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Thermal stability of carbonyl radicals Part I. Straight-chain and branched C₄ and C₅ acyl radicals

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The competition between thermal decomposition (k_{dis}) and O_2 addition (k_{O_2}) of linear and branched C_4 and C_5 alkanoyl (R-C(')O, R = alkyl) radicals has been studied in a photochemical reaction chamber made from stainless steel (v = 12 L). RCO radicals were prepared by continuous photolysis of Br₂–RC(O)H–O₂–NO₂–N₂ mixtures at wavelengths ≥ 420 nm. The products CO and RC(O)O₂NO₂ were analyzed by long-path IR absorption using an FT-IR spectrometer. Rate constant ratios k_{dis}/k_{O_2} were determined at 317 K for *n*-butyryl, *n*-pentanoyl, 3-methylbutyryl, 2-methylpropionyl and 2-methylbutyryl and at 6 temperatures between 293 and 317 K for 2,2-dimethylpropionyl (=pivaloyl, *t*-butyl-CO) radicals. Total pressures were 1 bar (M = N₂ + O₂). Adopting the literature value of k_{O_2} for acetyl, unimolecular decomposition rate constants k_{dis} were derived from the measured ratios k_{dis}/k_{O_2} . k_{dis} at 298 K, 1 bar, M = O₂ + N₂ increases by factors of 35, 54 and 24 for each H atom in CH₃CO which is consecutively replaced by a methyl group (corresponding to increasing branching of R). For the unimolecular decomposition of 2,2-dimethylpropionyl radicals, the Arrhenius expression $k_{dis}(t-butyl-CO) = 6.0 \times 10^{12} \exp(-41.6 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} (2\sigma)$ was derived for the temperature range 293–317 K and a total pressure of 1 bar (M = N₂ + O₂). The results on k_{dis}/k_{O_2} show that even for the thermally most unstable of the carbonyl radicals studied in this work, *i.e.* 2,2-dimethylpropionyl, only 1.8% decompose rather than add O₂ at 298 K and 1 bar in dry air.

Introduction

Aldehydes are common atmospheric trace gases. They are emitted from both biogenic and anthropogenic sources, and they are formed as intermediates in the atmospheric degradation of volatile organic compounds (VOC) (see *e.g.* refs. 1–3). A major loss process of aldehydes is abstraction by OH of the aldehydic H atom, leading to carbonyl radicals R-CO. Generally, carbonyl radicals can undergo two different loss processes in the atmosphere:

thermal decomposition

$$RCO + M \xrightarrow{\kappa_{dis}} R + CO + M$$
(1)

recombination with O₂

$$RCO + O_2 + M \xrightarrow{\kappa_{O_2}} RC(O)O_2 + M$$
 (2)

Depending on the chemical nature of R, the branching ratio $k_{\rm dis}/(k_{\rm O_2} \times [O_2])$ and thus the product distribution can be very different. Whereas reaction (1) leads to the degradation of the carbon chain by one unit, reaction (2) gives rise to the formation of acyl peroxynitrates, RC(O)O_2NO_2, which are typical constituents of photochemical smog and represent temporary reservoirs of NO_x, transporting NO_y from polluted to remote areas.⁴⁻⁶

Up to now, data on the branching ratio $k_{\rm dis}/(k_{\rm O_2} \times [O_2])$ under atmospheric conditions are very sparse. Depending on the structure of R, either channel may dominate $(k_{\rm dis} \ll k_{\rm O_2} \times [O_2])$ for $R = CH_3$, $k_{\rm dis} \gg k_{\rm O_2} \times [O_2]$ for $R = CH_3CO^{-8,9}$ or the contributions of both channels may be of the same order of magnitude (for $R = CX_3$, X = F, Cl^{-10-12}).

Experimental data on k_{O_2} exist only for CH₃CO and C₆H₅CO radicals,¹³⁻¹⁶ the IUPAC recommended value for the rate constant of reaction (2a),

$$CH_3CO + O_2 + M \rightarrow CH_3C(O)O_2 + M, \qquad (2a)$$

is 3.2×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K and infinite pressure.¹⁷ This value seems to be a reasonable estimate for k_{O_2} of longer chain carbonyl radicals at a total pressure of 1 bar.

Data on k_{dis} are uncertain: the thermal lifetime of CH₃CO at 298 K is of the order of several seconds,¹⁸ whereas the values for the thermal lifetime of C2H5CO at 298 K vary between 10^{-2} and 5×10^{-5} s.¹⁹⁻²¹ The only other published experimental results on k_{dis} we are aware of are from Cadman and coworkers,^{21,22} with thermal lifetimes in the order of 10^{-5} - 10^{-6} s at 298 K for several RCO radicals with four or five C atoms. If these latter figures are correct, CO elimination can be competitive with O_2 addition for highly branched RCO radicals at 298 K in 1 bar of synthetic air. In the present study, k_{dis}/k_{O_2} has been determined near room temperature for several RCO radicals with four or five C atoms (including the ones studied by Tomas et al.,23 accompanying paper) where the CO group is connected to primary, secondary or tertiary C atoms, *i.e.* for RCO with R = n-propyl, *n*-butyl, *i*-propyl, *i*-butyl, 2-butyl, *t*-butyl.

Experimental

The experiments were performed in a temperature controlled 12 L reaction chamber made from stainless steel (Fig. 1). The inner surface of the cell is electropolished to reduce adsorption and reactions on the walls. It is equipped with two light paths for absorption measurements in the IR and UV/VIS spectral regions, with optical pathlengths of 2 m each. For the IR measurements, light from the ever-glo[®] light source of an FT-IR spectrometer (Nicolet MAGNA 560) enters the absorption cell, is reflected by a gold-coated concave mirror (diameter = 50.8 mm, f = 1016 mm), leaves the absorption

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Fig. 1 Schematic diagram of the reaction chamber.

cell, re-enters the FT-IR spectrometer, and is detected by an MCT detector. The UV absorption light path was not applied in the present work.

The temperature of the absorption cell is controlled *via* a heating coil from copper surrounding the cell, using silicon oil as a heating liquid. A quartz tube of internal diameter of 22.5 mm which is closed at one end extends into the cell. A photolysis lamp can be placed in this quartz tube thus allowing gas mixtures in the photoreactor to be photolysed.

Carbonyl radicals RCO were generated by stationary photolysis of molecular bromine in the presence of the aldehyde RC(O)H and oxygen:

$$Br_2 + hv \rightarrow 2Br$$
 (3)

$$RC(O)H + Br \rightarrow RCO + HBr \tag{4}$$

Light of $\lambda \ge 420$ nm was used to photolyse Br₂ in order to avoid the photolysis of NO₂. For this purpose, a halogen lamp (55 W) and a long-pass cut-off filter were placed at the external end of the quartz tube rather than inserting the lamp into the tube.

The loss of RCO occurs via reactions (1), (2) and (5):

$$\operatorname{RCO} + \operatorname{M} \xrightarrow{k_{\operatorname{dis}}} \operatorname{R} + \operatorname{CO} + \operatorname{M}$$
(1)

$$\operatorname{RCO} + \operatorname{O}_2 + \operatorname{M} \xrightarrow{\operatorname{NO}_2} \operatorname{RC}(\operatorname{O})\operatorname{O}_2 + \operatorname{M}$$
 (2)

$$RC(O)O_2 + M \rightarrow RC(O)O_2NO_2 + M$$
(5)

The alkyl radicals formed in reaction (1) react in the same way as the acyl radicals, *i.e.* by consecutive addition of O_2 and NO_2 :

$$R + O_2 + M \rightarrow RO_2 + M \tag{6}$$

$$RO_2 + NO_2 + M \rightarrow RO_2NO_2 + M$$
(7)

The ratio k_{dis}/k_{O_2} was determined at 317 K for *n*-butyryl, *n*-pentanoyl, 3-methylbutyryl, 2-methylpropionyl, and 2methylbutyryl radicals and at six temperatures between 293 and 317 K for 2,2-dimethylpropionyl (= pivaloyl, *t*-butyl-CO) radicals according to the relationship

$$k_{\rm dis}/k_{\rm O_2} = [O_2] \times \Delta [CO]/\Delta [RC(O)O_2NO_2].$$
(I)

Standard photolysis times were 2 min; in several experiments 4 min of photolysis was applied. Conversion of the aldehydes was 8–20% during this time. Typical initial concentrations were: aldehydes = $(5.9-6.1) \times 10^{14}$ molecules cm⁻³, Br₂ = $(2-4) \times 10^{15}$ cm⁻³, NO₂ = $(6-20) \times 10^{13}$ molecules cm⁻³. The concentrations of aldehydes, CO, NO₂, NO and acyl peroxynitrates were determined from their IR absorptions. Absorption coefficients of appropriate IR band maxima of these gaseous compounds were determined in separate series of calibration measurements, in most cases based on pressure measurements of the pure compounds and Beer's law. The analysis of CO and the acyl peroxynitrates will be discussed in more detail in the following two sections.

Precise measurements of CO were essential to obtain reliable values of $k_{\rm dis}/k_{O_2}$ from eqn. (I) since the yield of channel (1) was low at many experimental conditions. The average absorbance of the P(5)–P(9) lines at 2124, 2120, 2116, 2112 and 2107 cm⁻¹ was used for calibration of the CO concentration. The calibration curve for T = 317 K and a total pressure of 1 bar is shown in Fig. 2; it is linear within the whole concentration range of the present work ((1–9) × 10¹³ molecules cm⁻³). The absorption coefficients of CO at 298 K were smaller by 1.5% as compared to 317 K; absorption coefficients at the other temperatures were derived from the values at 317 and 298 K by linear inter- and extrapolation. The detection limit of CO by this method was 7×10^{12} molecules cm⁻³.

Usually, the strongest IR bands of peroxynitrates are related to the peroxynitrate group and appear close to 800, 1300 and 1740 cm⁻¹. Since their positions can be very similar for different peroxynitrates, superposition of these product IR bands can occur for the acyl and alkyl peroxynitrates formed in reactions (5) and (7) and, eventually, for unidentified peroxynitrates deriving from side products. Even though alkyl peroxynitrates are thermally very short-lived $(1/k_{dis} \leq 1 \text{ s}^{24} \text{ at})$ 298 K and atmospheric pressure) as compared to acyl peroxynitrates $(1/k_{dis} about 40 min^{25} at the same conditions)$ and the time scale of the experiments, the actual lifetimes can be considerably longer in the absence of NO and the presence of excess NO_2 , due to the rapid recombination reactions (5) and (7). Thus IR spectra of acyl and alkyl peroxynitrates can overlap. It turned out, however, that the IR spectra of an acyl peroxynitrate $RC(O)O_2NO_2$ and the corresponding alkyl peroxynitrate RO₂NO₂ with the same R can be differentiated, in particular by the absence of the carbonyl band close to 1840 cm^{-1} in the alkyl peroxynitrate spectrum. Abstraction of the aldehydic H atom by Br atoms (reaction (4)) which leads to the formation of an acyl peroxynitrate is fast and selective.²⁶ Abstraction of non-aldehydic H atoms, however, leads to the formation of alkyl peroxynitrates of the structure $R'C(H)(O_2NO_2)R''C(O)H$ which also exhibit carbonyl bands. In a few experiments with an excess of oxygen present, *i.e.* with no measurable thermal decomposition of RCO, an excess of NO $(1 \times 10^{16} \text{ molecules cm}^{-3})$ was added to the reaction



Fig. 2 Calibration of the IR absorbance of CO at 317 K based on the average intensity of the P(5)-P(9) lines.

$$RC(O)O_2 + NO \rightarrow R + CO_2 + NO_2$$
(8)

$$RO_2 + NO \rightarrow RO + NO_2,$$
 (9)

and the effective lifetime of the peroxynitrate is identical to its thermal lifetime. In these experiments, a fast change of the typical peroxynitrate bands in the photolysis product spectra was *not* observed after the addition of NO, indicating the absence of short-lived alkyl peroxynitrates and thus setting an upper limit of about 10% for the initial abstraction of non-aldehydic H atoms by Br. Consequently, the observed carbonyl bands at 1840 cm⁻¹ were assigned to the desired acyl peroxynitrate product.

Pure samples of peroxynitrates are difficult to synthesize due to their thermal instability. For the calibration experiments, most of the acyl peroxynitrates were thus prepared *in situ* by photolysis of Br₂ in the presence of the corresponding aldehyde, NO₂ and an excess of O₂ (≥ 200 mbar). Under these conditions, thermal decomposition of RCO is negligible. A halogen lamp and cut-off filter combination ($\lambda \geq 420$ nm) was used in these experiments in order to avoid photolysis of NO₂ and the complications induced by its photolysis products NO and O₃. IR absorption coefficients of the peroxynitrates were then determined assuming a stoichiometric consumption of the aldehyde according to

$$RC(O)H + Br + O_2 + NO_2 \rightarrow RC(O)O_2NO_2 + HBr.$$

The validity of this assumption was supported by the absence of any unidentified product IR bands under these conditions. Intensity ratios of strong and weak IR absorption bands were independent of total absorbance thus suggesting that Beer's law is valid. n-Butyryl peroxynitrate was synthesized both in situ and by the wet chemical method described by Gaffney et $al.^{27}$ which is based on the reaction of *n*-butyric acid anhydride with H₂O₂ and HNO₃. Different from ref. 27, *n*-butyryl peroxynitrate was recondensed from its solution in n-tridecane at liquid nitrogen temperature before transferring it to the reaction cell. Attempts to prepare branched peroxynitrates by this method were not successful. The IR absorption coefficients of *n*-butyryl peroxynitrate from samples prepared by the wet chemical method were smaller by 15-20% as compared to the in-situ mixtures, possibly due to saturation of the IR bands since the mixing ratios were larger by a factor of 500 ²⁸ in this case. For the evaluation of the kinetic data, absorption coefficients based on the stoichiometric conversion of RC(O)H to RC(O)O₂NO₂ were used.

Reaction temperatures were measured in the gas phase with two platinum resistance gauges. Silicon oil was used as a heating liquid; the temperature distribution of the reactor walls including the end flanges was around the nominal value within a range of ± 0.5 K. At high temperatures, the accessible temperature region of the kinetic experiments was limited by the thermal instability of the acyl peroxynitrates.

The following chemicals were used as received from the manufacturer: Br_2 (Merck, 99.8%), CO (Messer Griesheim, 99.997%), NO (Messer Griesheim, 99.5%), NO₂ (Messer Griesheim, 98%), *n*-butyraldehyde (Aldrich, 99%), *i*-butyraldehyde (Aldrich, 98%), 2-methylbutyraldehyde (Aldrich, 95%), 3-methylbutyraldehyde (Merck, 98%), 2,2-dimethylpropionaldehyde (Aldrich, 97%), *n*-pentanal (Merck, 98%).

Results and discussion

Carbonyl radicals RCO were generated by stationary photolysis of molecular bromine in the presence of the aldehyde RC(H)O, O_2 and NO_2 , using nitrogen as a buffer gas. The RCO radicals formed in reaction (4) undergo reactions (1) and (2); the peroxy radicals are scavenged by NO_2 (reaction (5)).

In Fig. 3, IR spectra of a mixture of 0.025 mbar 2,2dimethylpropionaldehyde (= pivalaldehyde), 0.1 mbar Br_2 , 0.006 mbar NO_2 , 5.0 mbar O_2 , and 995 mbar N_2 before and after 4 min of photolysis at $\lambda \ge 420$ nm are shown. The loss of 2,2-dimethylpropionaldehyde is accompanied by the formation of CO and 2,2-dimethylpropionyl peroxynitrate, in accord with reactions (1), (2) and (5). The photolysis product spectra of other RC(O)H-Br₂-O₂-NO₂-N₂ mixtures were equivalent. IR spectra of the corresponding peroxynitrates are shown in Fig. 4. The positions of the predominant absorption bands are the following (in cm⁻¹): 2982, 1835, 1738, 1301, 1037, 796 (n-butyryl peroxynitrate); 2991, 1827, 1738, 1299, 1037, 797 (2-methylpropionyl peroxynitrate); 2975, 1832, 1736, 1301, 1049, 796 (n-pentanoyl peroxynitrate); 2975, 1831, 1736, 1302, 1048, 796 (3-methylbutyryl peroxynitrate); 2985, 1824, 1736, 1299, 1042, 1006, 796 (2-methylbutyryl peroxynitrate); 2989, 1820, 1737, 1301, 1058, 1011, 796 (2,2-dimethylpropionyl peroxynitrate). The IR spectrum of *n*-butyryl peroxynitrate is in good agreement with a spectrum published by Niki *et al.*²⁹

The ratios $k_{\rm dis}/k_{\rm O_2}$ were derived using eqn. (I). Since the yields of CO and RC(O)O2NO2 for the same carbonyl radicals strongly depend on the partial pressure of oxygen, experiments at different $[O_2]$ can be used to test the method and, eventually, to detect complications in the reaction mechanism. According to eqn. (I), the expression [O₂] $\times \Delta$ [CO]/ Δ [RC(O)O₂NO₂] should have an O₂ independent value which is equal to k_{dis}/k_{O_2} . In Figs. 5 and 6, this quantity is plotted as a function of oxygen partial pressure at 317 K for 3-methylbutyryl, 2-methylpropionyl, and 2-methylbutyryl, and at 317, 307 and 298 K for 2,2-dimethylpropionyl, demonstrating that $[O_2] \times \Delta [CO] / \Delta [RC(O)O_2NO_2]$ is in fact independent of the O₂ concentration. For 3-methylbutyryl, the CO yield was slightly above the detection limit, and for *n*-butyryl and *n*-pentanoyl only upper limits could be derived for the CO yields. In these cases, experiments were performed only at



Fig. 3 IR spectra of a mixture of 0.025 mbar 2,2-dimethylpropionaldehyde, 0.1 mbar Br_2 , 0.006 mbar NO_2 , 5.0 mbar O_2 , and 995 mbar N_2 before (top) and after (middle) 4 min of photolysis at $\lambda \ge 420$ nm; the product spectrum consists of absorptions from CO, 2,2-dimethylpropionyl peroxynitrate, *t*-butyl peroxynitrate, and residual 2,2-dimethylpropionaldehyde; bottom: reference spectrum of the product 2,2-dimethylpropionyl peroxynitrate.



Fig. 4 IR spectra of *n*-butyryl peroxynitrate, 2-methylpropionyl peroxynitrate, *n*-pentanoyl peroxynitrate, 3-methylbutyryl peroxynitrate, 2-methylbutyryl peroxynitrate, and 2,2-dimethylpropionyl peroxynitrate.

a single very low, yet well defined, O_2 partial pressure (0.25 mbar).

The data evaluation relies on the assumption that the acylperoxy radicals formed in reaction (2) are thermally stable under the conditions of the present experiments. Although there are no experimental data on the thermal decomposition rate constants of $RC(OO_2$ and virtually no data on the thermochemistry of $RC(OO_2$, there are several arguments in



Fig. 5 Determination of $k_{\rm dis}/k_{\rm O_2}$ for 2-methylbutyryl and 2-methylpropionyl radicals at 317 K, 1 bar (M = N₂ + O₂).

Table 1 Experimental results on k_{dis}/k_{O_2} at 1 bar, $M = O_2 + N_2$



Fig. 6 Determination of $k_{\rm dis}/k_{\rm O_2}$ for 2,2-dimethylpropionyl radicals at 317, 307 and 298 K, 1 bar (M = N₂ + O₂).

favour of the absence of reaction (-2),

$$RC(O)O_2 + M \rightarrow RCO + O_2 + M: \quad (-2)$$

(i) There is a recommendation for the heat of formation of $CH_3C(O)O_2^{30}$ based on MNDO calculations which corresponds to a $CH_3C(O)-O_2$ bond energy of 147 kJ mol⁻¹. This estimate must be wrong by about 90 kJ mol⁻¹ in order that reaction (-2) can compete with reaction (5).

(ii) Including reaction (-2) in the reaction mechanism, the assumption of quasistationary concentrations of $RC(O)O_2$ leads to the expression

$$\begin{split} \label{eq:constraint} \begin{split} \left[\mathrm{O}_2\right] \times \Delta \left[\mathrm{CO}\right] & \Delta \left[\mathrm{RC}(\mathrm{O})\mathrm{O}_2\mathrm{NO}_2\right] = (k_{\mathrm{dis}}/k_{\mathrm{O}_2}) \\ & \times \left\{1 + \left[k_{-2}/(k_5 \times \left[\mathrm{NO}_2\right])\right]\right\} \equiv (k_{\mathrm{dis}}/k_{\mathrm{O}_2})_{\mathrm{eff}} \end{split}$$

Thus the effective rate constant ratio $(k_{\rm dis}/k_{\rm O_2})_{\rm eff}$ should depend on the NO₂ concentration if the thermal decomposition of CH₃C(O)O₂ plays a role. However, varying [NO₂] by a factor of 10 did not change $(k_{\rm dis}/k_{\rm O_2})_{\rm eff}$ within the error limits (10%).

(iii) Recent experiments of Tomas *et al.*²³ on the competition between reactions (1) and (2) for 2,2-dimethylpropionyl and *i*-butyryl radicals were performed at considerably higher temperatures. An influence of reaction (-2) would have introduced inconsistencies to their observed $[RO_2]/[RC(O)O_2]$ ratios.

The results obtained for different carbonyl radicals are collected in Table 1. The stated error limits include (i) the statistical errors of k_{dis}/k_{O_2} (2σ , weighted by the uncertainties introduced by the measurement of the IR absorptions) as determined from the data in Figs. 5 and 6, equivalent data which are not shown in Fig. 6 for clarity exist for 2,2dimethylpropionyl at 312, 303, and 293 K, (ii) the statistical errors of the calibration curves for the IR absorptions of CO and the peroxynitrates, and (iii) the estimated systematic errors of these calibration curves; they do not include the error of k_{O_2} . Existing literature values for the rate constants of

	$k_{\rm dis}/k_{\rm O_2}/10^{15}$ molecule cm ⁻³					
R-CO	317 K	312 K	307 K	303 K	298 K	293 K
<i>n</i> -Butyryl (n -C ₃ H ₇ -CO) <i>n</i> -Pentanoyl (n -C ₄ H ₉ -CO) 3-Methylbutyryl (i -C ₄ H ₉ -CO) 2-Methylpropionyl (i -C ₃ H ₇ -CO) 2-Methylbutyryl (2 -C ₄ H ₉ -CO) 2,2-Dimethylpropionyl (t -C ₄ H ₉ -CO)		204 ± 30	155 ± 17	112 ± 14	93.7 ⁺²³	77.5 ± 13

reaction (2) (Table 2) suggest that there is no barrier (which could be different for different R) for the recombination of acyl radicals with O_2 . Thus it is expected that k_{O_2} does not strongly depend on R and the large range of $k_{\rm dis}/k_{O_2}$ values observed for RCO with varying R mainly reflect the different values of $k_{\rm dis}$, *i.e.* the different thermal stabilities of RCO. Using $k_{O_2} = 3.2 \times 10^{-12}$ molecule⁻¹ cm³ s⁻¹ as adopted from the literature data in Table 2, $k_{\rm dis}$ was calculated from the data in Table 1 and listed in Table 3.

For 2,2-dimethylpropionyl (=pivaloyl) radicals, the temperature dependence of k_{dis}/k_{O_2} was measured between 293 and 317 K. Using $k_{O_2} = 3.2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, independent of temperature, the Arrhenius expression

$$k_{\rm dis}(t-{\rm butyl-CO}) =$$

 $6.0 \times 10^{12} \exp(-41.6 \pm 5.9 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1} (2\sigma)$ (II)

resulted for this temperature range at a total pressure of 1 bar, $M = N_2 + O_2$. The Arrhenius plot is shown in Fig. 7. The error of k_{dis} at the mean temperature (306 K) is estimated to be $\pm 20\%$, excluding the error of the reference rate constant k_{O_2} .

 k_{O_2} . There are no experimental data on k_{dis}/k_{O_2} and only a few data on k_{dis} in the literature to compare with. The present upper limit of 7000 s⁻¹ for the thermal decomposition rate constant of *n*-butyryl at 298 K is very close to a thermochemical estimate by Forgeteg *et al.*³¹ Early data at elevated temperatures depend on the thermal decomposition rate constants of *n*-butyryl,²¹ 2-methylpropionyl (=*i*-butyryl),²¹ 3-methylbutyryl,²² and *n*-pentanoyl²² by Cadman and coworkers which, after extrapolation to room temperature, exceed the present values by nearly two orders of magnitude or more. In the work of Cadman *et al.*, rates of thermal decomposition of RCO were determined relative to the recombination of RCO with NF₂, the rate constant of which is not well known and was assumed to be extremely high $(1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-121,22})$. In addition, their experiments were performed at low pressures and elevated temperatures, and extrapolation to atmospheric pressure and room temperature may introduce considerable errors. In line with this, the activation energy measured by Cadman *et al.*²¹ for *i*-butyryl was relatively small as compared to the results of Tomas *et al.*²³ and *ab-initio* calculations of the activation barrier.³² Tomas *et al.*²³ studied the competition between reactions (1) and (2) for 2-methylpropionyl and 2,2-dimethylpropionyl by a completely different method with pulsed formation of RCO at higher temperatures and UV spectrometric detection of RC(O)O₂ and RO₂. Their activation energy for



Fig. 7 Arrhenius plot for the thermal decomposition rate constant of 2,2-dimethylpropionyl radicals; $p_{tot} = 1$ bar (M = N₂ + O₂).

Table 3 Estimated data on k_{dis} , total pressure 1 bar

	$k_{\rm dis}/{\rm s}^{-1},^a$ this work		
	317 K	298 K	- $k_{\rm dis}/{\rm s}^{-1}$, literature 298 K
n-Butyryl	<2300	<700 ^b	329810 ^c
n-Pentanoyl	<2300	<700 ^b	89722 ^{<i>d</i>,<i>e</i>}
3-Methylbutyryl	3200	1000 ^b	108041^{f}
2-Methylpropionyl	40300	12100 ^b	7574 ^g
(=i-butyryl)			775511 ^h
2-Methylbutyryl	52500	15800 ^b	
2,2-Dimethylpropionyl	880000	300000	89805 ⁱ

^a With $k_{0_2} = 3.2 \times 10^{-12}$ cm³ molecule⁻¹ s^{-1.17} ^b Converted from 317 K to 298 K using the activation energy $E_a = 49.6$ kJ mol⁻¹ of the reaction 2-methylpropionyl $\rightarrow i$ -propyl + CO from Tomas *et al.*²³ ^c Ref. 21, k_{∞} , extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 39.8$ kJ mol⁻¹. ^d Ref. 22, k_{∞} , extrapolated from the experimental temperature range 373–448 K to 298 K with $E_a = 42.9$ kJ mol⁻¹. ^e The pre-exponential factor given in the abstract of ref. 22 is different from the value $10^{12.47}$ s⁻¹ presented in Table 6 and the text of the same paper, $10^{12.47}$ s⁻¹ was adopted here. ^f Ref. 22, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ^e Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ^e Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ^e Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ^e Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ^e Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ^e Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ⁱ Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ⁱ Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ⁱ Ref. 23, extrapolated from the experimental temperature range 353–423 K to 298 K with $E_a = 40.5$ kJ mol⁻¹. ⁱ Ref. 23, extrapolated from the experimental temperature range 323–453 K to 298 K with $E_a = 40.5$ kJ mol⁻¹.

Since data on the thermochemistry and on thermal decomposition rate constants for carbonyl radicals are very sparse, it may be useful to derive rough estimates of the activation energies for the thermal decomposition of RCO from the kinetic data of Table 3. For the following discussion, it is assumed that the pre-exponential factors for k_{dis} at 1 bar of the different RCO radicals studied in this work are identical to the value measured for 2,2-dimethylpropionyl (see eqn. (II)).

According to this assumption, the difference in rate constants k_{dis} in Table 3 was assigned to differences in the high pressure activation energies E_a . The resulting activation energies are included in Table 4, together with literature values. Inspection of Table 4 suggests that the old values for E_a from Cadman *et al.*^{21,22} are probably low, and that the more recent results, both theoretical and experimental, are in quite good agreement (within a range of 5 kJ mol⁻¹).

In Table 5, the contributions of both pathways (1) and (2) are shown for atmospheric conditions. It is inferred from Table 5 that thermally distributed RCO radicals with R = alkyl, although becoming much more unstable with increased branching of the α -C atom of R, nearly exclusively add O₂ rather than decompose in the atmosphere. Only for heavily branched RCO radicals at elevated temperatures (*e.g.* RCO radicals deriving from certain biogenic emissions at *ca.* 40 °C) can the fraction of thermal decomposition possibly

reach 5–10%.

The formation of RCO radicals in reaction (4) is close to thermoneutral for $R = CH_3$.¹⁷ Preliminary experiments using Cl rather than Br atoms for the abstraction of the aldehydic H atom showed that there is an O₂ independent yield of CO (about 20% of the total RCO yield) even in the presence of 1 bar of O₂ where thermal decomposition of RCO should be negligible according to eqn. (I). Reaction (10),

$$RC(O)H + Cl \rightarrow RCO + HCl,$$
 (10)

is exothermic by about 60 kJ mol⁻¹, and a large fraction of the CO formed in these experiments can be the result of the spontaneous decomposition of chemically activated RCO radicals formed in reaction (10).

The reaction of aldehydes with OH radicals,

$$RC(O)H + OH \rightarrow RCO + H_2O,$$
 (11)

which is the most important bimolecular reaction to form RCO radicals in the atmosphere, is also strongly exothermic $(\Delta_{r, 298}H^{\circ} \approx 125 \text{ kJ mol}^{-1 33,34})$, and the RCO radicals from reaction (11) can be chemically activated, giving rise to spontaneous (*i.e.* non-thermal) decomposition, thus increasing the yields of CO as compared to the results from Table 5.

Conclusions

The thermal stability of RCO radicals strongly decreases with increasing branching at the C atom connected to the carbonyl group. Yet the thermal decomposition of RCO radicals is

Table 4 Experimental and theoretical activation energies of the reaction $RCO + M \rightarrow R + CO + M$ (in kJ mol⁻¹)

	Reference	Reference				
RCO	Bencsura et al. ¹⁸	Cadman <i>et al.</i> ^{21,22}	Tomas et al. ²³	Viscoltz ³²	This work	
Acetyl n-Propionyl n-Butyryl n-Pentanoyl 3-Methylbutyryl 2-Methyl- propionyl 2-Methylbutyryl 2,2-Dimethyl- propionyl	68.5 ^a	$\begin{array}{c} 46.4^{a,c,d} \\ 39.8^{a,c,d} \\ 42.9^{a,c,h} \\ 40.5^{a,c,h} \\ 40.8^{a,c,d} \end{array}$	$59.4^{a,f} 49.6^{e,f} 50.6^{a,f} 40.5^{e,f}$	$71.8^{a,b} \\ 64.9^{a,b} \\ 66.8^{a,b} \\ 57.4^{a,b} \\ 46.2^{a,b}$	$\geq 56.6^{e,f,g} \\ \geq 56.6^{e,f,g} \\ 55.7^{e,f,g} \\ 49.5^{e,f,g} \\ 48.9^{e,f,g} \\ 41.6^{e,f} \end{cases}$	

^{*a*} Infinite total pressure. ^{*b*} Ab initio, G2(MP2,SVP) method. ^{*c*} Rate constants measured relative to RCO + NF₂. ^{*d*} Ref. 21. ^{*e*} Total pressure 1 bar. ^{*f*} Rate constants measured relative to RCO + O₂. ^{*g*} Activation energy based on rate constant measured at 317 K and the pre-exponential factor measured for $t-C_4H_9CO$. ^{*h*} Ref. 22.

Table 5 Experimental results on $k_{dis}/(k_{O_2} \times [O_2])$ at 1 bar in synthetic air

RCO	$k_{\rm dis}/(k_{\rm O_2} \times [O_2])$ at 298 K, 1 bar of synthetic air	Ref.	% Decomposition of RCO at 298 K, 1 bar of synthetic air
Acetyl	ca. 0.0000004 ^a	18, 17	ca. 0.00004
n-Propionyl	0.000014^{b}	19, 17	0.0014
n-Butyryl	< 0.00004	This work	< 0.004
<i>n</i> -Pentanoyl	< 0.00004	This work	< 0.004
3-Methylbutyryl	0.00006	This work	0.006
2-Methylpropionyl	0.0008	This work	0.08
2-Methylbutyryl	0.0011	This work	0.11
2,2-Dimethylpropionyl	0.018	This work	1.8

^a k_{dis} from Bencsura et al.¹⁸ and k_{O_2} from Atkinson et al.¹⁷ ^b k_{dis} from Kerr and Lloyd¹⁹ and k_{O_2} from Atkinson et al.¹⁷

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