

Determination of the ultra violet absorption cross section of hexyl-ketohydroperoxides in solution in acetonitrile

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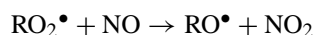
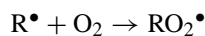
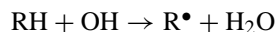
Abstract

Three hexyl-ketohydroperoxides, produced at 300°C by isomerization reactions in oxygen of hexyl-peroxy C₆H₁₃O₂• radicals (arising from *n*-hexane), were isolated through micro-preparative GC separation into two fractions: 2-hexanone-5-hydroperoxide, and mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide. Absorption cross sections versus UV wavelength (190–350 nm) were determined for these hexyl-ketohydroperoxides in solution in acetonitrile. Their absorption at wavelengths higher than 290 nm (being of tropospheric interest) is linked to the ketonic group and seems to be amplified by the peroxidic group. Photochemical data of alkyl-ketohydroperoxides might be introduced in tropospheric chemistry in order to model urban atmospheric pollution. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hexyl-ketohydroperoxides; Absorption cross section

1. Introduction

Atmospheric oxidation of hydrocarbons implies alkoxy RO radicals formed by the following reactions:



Through an oxidation process of paraffinic alkanes ($\geq \text{C}_4$) RH including two consecutive isomerization reactions, these alkoxy RO radicals lead to the formation of a carbonyl-hydroperoxide, also called ketohydroperoxide [1–5]. Rate constants of this isomerization process have been determined:

- for reaction $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OO}^\bullet \rightarrow \text{HOC}^\bullet\text{HCH}_2\text{CH}_2\text{CH}_2\text{OOH}$, this HORO₂ radical being formed from the *n*-butoxy *n*-C₄H₉O• radical, k_{isom} was found to be [2].

$$k_{\text{isom}} = 10^{11} \exp\left(-\frac{17600}{RT}\right) \text{ s}^{-1}$$

- for reaction $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OO}^\bullet)\text{CH}_3 \rightarrow \text{HOC}^\bullet\text{HCH}_2\text{CH}_2\text{CH}(\text{OOH})\text{CH}_3$, this HORO₂ radical being formed from the *n*-pentoxy *n*-C₅H₁₁O• radical, k_{isom} was found to be [3].

$$k_{\text{isom}} = (6.4 \pm 0.6) \times 10^{10} \exp\left(-\frac{(16900 \pm 700) \text{ cal mol}^{-1}}{RT}\right) \text{ s}^{-1}$$

- for reaction $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OO}^\bullet)\text{CH}_3 \rightarrow \text{CH}_3\text{C}^\bullet(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OOH})\text{CH}_3$, this HORO₂ radical being formed from the *s*-hexoxy *s*-C₆H₁₃O• radical, k_{isom} was found to be [5].

$$k_{\text{isom}} = 2.1 \times 10^{10} \exp\left(-\frac{14300}{RT}\right) \text{ s}^{-1}$$

Arrhenius parameters hereabove show that such isomerization reactions may exist in the troposphere during summer anticyclonic periods, characterized by bright sunshine and high temperature. It can even be assumed that isomerization reactions for secondary HORO₂ radicals issued from *s*-RO radicals like *s*-hexoxy can be predominant [3,5]. Under summer anticyclonic conditions, ketohydroperoxides are surely present and their decomposition may increase

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the concentration of tropospheric radicals [2,3], leading finally to increase tropospheric ozone. Atmospheric decomposition of ketohydroperoxides occurs by photolysis, mainly due to UV radiations. Up to now there exist no data on photodecomposition of that class of peroxides, bearing functional groups carbonyl C=O and hydroperoxide C–O–OH; the only UV absorption cross sections available being that of hydrogen peroxide H₂O₂ [6], that of methylhydroperoxide CH₃OOH [7], and that of hydroxy-methylhydroperoxide [8]. The determination of the UV absorption cross section of the hexanone-hydroperoxide was carried out, since *n*-hexane is a significant component of gasoline and solvents, able to be present in the troposphere and representative of large (\geq C₄) alkanes. Under the same conditions and in order to make comparisons, we measured also absorption cross sections of hydrogen peroxide H₂O₂ and of acetone CH₃COCH₃, as it is representative of a ketone [9].

However, the vapor pressure of this compound is very low, and its absorption on walls at room temperature can be important; so it was not possible to carry out this determination in the gas phase. The UV absorption cross section of hexyl-ketohydroperoxide was, therefore, measured in solution in acetonitrile CH₃CN, after micro-preparative separation (in order to purify the species) had been carried out.

2. Experimental

2.1. Preparation of hexyl-ketohydroperoxides

To obtain hexyl-ketohydroperoxides with a purity high enough to enable determination of their absorption spectra, micro-preparative separation was performed. The hexyl-ketohydroperoxides are produced by oxidation of *n*-hexane (puriss. \geq 99.5% (GC), supplied by Fluka) in O₂/N₂ mixtures, in the temperature range 270–300°C and under atmospheric pressure, in a flow reactor located in a thermoregulated oven. The experimental set-up was described elsewhere [10], a quartz reactor of i.d. 24 mm, length 320 mm. Products were continuously pumped through a capillary and trapped at the reactor outlet at –60°C. Recovered in acetonitrile, which is a very efficient solvent of ketohydroperoxides (whereas those species are practically insoluble in non-polar solvents such as *n*-pentane or *n*-hexane) they were analyzed by GC/MS. Operating conditions were chosen so as to produce a maximum of peroxides, and the least possible of products issued from their decomposition. Conditions were as follow: temperature=300°C, O₂ flow rate=500 ml min⁻¹, N₂ flow rate=550 ml min⁻¹, *n*-hexane flow rate (liquid)= 3.5×10^{-3} ml min⁻¹. Those conditions gave a residence time in the quartz vessel (volume 158 ml) of 4.3 s. The collected products after several hours of experimentation, represented ca. 0.2 ml of liquid.

2.2. Micropreparative separation of hexyl-ketohydroperoxides

Micropreparative GC separation of hexyl-ketohydroperoxides was performed on a Girdel 300 Gas Chromatograph. In front of the capillary column 15 m×0.53 mm×3 μm, DB-1 (J & W Scientific), carrier gas He 99.9999%, He front column pressure 0.3 bar, GC oven program from 60 to 120°C at a rate of 3°C min⁻¹, injector and FID detector at 200°C, a Ross injector enables to inject, in a splitless mode, several microlitres of the sample containing the species to be isolated. The FID detector is located, in parallel, at the main outlet of the column. When the peak corresponding to the wished product appears, a glass capillary tube is added to the main column outlet which makes the exit gas go through a cooler and then collected [11].

The GC/MS electronic impact (EI) chromatogram published elsewhere [4] includes a restrained number of peaks, and those marked 1, 2 and 3 were identified as hexyl-ketohydroperoxides. The separation is made by condensing the product in a first capillary tube during the time interval where the first Peak 1 is eluting, and in a second tube during the time interval where the second double Peak 2 and 3 is eluting. This work performed on 120 μl of sample enabled to isolate about 0.7 mg of 2-hexanone-5-hydroperoxide (1) and 1 mg of a mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide (2+3).

After isolation of the two volumes (1) and (2+3), their purity was checked by GC/MS: capillary column 25 m×0.2 mm×0.33 μm, HP-1 MS (Hewlett-Packard), carrier gas He 99.9999%, GC oven isotherm 50°C during 20 min, injector and transfer line at 120°C. The GC/MS (EI) chromatogram of Fig. 1 shows that: (i) the purity of the 2-hexanone-5-hydroperoxide is ca. 60–65% and (ii) the small peaks (corresponding to ketones or diones) eluting before Peaks 1 and 2 (the ketohydroperoxides) are practically negligible.

The GC/MS (EI) chromatogram of Fig. 2 (same GC conditions) shows that the purity of the mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide is about 90%, and that, here also, early eluting peaks can be neglected.

The mass spectra of the 2-hexanone-5-hydroperoxide, 2-hexanone-4-hydroperoxide and 3-hexanone-5-hydroperoxide were the same than those used for their identification [4].

2.3. Measurement of the UV molecular absorption of hexyl-ketohydroperoxides, acetone, and H₂O₂, in solution in acetonitrile

The products condensed inside the capillary tubes, according to the above described procedure, were weighed and recovered in acetonitrile, quality “far UV”, where they

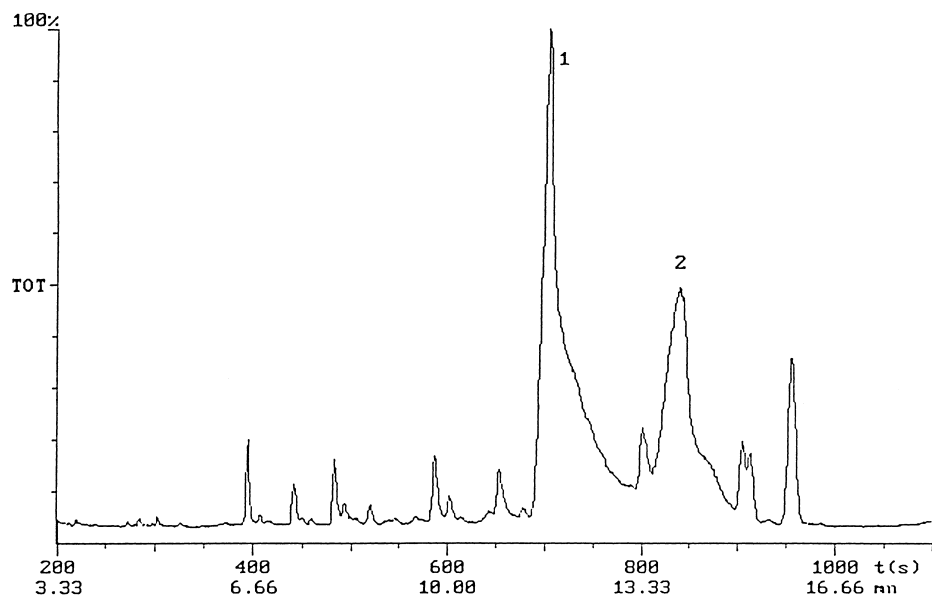


Fig. 1. GC/EIMS chromatogram of the products contained in the first sample and obtained by micropreparative separation: 1 2-hexanone-5-hydroperoxide, 2 2-hexanone-4-hydroperoxide.

are soluble. The first condensation 0.740 mg (2-hexanone-5-hydroperoxide) was solubilized in 50 μl of CH_3CN ; the second condensation 1.110 mg (mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide) was solubilized in 100 μl . Dilutions of these samples were made in order to measure the molecular absorption sections of the peroxides.

Absorbance is detected, by spectrophotometry, for wavelengths smaller than 350 nm. A UVIKON 933 spectrophotometer (Kontron Instruments) was used in

order to determine the absorption cross sections σ (10^{-20} cm^2 per molecule) versus UV wavelength λ (nm) of solutions in acetonitrile of (i) the 2-hexanone-5-hydroperoxide, (ii) the mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide, (iii) hydrogen peroxide H_2O_2 , and (iv) acetone CH_3COCH_3 . In Table 1, are summarized data concerning the 2-hexanone-5-hydroperoxide; on Fig. 3, are displayed the plot σ versus λ for the 2-hexanone-5-hydroperoxide, H_2O_2 and CH_3COCH_3 . For wavelengths increasing from 190 to 350 nm, it can be

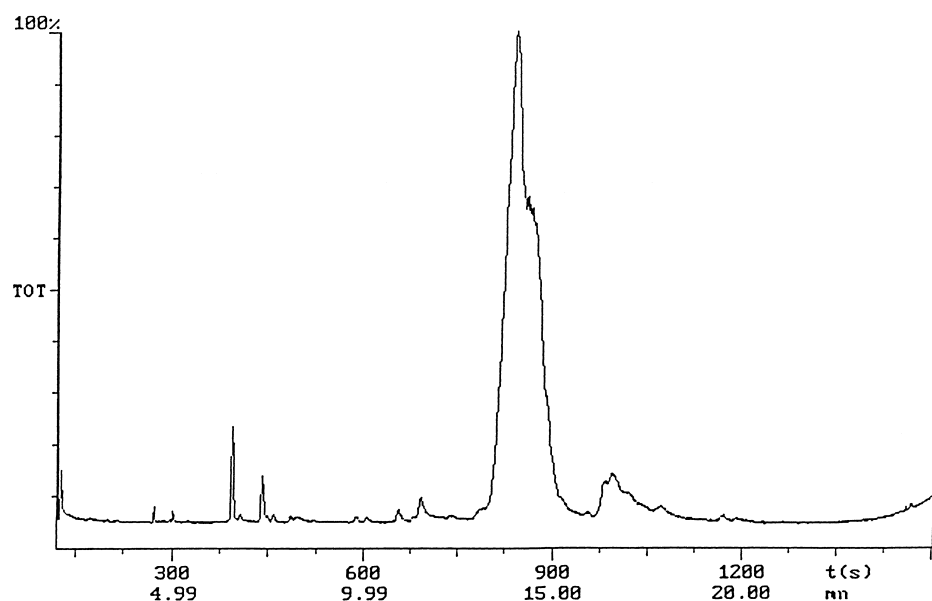


Fig. 2. GC/EIMS chromatogram of the products contained in the second sample and obtained by micropreparative separation: mixture of 2-hexanone-4-hydroperoxide and 3-hexanone-5-hydroperoxide.

Table 1
Absorption cross sections (10^{-20} cm² per molecule) vs. UV wavelength (nm) of the 2-hexanone-5-hydroperoxide in solution in acetonitrile

λ (nm)	σ (10^{-20} cm ² per molecule)	λ (nm)	σ (10^{-20} cm ² per molecule)	λ (nm)	σ (10^{-20} cm ² per molecule)
190	60.37	244	21.78	298	4.53
192	55.48	246	21.78	300	3.73
194	49.41	248	21.85	302	3.22
196	44.58	250	22.00	304	2.78
198	41.08	252	22.22	306	2.41
200	38.08	254	22.51	308	2.12
202	35.96	256	22.66	310	1.90
204	34.28	258	22.80	312	1.68
206	33.04	260	22.80	314	1.53
208	31.94	262	22.66	316	1.39
210	30.92	264	22.22	318	1.24
212	30.04	266	21.63	320	1.10
214	29.24	268	20.83	322	0.95
216	28.43	270	19.88	324	0.80
218	27.70	272	18.78	326	0.73
220	27.04	274	17.54	328	0.66
222	26.53	276	16.15	330	0.58
224	26.02	278	14.76	332	0.51
226	25.65	280	13.59	334	0.44
228	25.14	282	12.50	336	0.51
230	24.56	284	11.40	338	0.44
232	23.97	286	10.23	340	0.37
234	23.46	288	9.21	342	0.29
236	23.02	290	8.26	344	0.29
238	22.44	292	7.24	346	0.29
240	22.07	294	6.29	348	0.29
242	21.85	296	5.34	350	0.22

noticed that absorption cross sections of hydrogen peroxide are continuously and steeply decreasing (for $\lambda=290$ nm the value is ~ 0), whereas absorption cross sections of the 2-hexanone-5-hydroperoxide decrease steeply from 190 to 200 nm, but more slowly from 200 to 250 nm, go

through a maximum near 260 nm, and then decrease slowly again; for $\lambda \geq 290$ nm, absorption of the ketohydroperoxide remains important, about four times stronger, compared to that of acetone (which exhibits a maximum near 270 nm).

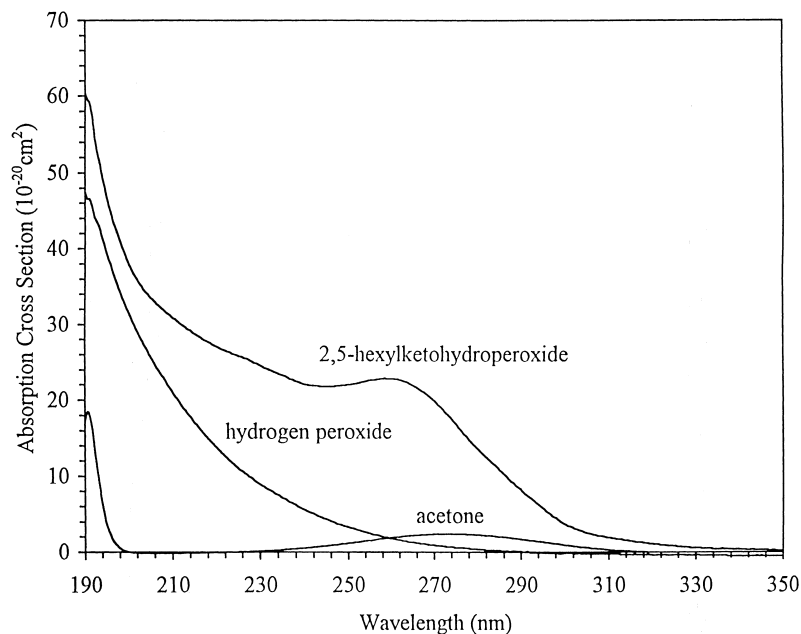


Fig. 3. Absorption cross sections σ (10^{-20} cm² per molecule) vs. UV wavelength λ (nm) of the 2-hexanone-5-hydroperoxide, of hydrogen peroxide and of acetone in solution in acetonitrile.

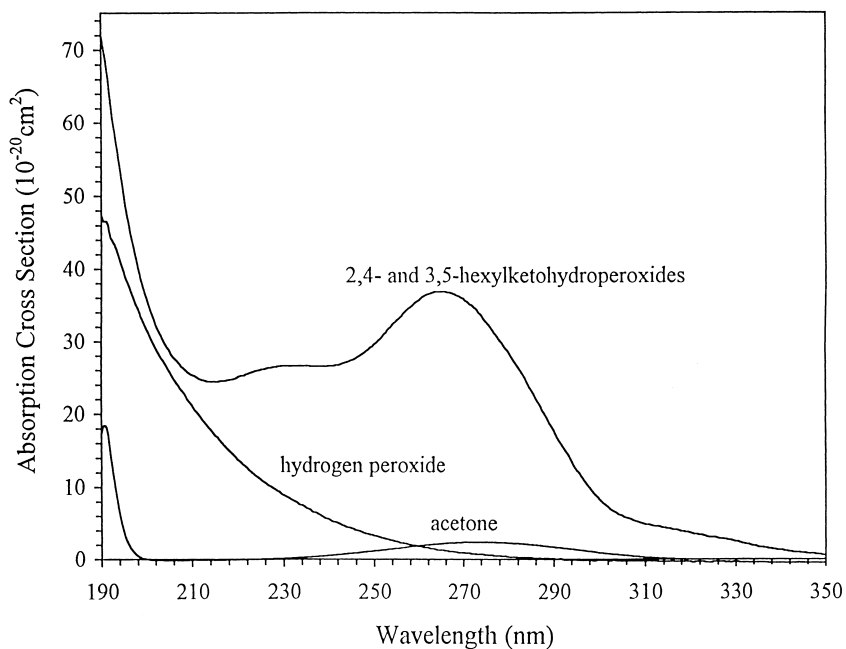


Fig. 4. Absorption cross sections σ (10^{-20} cm² per molecule) vs. UV wavelength λ (nm) of the mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide, of hydrogen peroxide and of acetone in solution in acetonitrile.

Table 2

Absorption cross sections (10^{-20} cm² per molecule) vs. UV wavelength (nm) of the mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide in solution in acetonitrile

λ (nm)	σ (10^{-20} cm ² per molecule)	λ (nm)	σ (10^{-20} cm ² per molecule)	λ (nm)	σ (10^{-20} cm ² per molecule)
190	71.96	244	27.11	298	9.87
192	62.99	246	27.71	300	8.37
194	54.02	248	28.60	302	7.28
196	46.45	250	29.60	304	6.38
198	40.47	252	30.90	306	5.78
200	35.88	254	32.29	308	5.28
202	32.39	256	33.49	310	4.88
204	29.70	258	34.68	312	4.58
206	27.71	260	35.68	314	4.39
208	26.31	262	36.48	316	4.19
210	25.32	264	36.78	318	3.89
212	24.72	266	36.78	320	3.69
214	24.42	268	36.48	322	3.39
216	24.52	270	35.88	324	3.09
218	24.72	272	34.88	326	2.99
220	25.12	274	33.59	328	2.79
222	25.51	276	31.89	330	2.49
224	25.91	278	30.10	332	2.19
226	26.21	280	28.31	334	1.89
228	26.41	282	26.31	336	1.69
230	26.61	284	24.22	338	1.50
232	26.61	286	21.93	340	1.30
234	26.61	288	19.83	342	1.10
236	26.51	290	17.54	344	1.00
238	26.51	292	15.45	346	0.80
240	26.61	294	13.46	348	0.70
242	26.71	296	11.56	350	0.60

Fig. 4 and Table 2 show that the mixture 2-hexanone-4-hydroperoxide/3-hexanone-5-hydroperoxide presents a steep decrease from 190 to 210 nm, then a plateau from 210 to 250 nm, a strong maximum near 265 nm, and after that a continuous decrease up to 350 nm. Here also, for $\lambda \geq 290$ nm, absorption of the mixture of ketohydroperoxides is about 10 times stronger than that of acetone.

3. Discussion

Hexyl-ketohydroperoxides are produced, through oxidation of *n*-hexane in O₂/N₂ mixtures at low temperature (270–300°C), in amounts high enough to permit micro-preparative separation, this separation (1–2 mg) enabling subsequent measurement of their UV absorption cross sections. It may be supposed that the ketohydroperoxide absorption looks like the sum of the peroxide absorption

and the ketone absorption, but modified by an amplification factor increasing the overall effect. It can be noticed, indeed, that the C=O group of the ketohydroperoxide provides a much stronger absorption than a ketone.

The comparison between our measurements of absorption cross sections of acetone and H₂O₂ in solution in acetonitrile, and the cross sections measured in gas phase [12,13] shows a shift due to the liquid phase: for both species, the absorption spectra obtained in the liquid phase are lower than those obtained in the gas phase, as shown in Table 3.

In tropospheric photochemistry, where only light of $\lambda \geq 290$ nm is available, the 2-hexanone-5-hydroperoxide absorption cross section is at least two times stronger than that of acetone measured in gaseous phase [12]. In the case of both 2-hexanone-4-hydroperoxide and 3-hexanone-5-hydroperoxide, their absorption is at least four times stronger.

The shift between the absorption cross sections in solution in acetonitrile and in gaseous phase allows to suppose that

Table 3

Absorption cross sections (10^{-20} cm² per molecule) vs. UV wavelength (nm) of acetone and hydrogen peroxide in solution in acetonitrile and in gaseous phase

λ (nm)	σ (10^{-20} cm ² per molecule) ^a	σ (10^{-20} cm ² per molecule) ^b	σ (10^{-20} cm ² per molecule) ^c	σ (10^{-20} cm ² per molecule) ^d
190	16.06	–	47.40	67.2
195	4.18	–	39.52	56.4
200	0.38	–	31.63	47.5
205	0.17	–	25.78	40.8
210	0.12	–	21.12	35.7
215	0.10	0.167	17.05	30.7
220	0.11	0.246	13.74	25.8
225	0.15	0.380	11.02	21.7
230	0.23	0.584	8.90	18.2
235	0.39	0.885	7.12	15.0
240	0.62	1.30	5.60	12.4
245	0.94	1.83	4.32	10.2
250	1.28	2.47	3.31	8.3
255	1.68	3.15	2.46	6.7
260	2.05	3.81	1.78	5.3
265	2.34	4.41	1.27	4.2
270	2.51	4.79	0.93	3.3
275	2.55	4.94	0.59	2.6
280	2.43	4.91	0.34	2.0
285	2.17	4.54	0.25	1.5
290	1.83	4.06	0.08	1.2
295	1.44	3.42	<0.08	0.90
300	1.01	2.67	<0.08	0.68
305	0.63	2.05	<0.08	0.51
310	0.34	1.36	<0.08	0.39
315	0.15	0.387	<0.08	0.29
320	0.05	0.455	<0.08	0.22
325	0.01	0.210	<0.08	0.16
330	<0.01	0.074	<0.08	0.13
335	<0.01	0.025	<0.08	0.10
340	<0.01	0.009	<0.08	0.07
345	<0.01	0.003	<0.08	0.05
350	<0.01	0.001	<0.08	0.04

^a This work; acetone in solution.

^b [12]; Acetone gas phase.

^c This work; H₂O₂ in solution.

^d [13]; H₂O₂ gas phase.

the absorption cross sections of the ketohydroperoxides are higher than those measured above. Therefore, in the range 290–350 nm, the solar UV radiations reaching the ground, the ketohydroperoxides, if they are formed (what is likely according to the Arrhenius parameters of their formation reactions, by isomerization), can absorb enough energy and may react.

The reaction rate of OH + ketohydroperoxide can be evaluated with the rate constant for methylhydroperoxide [14] and the OH concentration given by Kramp et al. [15]. Assuming (i) a photochemical absorption by the ketohydroperoxides calculated with our measured absorption cross section and the actinic flux in the troposphere [16], (ii) a quantum yield # 1 for this photochemical step, these pathways can be compared. Numerical estimations performed for the 2-hexanone-5-hydroperoxide and successively 20 and 30° for the zenith angle show that the ketohydroperoxide amount having absorbed the actinic flux is three to four times greater than the ketohydroperoxide consumed by the reaction with OH.

Gierczak et al. have shown that the acetone photolysis is a determining reaction in the stratosphere. In the troposphere, the main role is held by the reaction of OH with acetone. Since the absorption cross sections of ketohydroperoxides are larger than that of acetone it is possible that the role of those species has to be taken into account. In conclusion, to check our assumption on the role of ketohydroperoxides as a source of radicals [2,3], formation reactions of ketohydroperoxides and their photochemistry should be introduced in the mechanisms of tropospheric chemistry; and further investigations are needed in order to know the yield in radicals of those peroxides, during their photochemical decomposition.

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