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Journal of Photochemistry and Photobiology A: Chemistry 134 (2000) 31–36

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

The near-UV absorption cross sections for several ketones

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Received 2 December 1999; received in revised form 7 February 2000; accepted 21 February 2000

Abstract

The UV absorption cross sections of acetone, 2-butanone, 2,4-dimethyl-3-pentanone, 4-methyl-2-pentanone, and 5-methyl-2-hexanone are reported. The absorption spectra were measured by using a diode array spectrometer over the wavelength range 240–350 nm at room temperature (298±2) K. The obtained data were used to estimate the photolysis lifetimes of the studied ketones and compared to that with respect to the reaction with OH radicals. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: UV spectra; Acetone; 2-Butanone; 2,4-Dimethyl-3-pentanone; 4-Methyl-2-pentanone; 5-Methyl-2-hexanone

1. Introduction

Carbonyl compounds are important trace constituents in the troposphere. Their atmospheric photochemical transformations represent a major source of organic free radicals in the lower atmosphere [1,2]. They may control tropospheric ozone formation, enhance acidic deposition in remote areas by formation of organic acids, and long distances transport of nitrogen oxides. They may also play a role in the upper tropospheric budget of HO_x (e.g. [3]). Quantification of their atmospheric impact requires knowledge of their origin and their removal processes.

Ketones represent an important class of carbonyl compounds, they are widely used as solvents in industry, and a substantial proportion of them can then be emitted to the atmosphere. They are also formed in the troposphere by oxidation of non-methane hydrocarbons. Some of them are directly emitted from vegetation and biomass burning [4]. In the atmosphere, the oxidation of ketones is initiated either by reaction with OH or by photolysis. They have lifetimes in the range of 1 day up to months with respect to the loss via reaction with OH [5]. Their photodissociation rates in the atmosphere depend on their absorption cross sections, their primary quantum yields and actinic flux. A major uncertainty in the modelling of the chemistry of ketone in the lower atmosphere is in the values used for the absorption cross-sections for these molecules and their photolysis quantum yields [6,7]. The absorption cross sections of some ketones have been reported in the literature (e.g. [3,8–10]).

In the present paper, absorption cross-sections are presented for a series of aliphatic ketones, including acetone ($CH_3C(O)CH_3$), 2-butanone ($CH_3C(O)CH_2CH_3$), 2,4-dimethyl-3-pentanone ($(CH_3)_2CHC(O)CH(CH_3)_2$), 4-methyl-2-pentanone ($CH_3C(O)CH_2CH(CH_3)_2$), and 5-methyl-2-hexanone ($CH_3C(O)CH_2CH_2CH(CH_3)_2$). Cross-sections are reported at wavelength greater than 240 nm, at a temperature of (298±2) K. The obtained data are compared to the literature ones for acetone and 2-butanone. The photodissociation rates of the studied ketones for a representative set of atmospheric conditions are also estimated.

2. Experimental

The apparatus, technique and method of data analysis have been described in detail previously [11] and are briefly presented here.

Absorption measurements were made using a UV-Visible spectrophotometer (Chromex 250IS) equipped with a 1800 grooves/mm grating and a 1024 element diode array detector (Princeton Instrument, Inc.). The collimated output of a 30 W D_2 lamp (from Oriel) was passed through a 100 cm long and 2.5 cm diameter absorption cell and focused onto the entrance slit of the spectrometer. Spectral measurements were carried out at a spectral resolution of 0.04 nm by using a 20 μm entrance slit in the spectrometer. The spectrum was divided into four overlapping regions of about 40 nm in the

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PII: S1010-6030(00)00243-4

range 200–350 nm. The wavelength scale of the spectrometer was calibrated using the emission lines from low-pressure Zn (213.8 nm) and Hg (253.7, 313.2, 365 nm) pen-ray lamps and was accurate to 0.1 nm.

Absorption cross sections were calculated using the Beer–Lambert's law:

$$\sigma(\lambda) = -\frac{\ln[I(\lambda)/I_0(\lambda)]}{LC}$$

Where $\sigma(\lambda)$ is the absorption cross section (cm^2 per molecule) at wavelength λ, L is the path length in cm, and C is the concentration in molecule cm^{-3}. I and I_0 are the light intensities with and without ketone in the absorption cell, respectively. Each measurement of I and I_0 consisted of 10 to 20 scans of diode array and required at maximum 1 s to complete.

The reference spectrum I_0 was recorded after purging the absorption cell with He. The spectrum I was measured by two methods. In the called static method, I was measured when the absorption cell was filled with a fixed concentration of ketone, while in the second method, called dynamic, I was measured when a fixed pressure of ketone was flowed through the absorption cell. For each 40 nm region of the spectrum, absorption measurements were made at 10 different pressures, including six static and four dynamic. I_0 was recorded before and after each I measurement.

The pressure measurements were made using two capacitance manometers operating in the ranges 0–10 and 0–1000 Torr, respectively. The pressure range used in the measurements depended on the absorption cross sections of the studied ketone and its vapour pressure.

Acetone (>99.5%), 4-methyl-2-pentanone (>99.5%), 5-methyl-2-hexanone (99%), and 2,4-dimethyl-3-pentanone (98%) were from Aldrich, 2-butanone (>99.5%) was from Fluka. These compounds were further purified by repeated freeze, pump, and thaw cycles and fractional distillation before use.

3. Results and discussion

Absorption spectra were measured between 240 and 400 nm at (298±2) K. Because the deviation was very large beyond 350 nm due to small absorption cross sections, the cross sections are reported here only between 240 and 350 nm. The obtained spectrum for different ketones are shown in Fig. 1, and the cross section values are listed in Table 1 in 1 nm intervals. The precision of the experimental cross sections was calculated at each wavelength using the standard deviation for different measurements. In general, between 240 and 320 nm, the standard deviation of the measured absorption cross section was better than 5%. At λ>320 nm, the precision was worsened to 10% at the 90% confidence limit. The difference between the data obtained in the static and dynamic methods was within the estimated standard deviation. Independent determination of the absorption cross sections for each ketone at 253.7 and 313.2 nm using Hg pen ray lamp as the light source were also made. In these separate experiments, the earlier two lines were isolated from Hg lamp with band pass filters (254 and 313 nm, respectively) and the transmitted radiation were detected by a photodiode detector. The absorption cross sections of the ketones obtained by this method and obtained by continuous method (using D_2 lamp-diode array system) at corresponding wavelengths are listed in Table 2. The data obtained by the two methods were in good agreement.

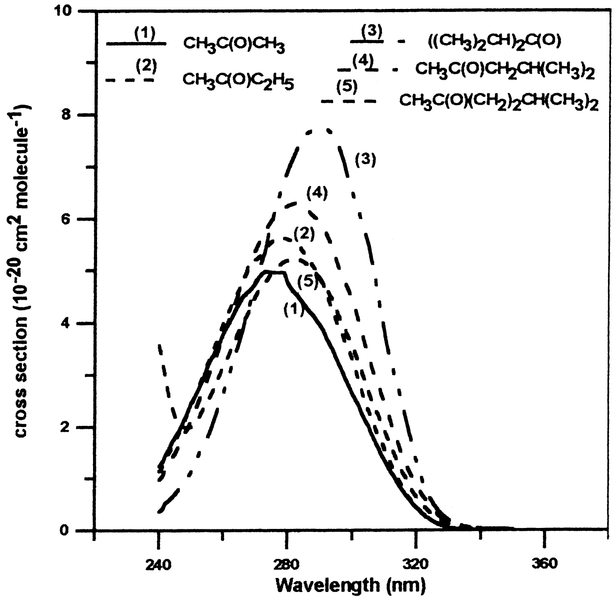

Fig. 1. Absorption cross section of acetone, 2-butanone, 2.4-dimethyl-3-pentanone, 4-methyl-2-pentanone, and 5-methyl-2-hexanone between 240 and 350 nm at (298±2) K.

In addition to random errors, the systematic ones also contribute to overall uncertainty in the absorption cross section measurements. In this study, the major sources of systematic errors are believed to be in operation of the capacitance manometer (<1%), and in the determination of the path length for the absorption cell (<1%). Absolute error in wavelength based on calibration of the spectrophotometer using the emission lines of Zn and Hg lamps, is estimated to be ±0.1 nm.

As expected for carbonyls, an absorption band centre at about 290 nm is observed for the ketones studied here resulting from a dipole forbidden n–π* electronic transition of C=O group. As shown in Fig. 1, the position of the maximum absorption depends on the nature of the rest of the molecules. The absorption bands of larger aliphatic ketones shift slightly to longer wavelength compared to acetone; presumably this is the consequence of larger alkyl have smaller resonance effects on π* level than that of methyl.

Absorption cross sections for acetone and 2-butanone have been reported in a number of previous studies (e.g. [3,8–10]). The agreement is reasonably good between the present results and those from the literature. The differences

Table 1
Absorption cross sections for acetone, 2-butanone, 2,4-dimethyl-3-pentanone, 4-methyl-2-pentanone, and 5-methyl-2-hexanone[a]

λ (nm)	$CH_3C(O)CH_3$	$CH_3C(O)C_2H_5$	$((CH_3)_2CH)_2C(O)$	$CH_3C(O)CH_2CH(CH_3)_2$	$CH_3C(O)(CH)_2CH(CH_3)_2$
240	1.233	1.131	0.360	0.962	3.578
241	1.319	1.230	0.407	1.048	3.235
242	1.449	1.377	0.517	1.182	2.926
243	1.561	1.493	0.581	1.281	2.587
244	1.684	1.607	0.636	1.382	2.382
245	1.807	1.726	0.694	1.488	2.211
246	1.912	1.859	0.787	1.606	2.083
247	2.030	2.000	0.884	1.731	2.017
248	2.179	2.136	0.954	1.860	1.998
249	2.330	2.276	1.032	1.996	1.989
250	2.463	2.416	1.135	2.134	2.005
251	2.571	2.569	1.276	2.280	2.056
252	2.687	2.732	1.429	2.433	2.150
253	2.833	2.893	1.550	2.589	2.272
254	2.993	3.049	1.663	2.752	2.385
255	3.154	3.203	1.788	2.919	2.492
256	3.293	3.355	1.946	3.087	2.604
257	3.412	3.512	2.136	3.255	2.733
258	3.540	3.667	2.313	3.421	2.886
259	3.664	3.829	2.484	3.594	3.031
260	3.794	3.991	2.658	3.774	3.175
261	3.925	4.147	2.837	3.955	3.315
262	4.040	4.288	3.050	4.135	3.452
263	4.155	4.417	3.275	4.304	3.598
264	4.287	4.529	3.469	4.463	3.745
265	4.408	4.654	3.661	4.623	3.868
266	4.503	4.791	3.865	4.790	3.986
267	4.575	4.940	4.088	4.962	4.111
268	4.614	5.067	4.340	5.130	4.248
269	4.681	5.159	4.577	5.279	4.397
270	4.769	5.220	4.791	5.414	4.525
271	4.867	5.269	5.001	5.539	4.622
272	4.947	5.331	5.207	5.654	4.701
273	4.994	5.401	5.415	5.772	4.777
274	4.979	5.518	5.737	5.895	4.855
275	4.968	5.573	5.926	5.990	4.970
276	4.969	5.608	6.187	6.083	5.046
277	4.955	5.645	6.404	6.140	5.091
278	4.967	5.647	6.612	6.191	5.148
279	4.955	5.634	6.794	6.230	5.185
280	4.767	5.616	6.959	6.262	5.209
281	4.661	5.588	7.107	6.292	5.223
282	4.596	5.554	7.241	6.313	5.233
283	4.529	5.504	7.374	6.319	5.227
284	4.447	5.438	7.503	6.300	5.205
285	4.365	5.348	7.601	6.252	5.170
286	4.273	5.252	7.669	6.186	5.119
287	4.205	5.158	7.702	6.117	5.051
288	4.133	5.072	7.723	6.050	4.985
289	4.032	4.979	7.727	5.990	4.917
290	3.958	4.870	7.731	5.921	4.843
291	3.852	4.733	7.733	5.832	4.761
292	3.717	4.568	7.719	5.710	4.663
293	3.599	4.385	7.672	5.555	4.543
294	3.467	4.204	7.590	5.377	4.403
295	3.330	4.039	7.477	5.202	4.252
296	3.182	3.891	7.320	5.036	4.105
297	3.042	3.749	7.121	4.880	3.969
298	2.915	3.610	6.904	4.734	3.832
299	2.769	3.460	6.688	4.589	3.697
300	2.627	3.282	6.478	4.426	3.561
301	2.527	3.085	6.284	4.235	3.404

Table 1 (*Continued*).

λ (nm)	$CH_3C(O)CH_3$	$CH_3C(O)C_2H_5$	$((CH_3)_2CH)_2C(O)$	$CH_3C(O)CH_2CH(CH_3)_2$	$CH_3C(O)(CH)_2CH(CH_3)_2$
302	2.406	2.882	6.108	4.027	3.230
303	2.262	2.685	5.930	3.807	3.049
304	2.134	2.495	5.719	3.578	2.869
305	2.016	2.320	5.473	3.364	2.691
306	1.874	2.167	5.183	3.164	2.528
307	1.727	2.022	4.858	2.987	2.374
308	1.596	1.816	4.502	2.815	2.245
309	1.476	1.731	4.138	2.641	2.101
310	1.353	1.583	3.801	2.466	1.957
311	1.238	1.425	3.501	2.286	1.797
312	1.117	1.283	3.243	2.101	1.639
313	1.028	1.144	3.015	1.914	1.483
314	0.917	1.014	2.808	1.719	1.339
315	0.817	0.904	2.586	1.549	1.191
316	0.736	0.790	2.328	1.394	1.066
317	0.659	0.684	2.072	1.227	0.976
318	0.573	0.595	1.816	1.098	0.823
319	0.496	0.514	1.562	0.981	0.727
320	0.436	0.439	1.321	0.870	0.639
321	0.374	0.373	1.107	0.765	0.560
322	0.313	0.315	0.922	0.667	0.484
323	0.261	0.262	0.760	0.576	0.420
324	0.218	0.216	0.655	0.492	0.357
325	0.181	0.176	0.543	0.413	0.298
326	0.147	0.145	0.446	0.345	0.245
327	0.114	0.118	0.366	0.285	0.201
328	0.088	0.096	0.299	0.235	0.171
329	0.066	0.077	0.245	0.193	0.145
330	0.056	0.061	0.201	0.158	0.120
331	0.043	0.048	0.166	0.129	0.103
332	0.032	0.037	0.137	0.104	0.088
333	0.028	0.029	0.113	0.082	0.074
334	0.022	0.022	0.094	0.064	0.101
335	0.016	0.016	0.079	0.050	0.050
336	0.012	0.013	0.066	0.039	0.043
337	0.009	0.009	0.057	0.035	0.036
338	0.009	0.007	0.049	0.031	0.033
339	0.008	0.005	0.043	0.028	0.030
340	0.007	0.003	0.040	0.026	0.030
341	0.006	0.002	0.037	0.026	0.031
342	0.005	0.002	0.035	0.024	0.043
343	0.004	0.001	0.034	0.025	0.035
344	0.003	–	0.033	0.025	0.032
345	0.003	–	0.031	0.025	0.033
346	0.002	–	0.030	0.023	0.034
347	0.002	–	0.029	0.021	0.030
348	0.002	–	0.026	0.022	0.029
349	0.002	–	0.024	0.022	0.026
350	0.002	–	0.022	0.023	0.025

[a] σ (10^{-20} cm^2 per molecule).

Table 2

Comparison of the absorption cross section for the series of ketones at 253.7 and 313.2 nm obtained by using Hg lamp/photodiode or D_2 lamp/diode array

Ketones	σ (253.7 nm) cm^2 per molecule		σ (313.2 nm) cm^2 per molecule	
	Photodiode	Diode array	Photodiode	Diode array
$CH_3C(O)CH_3$	2.94×10^{-20}	2.94×10^{-20}	1.10×10^{-20}	1.09×10^{-20}
$CH_3C(O)C_2H_5$	3.02×10^{-20}	3.01×10^{-20}	1.16×10^{-20}	1.12×10^{-20}
$((CH_3)_2CH)_2C(O)$	1.75×10^{-20}	1.63×10^{-20}	3.07×10^{-20}	2.97×10^{-20}
$CH_3C(O)CH_2CH(CH_3)_2$	2.77×10^{-20}	2.70×10^{-20}	1.88×10^{-20}	1.88×10^{-20}
$CH_3C(O)(CH)_2CH(CH_3)_2$	2.52×10^{-20}	2.47×10^{-20}	1.47×10^{-20}	1.42×10^{-20}

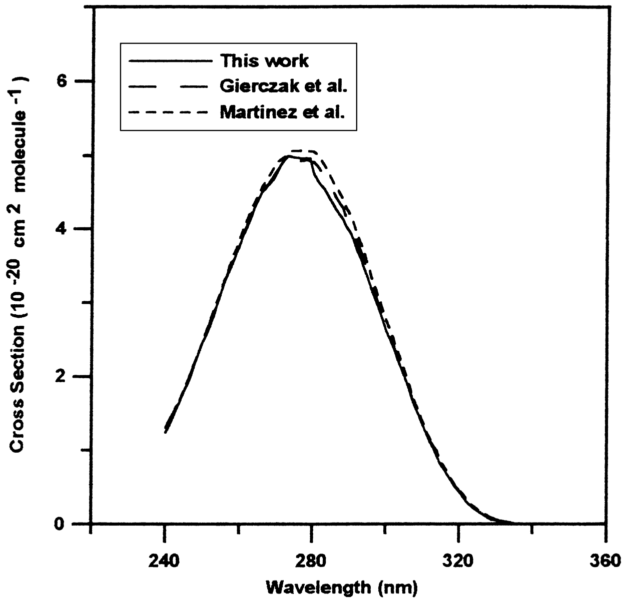

Fig. 2. Absorption cross section of acetone from Martinez et al. [9], Gierczak et al. [3], and this work.

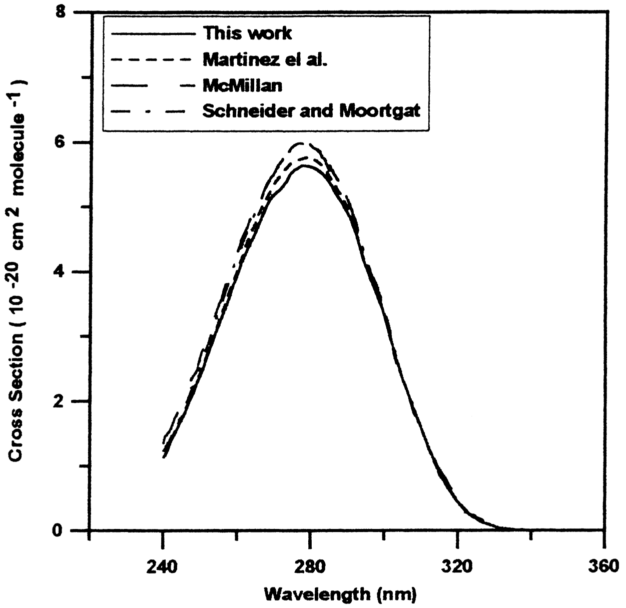

Fig. 3. Absorption cross section of butanone from McMillan reported in [8] from Schneider and Moortgat reported in [10] from Martinez et al. [9] and this work.

between different measurements for 2-butanone are around the maximum absorption (λ=277 nm). However, these differences are not large and fall within the combined uncertainties of different studies as shown in Figs. 2 and 3 where the data obtained in this work are presented along with those of Martinez et al. [9] and Gierczak et al. [3] for acetone (Fig. 2) and those of McMillan reported in reference [8], Martinez et al. [9] and that of Schneider and Moortgat reported by Raben and Moortgat [10] for 2-butanone (Fig. 3). The largest difference between different spectra of 2-butonone is at the maximum absorption and is less than 10%. To our knowledge, this work reports the first absorption spectra for the three other ketones.

The absorption cross sections from this study were used to calculate the photodissociation rate constants (k_p) for the ketones by using the following relationship.

$$k_{\mathrm{p}} = \int \sigma(\lambda)\phi(\lambda)J(\lambda)\,\mathrm{d}\lambda$$

where $\sigma(\lambda)$ is the absorption cross section for the molecule, $\phi(\lambda)$ is the primary quantum yield for photolysis, and $J(\lambda)$ is the actinic flux of solar radiation. The procedure for calculating was identical to that of previous studies [2,9]. The calculations were carried out under a representative set of atmospheric conditions (at noontime on 1 January and 1 July, cloudless and at sea level and a latitude of 40°N). The data for the actinic flux at the Earth's surface and zenith angle (θ=63° for 1 January and θ=16.9° for 1 July) are taken from Demerjian et al. [12]. Data for the primary quantum yields for acetone were taken from the recent extensive study of Gierczak et al. [3], who recommended the following expression for the acetone photodissociation quantum yield with pressure and wavelength:

$$\phi = \frac{1}{A(\lambda) + B(\lambda)\rho}$$

Table 3

Rate constants for photodissociation and reaction with OH radical for ketones under a typical atmospheric conditions

Ketones	$10^6 \times k_{\mathrm{p}}$ (s^{-1})$^{\mathrm{a}}$ (1 January)	$10^6 \times k_{\mathrm{p}}$ (s^{-1})$^{\mathrm{a}}$ (1 July)	$10^6 \times k_{\mathrm{OH}}$ (s^{-1})$^{\mathrm{b}}$
Acetone	0.14	0.59	0.06–0.6
2-Butanone	1.2	4.2	0.36–3.6
2.4-Dimethyl-3-pentanone	10.4	34	1.35–13.5
4-Methyl-2-pentanone	7.0	22.2	3.6–36.3
5-Methyl-2-hexanone	5.5	17.4	3.1–31

[a] k_{p}=Noontime photolysis rate constant at 40°N at sea level and under cloudless conditions. Data for primary quantum yields used in the calculation are discussed in the text.

[b] k_{OH}=Pseudo-first-order rate constant at T=298 K. assuming [OH]=0.3–3.0×10^6 molecule cm^{-3}. The OH reaction rate constant with 2.4-dimethyl-3-pentanone (k=4.5×10^{-12}). is from unpublished work from this laboratory. while the rate constant for the reaction of OH with the other ketones are from reference [5]. All k_{p} are the upper limits for phodissociation of ketones except for acetone and 2-butanone (see text).

where ρ is the number density of air (in molecule cm^{-3}),

$$A(\lambda) = -15.696 + 0.005707\lambda, \quad \text{for } 292 < \lambda(\text{nm}) < 308$$

$$A(\lambda) = -130.2 + 0.42884\lambda, \quad \text{for } 308 < \lambda(\text{nm}) < 337,$$

$$B(\lambda) = \exp(-88.81 + 0.15161\lambda), \quad \text{for } 292 < \lambda(\text{nm}) < 308,$$

$$B(\lambda) = \exp(-55.947 + 0.044913\lambda), \quad \text{for } 308 < \lambda(\text{nm}) < 337,$$

To estimate the primary quantum yield for acetone, we have used the above expression at 298 K and 760 Torr. For 2-butanone, we have used the photolysis quantum yield of 0.34 reported by Raben and Moortgat [10]. For other ketones, because no data on the primary quantum yields are available, only the upper limits for k_p are calculated by assuming $\phi(\lambda)$=1 at all wavelengths. The results are compared with the pseudo-first-order rate constants (k_{OH}) for reaction of ketones with hydroxyl radical at 25°C (Table 3). The tropospheric lifetimes of the studied ketones with respect to the reaction with OH were calculated using the rate constants (in cm^3 per molecule s^{-1}) at 298 K, for the reactions of OH with acetone (k=1.84$\times$10^{-13}), 2-butanone (k=1.19$\times$10^{-12}), 4-methyl-2-pentanone (k=1.21$\times$10^{-11}), and 5-methyl-2-hexanone (k=1.03$\times$10^{-11}), reported recently by Le Calvé et al. [5], and unpublished work from this laboratory for 2,4-dimethyl-3-pentanone (k=4.5$\times$10^{-12}), assuming an average OH concentration in the lower troposphere of 0.3–3.0$\times$10^6 molecule cm^{-3} [13].

The information listed in Table 3 can be used to qualitatively compare the relative importance of photolysis and reaction with hydroxyl radical for removal of ketones from troposphere. The loss process of acetone is mainly due to the OH reaction in the lower troposphere. The photolysis rate and that of reaction with OH are of the same order of magnitude with increasing altitude, indicating that both processes are important. Moreover, according to the data of Gierczak et al. [3], photolysis becomes more important at higher altitude than the reaction with OH. For the larger studied ketones, using a quantum yield of unity, the calculated upper limits for k_p are comparable to the pseudo-first-order rate constants of their reaction with OH. However, $\phi(\lambda)$ could be much smaller than unity, then photodissociation of the ketones becomes of minor importance as tropospheric sink. But at higher altitude, the importance of the photolysis could be of importance even with quantum yields smaller than unity as it was reported for acetone by Gierczak et al. [3]. Therefore, to accurately estimate the atmospheric impact of the ketones, measurements of their photodissociation quantum yields under atmospheric condition are required.

Acknowledgements

European Commission, French Ministry of Environment through the PREDIT-PRIMEQUAL programme, Programme de Recherches Avancées de Coopération Franco-Chinoise (PRA), and National Science Foundation of China (Grant No.4932703) are acknowledged for support.

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