FARADAY

Identification of an unexpected peroxide formed by successive isomerization reactions of the *n*-butoxy radical in oxygen

François Jorand,[a] Adolphe Heiss,[a] Krikor Sahetchian,[a]* Lucien Kerhoas[b] and Jacques Einhorn[b]
[a] *Laboratoire de Mécanique Physique, CNRS URA 879, Université P. & M. Curie (Paris 6), 2, Place de la Gare de Ceinture, 78210 Saint Cyr-l'Ecole, France*
[b] *Unité de Phytopharmacie et Médiateurs Chimiques, INRA, Route de St Cyr, 78026 Versailles Cedex, France*

A previously unreported peroxide, $C_4H_8O_3$ (**5**), has been identified and its mechanism of formation proposed. It is generated by two successive isomerization reactions of n-C_4H_9O radicals in O_2. These radicals are produced by di-n-$C_4H_9O{-}OC_4H_9$ pyrolysis at 480 K in a wall-passivated quartz vessel. The peroxide is collected, among other end-products, on a liquid-nitrogen trap and recovered in liquid acetonitrile. Analysis was carried out by GC–MS, GC–MS–MS [electron impact (EI) and NH_3 (or ND_3)–chemical ionization (CI) conditions] and GC–FTIR. After micropreparative GC separation of the titled peroxide, ^1H NMR and high-resolution EIMS were also obtained. The compound was identified as 3α-hydroxy-1,2-dioxane. The hydroperoxybutyraldehyde $OHC{-}(CH_2)_2{-}CH_2O_2H$ is proposed to be initially formed in the gas phase and to be in equilibrium with its cyclic form (six-membered ring peroxide), by far predominant in the liquid phase at room temperature. The implications of this hydroperoxybutyraldehyde in atmospheric pollution (due to the peroxide producing capability of radicals) and in combustion are discussed.

The impact of anthropogenic emissions on atmospheric pollution is one of the main problems facing mankind. With industrialization and steadily increasing road traffic, air quality is decreasing, in some cases becoming intolerable. This is mainly due to the huge consumption of hydrocarbons (energy, transport, solvents, *etc.*) and, as a consequence, many unburned materials contribute to the formation of pollutants such as ozone, peracids, peroxyacetyl nitrate, *etc.*

It is, therefore, essential to know and understand the transformation and degradation mechanisms of hydrocarbons emitted into the troposphere. For several decades, increasing importance has been given to the isomerization reactions of R, RO and RO_2,[1–4] which explain the formation of many intermediates or end-products. This applies also to processes leading to autoignition in motor engines where peroxides as well as carbonyl compounds and many other O-heterocyclic species, like oxirans, oxetans, epoxides and furans, are formed.

In this paper, we confine ourselves to the reactions of alkoxy (RO) radicals, which are at the origin of many atmospheric pollutants. These radicals are produced by the following reaction pathways:

$$RO_2 + RO_2 \rightarrow 2RO + O_2$$

$$RO_2H \rightarrow RO + OH$$

$$RO_2 + NO \rightarrow RO + NO_2$$

RO radicals contribute to the formation of pollutants *via* oxidation, decomposition and isomerization reactions. Isomerization was claimed[5] in 1976 in the photooxidation of C_4–C_6 alkanes under simulated atmospheric conditions in the presence of NO_x. During the last twenty years, experimental or thermochemical investigations have taken into account unimolecular isomerization (mainly *via* a 1,5-H shift) for a variety of RO radicals.[6–13]

Only methoxy, ethoxy and propoxy radicals[14–16] have been observed by optical methods at low pressures. RO radicals with a carbon chain length $\geq C_4$ have never been observed and identified spectroscopically, and investigations can only be made by indirect methods. The radicals must be produced in a safe and unequivocal way and analysis of their products is required to determine the pathways involved. As the concentration of RO radicals cannot be determined, relative rate constants must be used.

Recently, the debate on isomerization reactions has been relaunched by new experimental data.[17–20] Our previous work on the reactions of the *n*-butoxy radical in oxygen has indicated the importance of isomerization in the formation of pollutants.[17] Among the products of isomerization, we found a compound having a relative molar mass, M_r, of 104 (presumably of formula $C_4H_8O_3$) remaining to be identified. The formation of hydroxycarbonyls, due to isomerization[20] reactions of the alkoxy radicals of C_4–C_8 *n*-alkanes, was shown to be important in the presence of NO at initial concentrations of $(2.4–4.8) \times 10^{13}$ molecule cm^{-3}, in air at room temperature.

The aim of the present work is to elaborate experimental conditions which might enable preparation of sufficient $M_r = 104$ compound to identify it. The elementary reactions necessary for its formation and involved in its consumption could then be discussed and introduced into kinetic models of atmospheric chemistry and combustion.

Experimental

Experimental set-up

The experimental set-up has been described elsewhere.[17] Briefly, n-C_4H_9O radicals are formed by the pyrolysis of di-*n*-butylperoxide (synthesized according to Welch *et al.*[21]) in O_2–N_2 mixtures. Gaseous flows are electronically regulated by mass-flow controllers from Air Liquide–Alphagaz. Nitrogen carries the diperoxide and is mixed with oxygen. The mixture then passes through the vessel under atmospheric pressure. At the vessel outlet, gas is sampled through a microprobe and all condensable species are trapped by liquid nitrogen on the cold finger of a dismountable Dewar. The trapped products are solubilized with acetronitrile for analysis.

Quartz vessels (inner diameter, id, of 10, 20 and 60 mm) with walls either passivated or not towards reactions of radicals, have been used, as well as a 10 mm id Pyrex vessel. The passivation of the walls consisted of coating them with boric acid and treatment *via* the slow hydrogen–oxygen reaction carried out at *ca.* 773 K.[12,17]

To obtain the highest possible concentration of the M_r = 104 peroxide, pyrolysis has been performed using a high concentration of the initial peroxide [(2–3) × 10^{14} particle cm^{-3}] in the quartz vessel with passivated walls and with a residence time of the mixture providing a high consumption of RO_2R and of RO. Secondary and side-reaction products of the RO present in high concentration are not negligible, but do not hinder further separation. An overall flow of 100 ml min^{-1} was used: 70 ml min^{-1} nitrogen, carrying RO_2R, mixed with 30 ml min^{-1} oxygen. The temperature was 480 K in the vessel, its id 20 mm and the residence time about 30 s. Eight experiments were performed, each consisting of trapping products for about 2 h. We thus obtained a sufficient amount of the M_r = 104 species to separate it from other products by a micropreparative method.

Identification

Conventional GC–MS and GC–MS–MS spectra were obtained with a Nermag R-30-10 (Quad Service, Poissy, France) triple quadrupole instrument. Source conditions were set as follows: temperature = 463 K (EI mode) and 413 K (CI mode); filament current = 0.2 mA (EI) and 0.1 mA (CI); electron energy = 70 eV (EI) or 95 eV (CI). NH_3 (or ND_3) was used as reagent gas for CI at 10^{-4} Torr measured in the source housing. For MS–MS experiments, collisionally activated decomposition was achieved with Ar as collision gas at 3.5 × 10^{-2} Torr and 25 eV collision energy. Samples were introduced *via* GC by a split–splitless injection using a 30 m × 0.32 mm DB5 MS (J & W Scientific, Fisons) silica-fused capillary column at 313 K (4 min) and up to 423 K (5 K min^{-1}) and He as carrier gas.

Micropreparative GC was performed on Girdel 300 equipment using a 15 m × 0.53 mm DB5 column under isothermal conditions (333 K) and a fraction collector.[22] ^{1}H NMR spectra were obtained on Varian Gemini 300 MHz equipment with C_6D_6 as the solvent.

Results

As shown by the GC–MS chromatogram obtained under EI conditions (Fig. 1), the compound (**5**) to be identified is the predominant compound being formed. In our chromatographic conditions (*e.g.* apolar stationary phase), it elutes at 13.7 min between butyrolactone (11.7 min) previously identified as a secondary by-product and residual di-*n*-butylperoxide (16.1 min). The other by-products include *n*-butanal, *n*-butanol[17] and presumably *n*-propylhydroperoxide.[17]

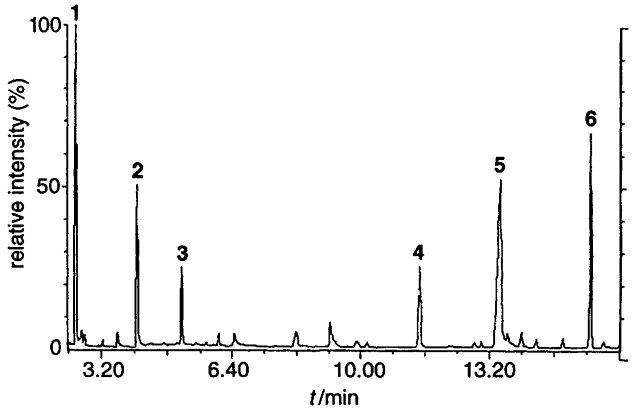


Fig. 1 GC–EIMS chromatogram showing the formation of the peroxide (**5**) after pyrolysis of di-*n*-butylperoxide (**6**) (by-products: **1**, *n*-butanal; **2**, *n*-butanol; **3**, *n*-propylhydroperoxide; and **4**, butyrolactone)

The EI spectrum (Fig. 2) exhibits ions at *m*/*z* 104 (low abundance: $M^{\cdot+}$), 87, 71, 69, 57, 47 and 29. Ion *m*/*z* 87 could be interpreted as $[M - {}^{\cdot}OH]^+$ and ion at *m*/*z* 69 as resulting from consecutive losses of $^{\cdot}OH$ and H_2O. Ion *m*/*z* 71 could correspond to $[M - {}^{\cdot}OOH]^+$ whereas ion *m*/*z* 57 was tentatively assigned as $[M - {}^{\cdot}CH_2O_2H]^+$ or $[M - {}^{\cdot}OH - CH_2O]^+$. At this stage, it has to be pointed out that hydroperoxide structures (see examined standards or library of spectra) are rather (and significantly) characterized by $[M - H_2O]^+$ and $[M - {}^{\cdot}OOH]^+$ ions.

The NH_3–CI spectrum [Fig. 3(*a*)] gave ions at *m*/*z* 139 (low abundance), 122 (major), 104, 88 and 71 (low abundance). The first three could *a priori* correspond to $[MNH_4, NH_3]^+$ $[MNH_4]^+$ and $[MNH_4 - H_2O]^+$. Ion *m*/*z* 88 might be produced by decomposition of the adduct ion $[MNH_4]^+$ by loss of H_2O_2 which, after further loss of NH_3, would give rise to ion *m*/*z* 71. These assumptions agreed perfectly with the shifts observed under ND_3–CI (replacement of the reagent gas by a deuterium prelabelled one) [Fig. 3(*b*)] since the following ions were obtained: *m*/*z* 147 (+8 u), 127 (+5 u), 108 (+4 u), 91

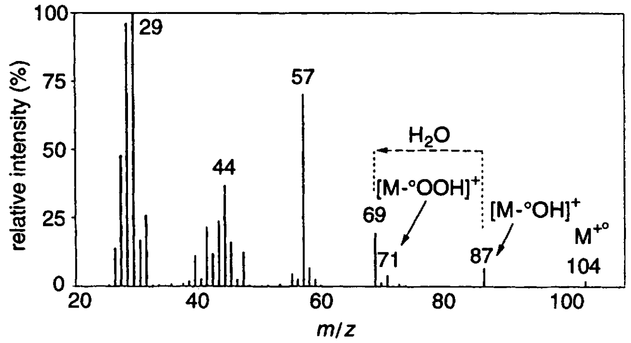


Fig. 2 EI mass spectrum of peroxide **5**

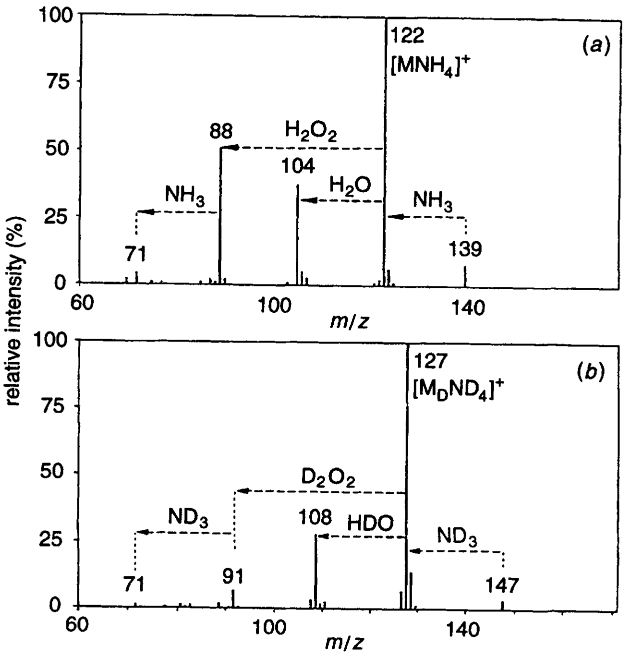


Fig. 3 NH_3 (*a*) and ND_3 (*b*) CI mass spectra of peroxide **5**

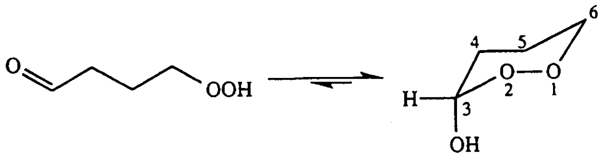


Fig. 4 Structure of peroxide **5** and corresponding acyclic form

(+3 u) and 71 (unchanged). Furthermore, this behaviour indicated the presence of one mobile hydrogen according to the new *m*/*z* values obtained for the adduct ions (1 u supplementary shift due to H–D exchange). On the other hand, it was clearly demonstrated that the relative molecular mass was 104. Note also that under the last conditions the losses generated from ion *m*/*z* 127 become either D_2O_2 and HDO (one hydrogen coming necessarily from the initial substrate) to give ions at *m*/*z* 91 and 108, respectively.

Some MS–MS experiments were performed using a triple quadrupole instrument to study the above ions *m*/*z* 122, 104 and 88 obtained under NH_3–CI source conditions, and comparison was carried out with the deuterium-labelled medium. This confirmed again the above statements. Interestingly, the decomposition of ions 122 and 104 also showed the formation of ion NH_4^+ (ND_4^+ under ND_3–CI).

High-resolution GC–EIMS measurement of the molecular ion led to the unambiguous assignment of the $C_4H_8O_3$ crude formula (found, 104.0485; requires, 104.0473).

All these indications are in favour of a six-membered ring peroxide with an α-hydroxy group (hemi-ketal-like compound) rather than a bifunctional non-cyclic hydroperoxide. Such a structure would, for instance, be consistent with the production of $[M{-}{}^{\bullet}OH]^+$ by EI-MS which is known not to occur with hydroperoxides.

Since the occurrence of a cyclic peroxide was quite unexpected in this context, some complementary work to achieve its identification was performed after isolation by micropreparative GC.

At first, its thermal transformation ability was studied by GC by varying injection-port temperatures. Indeed, the peroxide was injected without any degradation, *i.e.* at 498 K, but appeared to be partly or totally transformed at 598 and 673 K, respectively. Butyrolactone formation as one of the main degradation products (by elimination of H_2O) was the most interesting feature.

The ^1H NMR spectrum together with decoupling experiments led to the following interpretation in complete agreement with the assumed structure δ_H 4.95 (H-3 m), 3.78 (2 H, H-6 m), 2.63 (OH, d, *J* 5.2 Hz), 1.3–1.6 (3 H, H-4, H′-4, H-5 m) and 1.12 (H′-5 m). The moderate or low values (<6 Hz) of the coupling constants occurring for H-3 and the observation of a long-range coupling with one of the H-6 protons indicate an equatorial position for H-3.

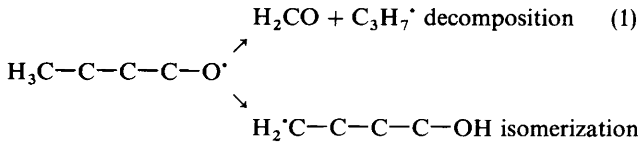
Finally, GC–FTIR measurements indicated to some extent the presence of an aldehyde (absorption at 1747 cm^{-1} of moderate intensity and small complementary ones at 2725 and 2824 cm^{-1}). It is thus likely that both the linear (with hydroperoxide and aldehyde functions) and cyclic forms of the investigated peroxide co-exist (Fig. 4) in the gas phase (but not in the liquid one: *cf.* NMR). The presence of the $[M - {}^{\bullet}OOH]^+$ and $[M - {}^{\bullet}CH_2O_2H]^+$ ions in the EI spectrum may probably also be explained by the same statement.

Discussion

Reaction mechanism

Identification of the $C_4H_8O_3$ peroxide being achieved, the following is concerned with its formation in the gas phase, the experimental conditions which enabled this compound to be observed and the role it might play in atmospheric pollution and in combustion. H atoms playing no significant role are not mentioned in the further developed formulas.

We showed in a previous work[17] that the reactions of *n*-butoxy radical in oxygen run through two pathways: decomposition and isomerization:



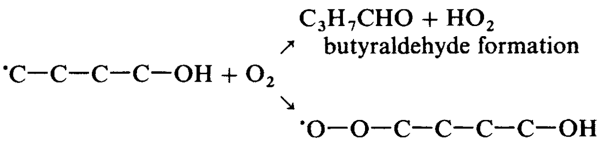
$$H_3C{-}C{-}C{-}C{-}O^{\bullet} \nearrow H_2CO + C_3H_7^{\bullet} \text{ decomposition} \quad (1)$$

$$H_3C{-}C{-}C{-}C{-}O^{\bullet} \searrow H_2{}^{\bullet}C{-}C{-}C{-}C{-}OH \text{ isomerization} \quad (2)$$

Between these two reactions, there is a difference of activation energies of $\Delta E = 7.7 \pm 0.1$ kcal mol^{-1}. At room temperature, oxidation as a third pathway has a minor importance and cannot be ruled out.

$$C{-}C{-}C{-}C{-}O^{\bullet} + O_2 \rightarrow HO_2 + C_3H_7CHO \quad (3)$$

The isomerized radical from reaction (2) reacts with oxygen:



$${}^{\bullet}C{-}C{-}C{-}C{-}OH + O_2 \nearrow C_3H_7CHO + HO_2 \text{ butyraldehyde formation} \quad (4)$$

$${}^{\bullet}C{-}C{-}C{-}C{-}OH + O_2 \searrow {}^{\bullet}O{-}O{-}C{-}C{-}C{-}C{-}OH \quad (5)$$

The butyraldehyde : butyraldehyde + isomerization products ratio is 0.290 ± 0.035 which is independent of oxygen concentration from 448 to 496 K in a vessel with passivated walls. The above peroxidic radical from reaction (5) isomerizes:

$${}^{\bullet}O{-}O{-}C{-}C{-}C{-}CH_2{-}OH \rightarrow H{-}O{-}O{-}C{-}C{-}C{-}{}^{\bullet}CH{-}OH \quad (6)$$

In the $-CH_2-OH$ group, the remaining C—H bonds are weakened (4–5 kcal mol)† by the presence of OH thus favouring isomerization.[23]

The radical formed in reaction (6) reacts in turn with oxygen giving the peroxide identified in this paper (*i.e.* $M_r = 104$):

$$H{-}O{-}O{-}C{-}C{-}C{-}C^{\bullet}{-}OH + O_2 \rightarrow HO_2 + C_4H_8O_3 \quad (7)$$

This compound, obtained after condensation, was identified as 3α-hydroxy-1,2-dioxane. It may, however, be assumed to be initially formed in the gas phase as an aldehyde–hydroperoxide structure which would then equilibrate with its cyclic form (see Fig. 4).

In the literature, cyclic peroxides were observed either as products of an ozonolysis reaction, *i.e.* diozonolysis of cyclic conjugated dialkenes in methanol[24] or as natural products, *i.e.* 1,2-dioxane carboxylates.[25] *Ab initio* calculations about conformations of cyclic peroxides, including various 1,2-dioxacyclohexanes have also been performed.[26] However, to our knowledge, no experimental data have ever been published about a six-membered cyclic peroxide in gas-phase chemistry.

We propose to introduce reactions (4)–(7) into the combustion and pollution chemical mechanisms. The thermal or photochemical decomposition of the peroxide identified should yield two radicals thus acting as a new source of

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† 1 cal = 4.184 J.

Table 1 Ratio of $HOR_{-H}O_2$ reaction rate with NO w_8 *vs.* isomerization rate, w_6, at atmospheric temperatures

T/K	k_6	k_8[NO]	w_6/w_8
273	10^{-3}	0.487	0.002
283	3.13×10^{-3}	0.476	0.006
293	9.04×10^{-3}	0.466	0.019
303	2.4×10^{-2}	0.457	0.053
313	6.16×10^{-2}	0.448	0.137
323	1.47×10^{-1}	0.440	0.334

$w_6 = k_6[HOR_{-H}O_2]$; $w_8 = k_8[NO][HOR_{-H}O_2]$; [NO] = 3 μg m^{-3}.

radical species involved in the combustion and atmospheric pollution processes.

Specific experimental details favouring the second isomerization

The importance of isomerization reactions for *n*-RO_2 radicals has been shown during the slow oxidation of *n*-alkanes and for autoignition in motor engines. In the case of *n*-heptane, isomerization yielded an oxohydroperoxide.[27] Carter *et al.*[5] demonstrated that this reaction is negligible under atmospheric conditions.

The set of experimental conditions being used to observe the above peroxide and afterwards to produce it in large amounts has the following specific characteristics: RO radicals are formed by thermal decomposition so that NO is not needed and excited species do not occur; the reactor walls are passivated rendering heterogeneous reactions negligible; the concentration of radicals is sufficiently low that radical–radical reactions are also negligible and temperature is chosen to ensure sufficient isomerization *vs.* thermal decomposition of the final peroxidic species. These conditions are quite specific, which explains why a two-isomerization sequence of RO radicals has never been reported previously.

The specific nature of these conditions, and especially the absence of NO and low concentrations of radicals, explains why hydroxycarbonyl species, such as $HOCH_2CH_2CH_2CHO$, expected to occur according to recent environmental chamber investigations,[20] were not observed under our conditions. In our experiments at 480 K, the concentration of RO_2 radicals (where RO_2 is $HOCH_2CH_2CH_2CH_2OO^{\bullet}$, the 4-hydroxy-1-butyl peroxy) can be estimated to be *ca.* 10^9 particle cm^{-3}. It ensures that an estimation of the ratio $k_{isom}[RO_2] : k_{RO_2+RO_2}[RO_2]^2$ which is equal to $k_{isom} : k_{RO_2+RO_2}[RO_2]$ gives a value of *ca.* 10^6, in agreement with the predominance of the second isomerization leading to the unexpected peroxide identified in this work.

Table 2 NO concentration required to give $w_6/w_8 = 0.1$ at atmospheric temperatures

T/K	NO/μg m^{-3}
273	0.06
283	0.18
293	0.57
303	1.59
313	4.11
323	10.0

Table 3 Ratio of *n*-butoxy isomerization reaction rate *vs.* thermal decomposition rate

T/K	k_2	k_1	w_2/w_1
373	2.7×10^6	5.9×10^4	42.5
473	4.2×10^7	8.2×10^6	5.14
573	2.5×10^8	2.0×10^8	1.25
673	8.9×10^8	1.9×10^9	0.45
773	2.2×10^9	1.0×10^{10}	0.218
873	4.6×10^9	3.7×10^{10}	0.123

$w_2 = k_2$[*n*-butoxy]; $w_1 = k_1$[*n*-butoxy].

The temperature range (343–503 K) is intermediate between that of the atmosphere and that of slow oxidation of hydrocarbons. Extrapolation of the established reaction rates enables us to use the elaborated mechanism in both areas.

Role of introduced reactions

In atmospheric pollution. The only source of ozone is $O + O_2 + M \rightarrow O_3 + M$. The O atom comes from $NO_2 \rightarrow NO + O$. NO_2 is formed by two reactions:

$$NO + RO_2 \rightarrow RO + NO_2$$

$$NO + HO_2 \rightarrow OH + NO_2$$

There are two origins of RO_2 radicals: the oxidation of hydrocarbons:

$$RH + OH \rightarrow R + H_2O$$

$$R + O_2 \rightarrow RO_2$$

and reaction (5), directly consecutive to the isomerization of RO and subsequent addition of O_2, yielding a radical, which can be written $HOR_{-H}O_2$. Furthermore, HO_2 present in the mixture comes from RO *via* reactions (3) and (4) and from other reactions indirectly induced by RO. In this set, the role of reaction:

$$HOR_{-H}O_2 + NO \rightarrow HOR_{-H}O + NO_2 \qquad (8)$$

can be a non-negligible part of the total ozone formed by the presence of hydrocarbons. The rate constant of this reaction is well known:[28] $k_8 = 4.2 \times 10^{-12} \exp(180/T)$ cm^3 $molecule^{-1}$ s^{-1}, where T is reaction temperature. This reaction is in competition with the isomerization of $HOR_{-H}O_2$, *e.g.* reaction (6). Its rate constant k_6 is estimated from our experiments:[17] $k_6 = 10^{11} \exp(-17600/RT)$ s^{-1}, where R is the gas constant. Reaction (6) gives a peroxide from which two radicals can appear per molecule *via* further decomposition reactions.

According to these values, reaction rates can be calculated at different temperatures with an atmospheric NO concentration of 3 μg m^{-3}, which is the lowest value measured by AIRPARIF (which supervises the air quality in Paris and its suburbs). At this low NO concentration, the tropospheric ozone concentration is always the most important.[29]

The behaviour of this set of reactions in atmospheric conditions is shown in Tables 1 and 2, which indicate the following. (i) The rate of isomerization increases strongly with temperature. (ii) At 303 K with low NO concentration, one tenth of the reacting $HOR_{-H}O_2$ radicals isomerizes. This isomerization can induce the formation of two radicals contributing to an increase of radical concentration, and thus of secondary pollutants. Thus, the role of the second isomerization increases when NO in the atmosphere is low and the production of peroxides, and afterwards radicals and pollutants, is more important. (iii) If temperature increases, isomerization reaction (6) keeps its role even when NO amounts are important (summer conditions of urban atmosphere). Simulation of a chemical mechanism will enable an accurate evaluation of the role played by the successive isomerizations in the whole process.

In combustion processes. In the range 400–900 K, the oxidation reaction (3) of the *n*-butoxy radical is negligible compared with the decomposition reaction (1) and the isomerization reaction (2). Their rate constants are:[17] $k_1 = 8 \times 10^{14} \exp(-17400/RT)$ s^{-1} and $k_2 = 1.3 \times 10^{12} \exp(-9700/RT)$ s^{-1}. According to these values, reaction rates can be calculated at different temperatures in the preflame area (see Table 3). At 573 K, their rates are almost equivalent, and at 873 K, despite the increase of the decomposition rate, the isomerization remains significant. In this temperature range, reactions (5) and (6) yield the peroxide given by the successive isomerization reactions. Isomerization plays an important role in the whole area of preflame reactions.

Conclusion

A new compound resulting from the oxidation of the *n*-butoxy radical in O_2 was shown to be produced under well chosen conditions (temperature, production process, passivation of reactor walls, *etc.*). The amounts obtained enabled its isolation and identification using a combination of modern spectral techniques. Its formation is probably explained by the occurrence of two successive isomerizations yielding an aldehyde–hydroperoxide in equilibrium with a cyclic peroxide structure.

This compound can decompose and thus yields two radicals per molecule. This multiplication of radicals is enhanced by low NO concentration in the atmosphere and high temperature. In summer, such reactions can be harmful. Therefore formation and decomposition reactions of the aldehyde–hydroperoxide must be included in kinetic models for atmospheric pollution and combustion. Further work on higher alkoxy radicals is needed to generalize these models.

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