10^{3}	
2-Propoxyl (CH ₃ O•)	1.4×10^{2}	7.3	1.3×10^{2}	4.7×10^{2}	91	69	
2-Butoxyl (CH ₃ O•)	1.3×10^{2}	14	31	36	91	1.7×10^{2}	
2-Butoxyl ($C_2H_5O^{\bullet}$)	1.8×10^4	2.3×10^4	3.5×10^4	1.6×10^{4}	1.7×10^{4}	1.0×10^4	
<i>t</i> -Butoxyl (CH ₃ O•)	2.0×10^{3}	140	3.0×10^{3}	2.0×10^{2f}	9.5×10^{3}	1.2×10^{3}	
2-Methyl-2-butoxyl ($C_2H_5O^{\bullet}$)	3.4×10^4	6.5×10^{4}	9.4×10^5	1.1×10^{4f}	5.9×10^{5}	3.2×10^4	
2-Methyl-2-butoxyl (CH ₃ O•)	7.0×10^{2}	100	1.1×10^{4}	2.0×10^{2f}	6.3×10^{3}	1.3×10^{3}	
<i>i</i> -Butoxyl (<i>i</i> - $C_3H_7O^{\bullet}$)	1.2×10^{4}	3.4×10^4	5.7×10^{4}	2.0×10^{2f}	9.3×10^4	1.3×10^4	
2-Pentoxyl $(n-C_3H_7O^{\bullet})$	7.5×10^{3}	3.3×10^4	2.2×10^4	9.0×10^{3}	1.7×10^{4}	1.1×10^4	
3-Pentoxyl ($C_2H_5O^{\bullet}$)	3.3×10^4	1.6×10^{4}	3.4×10^4	3.9×10^{4}	3.4×10^4	3.7×10^{4}	

^{*a*} Radical decomposition product shown in parentheses; ^{*b*} Data taken from Table 1 of Johnson *et al.*;^{30 *c*} Ref. 7; ^{*d*} Ref. 33; ^{*e*} Ref. 48, rate coefficients calculated using SAR to estimated decomposition barrier (298 K, 760 Torr) and *A* factors reported by the authors; ^{*f*} Rate coefficients calculated using SAR to estimated decomposition barrier (298 K, 760 Torr) and *A* factors of 1×10^{13} s⁻¹ per degenerate reaction channel; ^{*g*} Ref. 34; Rate coefficients calculated using expression (E5) and multiplying by reaction path degeneracy.

provides some validation of our choice of reference reaction *i.e.* a reaction whose kinetics were estimated. A 298 K value for k_5 of 2.2×10^4 s⁻¹, estimated relative to the isomerisation of 2-methyl-2-pentoxyl, is consistent with the correlation plot in Fig. 5, as is the 298 K value for k_6 . The solid line in Fig. 5 (represented below by expression (E5)) is not that previously presented by Johnson *et al.*³⁰ but represents a re-calculated second order polynomial taking account of the revised value of k_2 and including the values of k_5 and k_6 .

$$\ln(k/\theta/s^{-1}) = -1.22 (\text{IP}_{\text{mean}})^2 + 17.64 (\text{IP}_{\text{mean}}) - 49.93$$
(E5)

Here, θ is the reaction path degeneracy for a given decomposition channel and IP_{mean} is the average ionisation potential of the carbonyl and alkyl radical fragments. In all but one case (the kinetics of the decomposition of *t*-butoxyl) the plotted rate data agree with expression (E5) within a factor of two of the experimentally determined rate coefficients.

Other SARs for alkoxyl radical decomposition kinetics have recently been presented by Méreau *et al.*³³ (who re-parameterised the Choo and Benson⁴⁶-type expression by replacing the reaction enthalpy with a term which takes into account the "class" of alkoxyl radical-"class" referring to primary, secondary or tertiary substitution at the alkoxyl C atom), Somnitz and Zellner⁴⁸ (who related reaction barriers to differences in carbon chain lengths of the carbonyl and radical fragments), and Peeters *et al.*³⁴ (who correlated reaction barriers with the numbers of alkyl-, hydroxyl- and/or oxo-substituents on the α - and β -carbon atoms of the breaking bond). As a comparison, decomposition rate coefficients (for 298 K and 760 Torr) have been estimated using the SARs of Atkinson,⁷ Méreau,³ Somnitz and Zellner,⁴⁸ Peeters et al.³⁴ and Johnson et al.³⁰ for the following radicals for which the experimental rate data are available (see Table 1 of Johnson *et al.*³⁰): ethoxyl, *n*-propoxyl, i-propoxyl, 2-butoxyl (2 channels), t-butoxyl, i-butoxyl, 2methyl-2-butoxyl (2 channels), 2-pentoxyl, and 3-pentoxyl. Experimental and estimated rate coefficients are listed in Table 4, and estimated rate coefficients are plotted against the measured values in Fig. 6 (as a log-log plot).

As can be seen in this figure each of the SARs captures the general variation observed in decomposition rate coefficients which span some five orders of magnitude—but with varying degrees of accuracy. The Atkinson SAR appears to be the least reliable whereas the Johnson *et al.* SAR is able to predict rate coefficients that are within a factor of three of the measured values in all cases for the data in Fig. 6. The SARs of Méreau et al., Somnitz and Zellner, and Peeters et al. also predict rate data to within around a factor of three of their measured values for the majority of reactions considered. There are, however, some notable exceptions. The method of Somnitz and Zellner underestimates the rate coefficients for the decomposition of t-butoxyl and i-butoxyl by factors of 10 and 60, respectively, and the reasons for this are not clear, although their SAR was formulated using theoretically calculated data for straightchain alkoxyl radicals up to C5. The methods of Méreau et al. and Peeters et al. overestimate the rate coefficients for both decomposition channels of 2-methyl-2-butoxyl by factors of around 20 to 30. Again the reasons for this are unclear, but the SAR predictions merely reflect the fact that, as described in the Introduction section, the theoretically calculated rate data also overestimate the experimental determinations. Thus, on the evidence of the agreement between predictions and available experimental determinations, the correlation-type SAR updated in the present paper appears to be the most reliable method for estimating room temperature rate coefficients for the decomposition of simple alkoxyl radicals.



Fig. 6 Log–log plot of estimated (298 K) alkoxyl radical decomposition rate coefficients *vs.* experimentally determined rate coefficients for a series of simple alkoxyl radicals. Data are included for the decomposition of ethoxyl, *n*-propoxyl, *i*-propoxyl, 2-butoxyl (2 channels), *t*-butoxyl, *i*-butoxyl, 2-methyl-2-butoxyl (2 channels), 2-pentoxyl, and 3-pentoxyl radicals (see text).

Conclusions

The relative-kinetics of the decomposition of 2-methyl-2-butoxyl have been re-investigated using the near-UV photolysis of dilute (ppmv) mixtures of 2-methyl-2-butyl nitrite as the source of alkoxyl radicals. Yields of acetone and butanone were measured at a total pressure of 1 atm and as a function of temperature between 280 and 340 K. The relative rate coefficient (k_1/k_2) obtained at 298 K is around a factor of 20 smaller than that estimated by Atkinson⁷ by extrapolation of the higher temperature data of Batt et al.³¹ Previous experimental determinations of k_1/k_2 in which 2-methyl-2-butoxyl was produced from the thermal decomposition of dialkyl peroxide precursors are consistent with the temperature-dependence of the relative rate coefficients measured in the present investigation. Results from other studies in which the alkoxyl radical was produced from the photolysis of dialkyl peroxides or alkyl nitrites, or from the thermal decomposition alkyl nitrite precursors are not consistent with the temperature-dependent values of k_1/k_2 measured in the present investigation. It seems likely that these differences are attributable to the effects of chemical activation in alkoxyl radicals (when formed from the UV photolysis of organic peroxide precursors) or to additional carbonyl-forming chemistry occurring in the presence of high concentrations of alkyl nitrite precursors. The 298 K value of k_1 derived form the data of Batt *et al.*³¹ is consistent with a nonlinear correlation, between the logarithm of the rate coefficient and the average IP of the reaction products, previously presented by this laboratory.³⁰ The 298 K value of k_2 —derived from this latter value for k_1 and the relative rate coefficient determined in the present investigation-is also consistent with the kinetic correlation plot. Rate coefficients have also been estimated for the two decomposition channels of the 2-methyl-2-pentoxyl radical (R5,6) using the isomerisation of this radical as an estimated kinetic reference. Once again, the estimated 298 K values of k_5 and k_6 are consistent with the non-linear kinetic correlation which lends support to the choice of an estimated rate coefficient as the kinetic reference. The 298 K rate coefficient for the decomposition of 2-methyl-2-pentoxyl to acetone and *n*-propyl (k_5) is similar to that for the decomposition of 2methyl-2-butoxyl to acetone and ethyl (k_1) which is not unexpected as both reactions give similar products (with similar values for IP_{mean}). The expression presented by Johnson *et al.*³⁰ for the estimation of 298 K rate coefficients for the decomposition of simple alkoxyl radicals has been updated to incorporate the revised and previously unreported rate data. This correlation-type SAR appears to be the most accurate, currently reported, SAR method for estimating (298 K) decomposition rate coefficients for simple alkoxyl radicals, for which experimental rate data are available at this time.

Acknowledgements

The authors would like to acknowledge the NERC and the EU for funding under the UTLS thematic programme and UTO-PIHAN-ACT project (EVK2-CT2001-00099), respectively.

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