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Atmospheric organic-phase photo-sensitized epoxidation of alkenes by α-dicarbonyls

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**Photo-sensitized
epoxidation by
α-dicarbonyls**

G. Yu and F. N. Keutsch

Abstract

We report a new pathway of epoxide formation in organic phases via catalytic oxidation of alkenes by air with α-dicarbonyls as photo-sensitizers. Epoxide yields as high as 100 % in 30 min of exposure to a solar simulator operating at the equivalent of 48.5° zenith angle are observed. The rate constants are proportional to light intensity and inversely proportional to temperature. The reaction rate is 0th order with respect to alkenes, implying that alkenes with small concentrations may rapidly be converted to epoxides in the organic phase. Based on a statistical estimate of α-dicarbonyl concentrations in secondary organic aerosol, we propose that this reaction could be highly effective under ambient conditions: the 0th-order lifetimes of organic-phase alkenes are estimated to be as low as 10 min, significantly shorter than their gas-phase 1st-order lifetimes, which are typically hours to days. The formation of epoxides in organic particles is expected to increase their hygroscopicity and ability to act as cloud condensation nuclei. Epoxides in deliquesced particles can subsequently form polyalcohols, oligomers, organosulphates and organonitrates, increasing the organic mass in the atmospheric waters.

1 Introduction

Organic material comprises 20–90 % of the non-refractory submicron aerosol mass and is distributed ubiquitously worldwide (Zhang et al., 2007; Kanakidou et al., 2005). It is well known that the majority of organic aerosol (OA) is formed via condensation of products from the oxidation of volatile organic compounds (VOCs) in the atmosphere. The aerosols formed in this manner are referred to as secondary organic aerosol (SOA). Epoxides have recently been suggested to contribute to SOA mass via aqueous-phase ring-opening reactions, especially in acidic conditions, to form polyalcohols, oligomers, organosulfates and organonitrates, especially in isoprene-derived SOA (Paulot et al., 2009; Minerath and Elrod, 2009; Minerath et al., 2009; Iinuma et al.,

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2009; Eddingsaas et al., 2010; Surratt et al., 2010; Lin et al., 2012). Conventionally, epoxides are considered to be formed from gas-phase oxidation of alkenes by OH, $O(^3P)$, ozone or nitrate radicals (Minerath and Elrod, 2009; Paulot et al., 2009). This gas-phase conversion of alkenes to epoxides and subsequent chemical transformations increases aqueous solubility and decreases vapour pressures of compounds, and therefore increases the tendency to contribute to SOA.

Conversion of alkenes into epoxides in the condensed phase has been reported in the synthetic organic literature, e.g., by Shimizu and Bartlett (1976), who demonstrated photo-epoxidation of olefins sensitized by α-dicarbonyls, specifically biacetyl, in organic solvents. The authors bubbled oxygen through mixtures of various olefins and biacetyl in organic solvents at 0 °C while exposing the solution to 254 nm light, which resulted in > 50 % yield of epoxides. The importance of this condensed phase reaction scheme has not been investigated in the context of atmospheric chemistry, even though the conditions used by Shimizu and Bartlett are not uncommon in the atmosphere: (1) organic aerosol present in the atmosphere can readily serve as organic solvent; (2) the oxidized organic molecules in the aerosol include α-dicarbonyls, which can reach a large concentration as shown later in this work; (3) the temperature of the work by Shimizu and Bartlett was 0 °C, close to atmospheric temperatures near or not far above the surface; and (4) sunlight and oxygen (air) are both abundant in the atmosphere. For these reasons, the proposed pathway of epoxide formation in the organic phase is likely to take place in the atmosphere. In this work, we use primarily biacetyl as well as other α-dicarbonyls to revisit the experiments of Shimizu and Bartlett under atmospherically relevant conditions via NMR spectroscopy, study the kinetics of the reaction, quantify temperature and wavelength dependence, and discuss atmospheric implications.

2 Experimental method

All reagents were obtained from Sigma-Aldrich and used without further purification. The studied alkenes include (+)-α-pinene (referred to as α-pinene in the rest of this work), isoprene, methyl vinyl ketone (MVK), 1-dodecene and oleic acid. The α-dicarbonyls studied include biacetyl, methylglyoxal, 2,3-pentanedione, 1,2-cyclohexanedione as well as pyruvic acid, an α-keto carboxylic acid. UV-Vis absorbance measurements showed that glass beakers and NMR tubes used in this study effectively blocked light < 290 nm (transmittance < 0.1 %), and thus eliminate UV wavelengths that are not relevant for the troposphere. Each of the alkenes (50–200 mM) was dissolved in 1 ml CDCl$_3$ with biacetyl (50–200 mM) in an NMR tube. The resulting mixture was placed in a water bath with controlled temperature. Air was bubbled through the NMR tube and the tube was exposed to a light source for 30 min for experiments aimed at determining epoxide yields. The light sources used in this study included a broadband UV lamp centred at 350 nm (ENF-240C, Spectroline), a diode laser at 445.5 ± 0.5 nm (DL-445-050-O, CrystaLaser, 50 mW), and an adjustable solar simulator (model 91160, Newport) simulating AM1.5G (Air Mass 1.5 Global) solar spectrum, the equivalent of the global average solar spectrum at 48.5° zenith angle. After exposure, ~ 10–30 % of the solution had evaporated, depending on temperature. The solution was then analyzed by a Varian 500 MHz NMR spectrometer. All NMR spectra were taken quantitatively according to Yu et al. (2011), with 25 s relaxation delay and 45° pulse flip angle. Reaction yields were calculated by the equation:

$$\text{Yield} = \frac{I_{\text{product}}}{I_{\text{product}} + I_{\text{alkene}}} \times 100\% \tag{1}$$

Where I is the integrated peak area of alkene or oxidation product in the NMR spectrum normalized by the number of hydrogen atoms corresponding to this peak. I is proportional to the concentration of the corresponding compound. A dark experiment with air bubbled through a reaction mixture that had previously been irradiated for 30 min with

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the UV lamp showed no difference between relative *I* of the product and alkene, indicating that the difference of the evaporation rates between the reactants and products under these conditions was negligible.

Kinetic studies were conducted with α-pinene, biacetyl and the UV lamp described previously. The mixtures were analyzed at 10, 20, 30, 50, 70, and 135 min of UV exposure, and the effect of temperature was determined using a temperature-controlled water bath.

3   Results and discussion

3.1   Reaction products and mechanisms

The yields after 30 min of UV exposure vary between different alkenes, and although all of the studied alkenes form oxidation products, not all of them form epoxides (Table 1). A sample NMR spectrum of α-pinene after irradiation is shown in Fig. 1. The observation that conjugated alkenes form aldehydes and non-conjugated alkenes form epoxides is expected, as previous work indicates that conjugated alkenes undergo isomerisation between *cis*- and *trans*-conformations (Shimizu and Bartlett, 1976; Nojima and Isogami, 1993) with small or no yield of epoxide. In contrast to the study of Shimizu and Bartlett – who suggested that biacetyl was completely photolyzed as judged by the disappearance of the yellow colour – we observed that the reaction mixture remained yellow, indicating that photolysis of biacetyl was minimal under our conditions. This is confirmed by NMR spectra showing low concentrations of biacetyl photolysis products (black line in Fig. 1) after irradiation. This is likely because the glassware used in this study blocked UV with wavelengths < 290 nm, which are mostly responsible for photolyzing biacetyl (Noyes et al., 1956). The yield within 30 min of exposure to long-wavelength light using the UV lamp is far less than the yields reported by Shimizu and Bartlett, who achieved almost 100 % yield. This difference results from the low power

of the UV lamp used in our work. We show later (Sect. 3.3) that the yield can reach 100 % in 30 min at realistic irradiation levels using the solar simulator.

We conducted control experiments with α-pinene (Table S1), which confirmed that the reaction requires an α-dicarbonyl, air, and irradiation. Without biacetyl or UV light, only 0.2 % epoxide was observed (exp. 4 and 5 in Table S1), consistent with the amount of epoxide found in the commercial α-pinene (exp. 2). Reaction without air bubbling through gave ~ 2 % yield, which is likely from the residual air in the NMR tube. We note that, in ambient aerosol, diffusion of air is likely to be fast enough that oxygen availability is not a limiting factor; in this context, the experimental conditions are appropriate. Pure oxygen gas instead of air was not observed to increase yield (exp. 6), also consistent with the assumption that oxygen diffusion was not a limiting factor.

The mechanism of this α-dicarbonyl photo-sensitized epoxidation is a long-debated topic (Shimizu and Bartlett, 1976; Koo and Schuster, 1979; Bartlett and Becherer, 1978; Sawaki and Foote, 1983), but it is certain that singlet oxygen ($^1O_2$) is not involved and that the most likely pathway is through radicals. Sawaki and Foote (1983) concluded that an acylperoxy radical ($CH_3C(=O)OO\cdot$), formed from acyl radicals ($CH_3C(=O)\cdot$) generated via photolysis of biacetyl, was responsible for epoxidation according to isotopic labelling studies. However, since we use longer wavelengths in this study than the 254 nm light used in previous studies, absorption is more likely to produce an excited biacetyl triplet state as opposed to photolysis that produces acyl radicals. The dominant reaction pathway under the experimental conditions in this work is consistent with the one Shimizu and Bartlett suggested originally, involving a triplet state of biacetyl (Fig. 2). Characterizing the actual reaction mechanism would require isotopic labelling studies, which is beyond the scope of this work.

Crucial to this reaction is the capability of α-dicarbonyls to undergo rapid intersystem crossing from an excited singlet state to a triplet state, which readily reacts with triplet oxygen to form the key intermediate, the oxyperoxy biradical (red structure in Fig. 2). This intersystem crossing is a distinctive property of α-dicarbonyls, making them active as photo-sensitizers while monocarbonyls are not.

3.2 Kinetic studies

Kinetic experiments using the initial rate method were conducted using α-pinene. We varied the concentrations of α-pinene and biacetyl, and determined the epoxide yield after 30 min of UV exposure. The results (Table S2) demonstrate that the reaction rate is proportional to biacetyl concentration and does not depend on initial α-pinene concentration; therefore, the reaction rate is 1st order with respect to biacetyl and 0th order with respect to alkene. Experiments conducted with 1-dodecene also demonstrated 0th order kinetics with respect to alkene. This behaviour is consistent with the rate limiting step being the production of radicals, which depends only on the concentration of biacetyl and the irradiation power.

In addition, time-dependent experiments (integrated rate law method) were conducted using 0.1 M biacetyl and 0.1 M α-pinene. The time dependent epoxide concentration is shown in Fig. 3. The linear fit is consistent with a constant reaction rate throughout the course of the reaction. Considering biacetyl is a catalyst (with negligible photolysis) whose concentration remains constant while the concentration of α-pinene decreases as the reaction progresses, this constant reaction rate is consistent with the 0th reaction order with respect to α-pinene. The deviation from linearity after 30 min is likely an artefact of solvent evaporation.

The reaction rate also depends on the alkene being oxidized. As shown in Table 1, α-pinene reacts the fastest and oleic acid reacts the slowest. This is likely due to a combination of electronic and steric effects. Alkyl groups provide higher electron density for the double bond and thus higher reactivity with respect to electrophilic radicals, as seen in the high reactivity of the triple alkyl-substituted α-pinene. α-pinene also has a constrained ring structure and low steric hindrance. However, the comparison between oleic acid and 1-dodecene shows that the reactivity is influenced by competing effects that we are not able to quantify.

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The reaction rate can then be expressed by the following equation:

$$R = \frac{d[\text{epoxide}]}{dt} = k[\text{biacetyl}] \tag{2}$$

Where R is the reaction rate in M s^{-1}, [] denotes concentration in M, and k represents the first order rate constant in s^{-1}. The measured rate constants between biacetyl and alkenes are: $2.2 \times 10^{-5}\,\text{s}^{-1}$ for α-pinene, $1.3 \times 10^{-5}\,\text{s}^{-1}$ for 1-dodecene and $1.2 \times 10^{-6}\,\text{s}^{-1}$ for oleic acid.

We also measured the temperature dependent rate constant for α-pinene epoxidation (Fig. 4). We used two UV lamps of the same model but with slightly different power distribution for exposure. Lamp B has a small feature at 404.3 nm (see Fig. S2) that results in efficient formation of the biacetyl triplet state and causes higher reaction rate constants. The comparison between the two UV lamps therefore also further highlights that the biacetyl triplet state is responsible for the epoxidation of alkenes. The reaction rate decreases as temperature increases, indicating a negative activation energy of the reaction, which is not unusual for radical reactions. This effect is also relevant for atmospheric implications, as colder air-masses may be more likely to form epoxides in organic particles.

3.3 Wavelength dependence

All experiments discussed previously were conducted with a UV lamp (Spectroline model ENF-240C, broadband UV centred at 350 nm), and the peak intensity at 15 cm away from the lamp is $300\,\mu\text{W cm}^{-2}$. Measured spectra are shown in Figs. S1 and S2. We also conducted experiments using α-pinene and biacetyl with other light sources, including a 50 mW power diode laser at 445.5 nm ideal for formation of triplet biacetyl but below the photodissociation threshold, and a solar simulator with adjustable power simulating an AM 1.5G solar spectrum at an equivalent output power and spectral distribution of the Sun at 48.5° zenith angle. The solar simulator experiments showed that the reaction rate constant scales with light power (Fig. S3) with an equation of

$k = 3.48 \times 10^{-4} P - 5.45 \times 10^{-5}$, where k is the rate constant in Eq. (2) with unit of s^{-1}, and P is the light power scaled to solar power (i.e., 1 is equivalent to the power from the Sun at 48.5° zenith angle). The R^2 for the fitting is 0.99. The rate constant of α-pinene for Eq. (2) at 100 % solar power at 48.5° zenith angle is then calculated to be 2.9×10^{-4} s^{-1}.

Table 2 shows a list of the reaction rate constants obtained with different light sources. It is clear that the epoxide formation rate qualitatively scales with the power of the light source, considering the three light sources have different spectral distribution (see Fig. S1) that excite biacetyl with very different efficiencies. The efficiency is especially low for the UV lamp, as the output does not overlap with the absorption cross section of biacetyl significantly.

3.4 Solvent and other α-dicarbonyls

We conducted α-pinene epoxidation experiments in benzene and compared the results with the reaction in chloroform to evaluate the effect of solvents. Initial concentrations of α-pinene and biacetyl were 0.055 M and 0.18 M, respectively, and the reaction was performed at 0 °C. The resulting yield (10 %) is not significantly different than that in CDCl$_3$ (11 %). Even though benzene and CDCl$_3$ provide similar reaction rates, the effect of other solvents on this photo-epoxidation remains unclear. However, based on the two organic solvents studied in this work, it can be extrapolated that organic aerosol in the atmosphere would be able to serve as the solvent for this epoxidation.

As the triplet state of α-dicarbonyls is critical for this reaction, other α-dicarbonyls, including ketones and aldehydes, should also act as photo-sensitizers. Except for pyruvic acid (discussed later) all studied α-dicarbonyls have an absorption feature between 350 and 450 nm (Fig. 5), which is responsible for the generation of the triplet state as discussed earlier. Experiments with these α-dicarbonyls confirmed that, as expected, α-dicarbonyls in general can act as photo-sensitizers (Table 3). There are four important observations: (1) biacetyl and 2,3-pentanedione showed similar reactivity,

consistent with their similar absorption cross sections (Fig. 5) and intersystem crossing quantum yields (Richtol and Klappmei, 1966). (2) Methylglyoxal showed a lower reactivity because the commercial methylglyoxal obtained was in aqueous solution, which was not miscible with $CDCl_3$. As methylglyoxal readily hydrates in aqueous solutions (Yu et al., 2011), it will preferentially partition to the aqueous phase, significantly decreasing its effective concentration in $CDCl_3$, resulting in the observed low rate constant. (3) The carbonyls in 1,2-cyclohexanedione are at torsional angles that shift the absorption and affect the triplet state dynamics (Verheijdt and Cerfontain, 1982), which explains the lower yield. (4) Pyruvic acid showed no reactivity when exposed to either UV lamp or solar simulator, due to the different electronic states for carboxylic acids compared to ketones or aldehydes, although its ester has been reported to undergo intersystem crossing and phosphoresce (Hammond et al., 1961). According to these results, only ketone or aldehyde carbonyl groups in *α*-dicarbonyls participate in this reaction, and the carbonyl groups in carboxylic acids, and likely esters or amides, are inefficient photo-sensitizers.

4   Conclusions and atmospheric relevance

In this work, we show that alkenes undergo organic-phase photo-sensitized epoxidation in the presence of *α*-dicarbonyls, air and sunlight. The epoxide formation yield can reach as high as 100 % in 30 min with simulated sunlight, implying a short lifetime for condensed-phase alkenes in the presence of photosensitizers. We used *α*-pinene as a model alkene to study the reaction kinetics, and confirmed the role of triplet state *α*-dicarbonyl in photo-epoxidation. We measured the rate constants for epoxide formation from *α*-pinene, 1-dodecene and oleic acid. We also showed that the reaction rate constant is inversely proportional to temperature and scales with irradiation power. The reaction kinetics were determined to be 0th order in alkene concentration and 1st order in *α*-dicarbonyl concentration, suggesting that activation of the photosensitizing agent is the rate-limiting step.

The fact that other α-dicarbonyls in addition to biacetyl are also active photo-sensitizers highlights the potential atmospheric significance of this reaction. We estimate the concentration of α-dicarbonyls in typical low-volatility oxidized organic aerosol (LV-OOA) by assuming that LV-OOA has 8–12 carbon atoms in a molecule with an O:C ratio of 0.8, and that 20 % of the oxygen atoms are carbonyl oxygens (Kroll et al., 2011; Donahue et al., 2011). We then treat all molecules as straight-chain organic compounds with a statistically even distribution of oxygenated functional groups. These two assumptions allow us to simplify a complicated system to assess the relevance of the reactions studied. Statistical calculations show that 17 % of the LV-OOA molecules contain α-dicarbonyl groups under these assumptions. If we take the average formula, $C_{10}H_{14}O_8$ (number of H atoms in a molecule is undefined, but it does not affect the molecular weight significantly), the molecular weight is 262 g mol^{-1}. Assuming the particles have a density of 1.5 g ml^{-1}, the total molar concentration of organic material in LV-OOA is $\sim$ 6 M. 17 % of the molecules are α-dicarbonyls, meaning that α-dicarbonyl concentration in LV-OOA particles can be as high as 1 M, far exceeding the concentrations studied in this work. Considering that the reaction rate depends linearly on the concentration of α-dicarbonyls, the potential reaction rate is expected to be very high. The same statistical estimation for semi-volatile oxidized organic aerosol (SV-OOA), assumed to have typically 6–12 carbon atoms in a molecule with 0.5 O:C ratio and 1/3 of the oxygen atoms being carbonyl oxygen, shows that 20 % of the molecules contain α-dicarbonyl groups. Using an average formula $C_9H_{14}O_{4.5}$, the estimated α-dicarbonyl concentration can reach 1.5 M, which is even higher than that in LV-OOA. Although these estimates are uncertain, they highlight that high α-dicarbonyl concentrations are expected in ambient SOA.

Due to the presence of abundant α-dicarbonyls, organic phase solvent, air and sunlight in the atmosphere, this reaction is expected to occur in particles containing LV-OOA and SV-OOA. Although the concentration of alkenes may be low in these particles due to their short atmospheric lifetimes, our work shows that low concentrations of alkenes can reach 100 % conversion to epoxide under these conditions. If we assume

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that conversion of alkenes by aerosol-phase α-dicarbonyls to epoxides is analogous to that of biacetyl and 1-dodecene with the solar simulator, the estimated rate constant is $1.7 \times 10^{-4}\,\mathrm{s}^{-1}$. The 0th-order lifetime of alkenes is $5.9 \times 10^3 \times$ [alkene] seconds, where [alkene] is the total alkene molarity in the OA particles. Note that this lifetime described here is not the e-folding lifetime for 1st order reactions; it is the total time for alkenes to be completely converted. If [alkene] is 0.1 M, the 0th-order lifetime with regard to this photo-sensitized epoxidation is estimated to be 10 min, significantly shorter than the gas-phase lifetimes of alkenes with respect to reactions with OH, O_3 or NO_3, which are hours to days (Seinfeld and Pandis, 1998). If [alkene] is even smaller, the lifetime will be even shorter. The organic-phase alkenes in the atmosphere will form epoxide much more rapidly than other oxidants can oxidize them. In addition, organic aerosol may serve as a potential sink of atmospheric alkenes by rapid conversion of condensed alkenes to epoxides. At high organic aerosol load, this reaction may even compete with gas-phase alkene oxidation.

Moreover, the formation of epoxides in organic-phase particles will increase hygroscopicity, and therefore increase the potential of these particles to act as cloud condensation nuclei (CCN). The resulting epoxides in deliquesced particles are readily hydrolyzed or attacked by water, sulphate or nitrate ions catalyzed by acids to form polyalcohols, oligomers, organosulphates, or organonitrates (Iinuma et al., 2009; Minerath et al., 2009; Minerath and Elrod, 2009; Eddingsaas et al., 2010; Lin et al., 2012). Organosulfates have been recently proposed to contribute substantially to organic aerosol mass, by as much as 30 % at some locations (Surratt et al., 2008). Laboratory studies show that organosulphate formation likely occurs via the ring-opening reaction of epoxides by the nucleophilic attack of sulphate ion with acidic catalysis, which requires a large source of precursor epoxides. The fast photo-sensitized epoxidation described in this work may contribute to observed organosulphates. To the authors' knowledge this epoxide formation pathway has not previously been considered in atmospheric processes. Further studies of this reaction, in particular chamber aerosol studies as well as field measurements of organic-phase epoxides, are needed

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to quantify the role of this mechanism in the atmosphere. In addition, this study high-lights that further investigations of aerosol organic photochemistry within the context of atmospheric processes are needed.

Supplementary material related to this article is available online at:
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Table 1. Oxidation products identified for alkenes studied in this work. Reactions were performed in 0.1 M alkene and 0.1 M biacetyl solution in CDCl$_3$ with the Spectroline UV lamp.
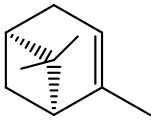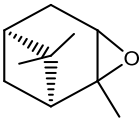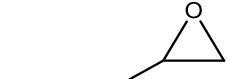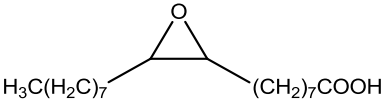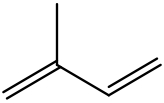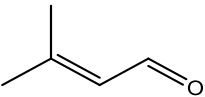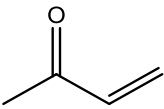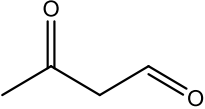
Alkane	Oxidation product	Yield in 30 min
(α-pinene)		4.1 %
CH$_3$(CH$_2$)$_9$ (1-dodecene)	CH$_3$(CH$_2$)$_9$	2.2 %
H$_3$C(H$_2$C)$_7$ (CH$_2$)$_7$COOH (oleic acid)	H$_3$C(H$_2$C)$_7$ (CH$_2$)$_7$COOH	0.6 %
(isoprene)		4.5 %
(MVK)		1.3 %

Table 2. Epoxide formation rate constant in CDCl$_3$ solutions of 0.055 M α-pinene and 0.18 M biacetyl for different light sources. Yields were collected after 30 min of exposure.

Light source	Power	Total power**	Yield	Rate constant, $10^{-5}\,\text{s}^{-1}$
UV lamp	$< 20\,\text{mW cm}^{-2}$*	$< 60\,\text{mW}$	11 %	2.2
Diode laser (445.471 nm)	50 mW	50 mW	14 %	2.4
Solar simulator	$100\,\text{mW cm}^{-2}$	500 mW	100 %	29

* Estimated from the power distribution spectrum and peak power provided by the company, $300\,\mu\text{W cm}^{-2}$.
** The estimated cross section of the NMR tube exposed to the UV lamp is $3\,\text{cm}^2$, and $5\,\text{cm}^2$ for the solar simulator.

Table 3. Epoxidation rate constants observed for different α-dicarbonyls in CDCl$_3$ solutions of 0.055 M α-pinene and 0.18 M α-dicarbonyl.

α-dicarbonyl	biacetyl	2,3-pentanedione	Methylglyoxal*	1,2-cyclohexanedione
Reaction rate, $\times 10^{-5}\,\text{s}^{-1}$	2.2	3.1	0.19	0.50

* Methylglyoxal was commercially obtained in aqueous solution, which was not miscible with CDCl$_3$. The observed low reaction rate was due to the preferential partitioning of methylglyoxal into the aqueous phase, causing the effective concentration of methylglyoxal lower than 0.18 M. See text.
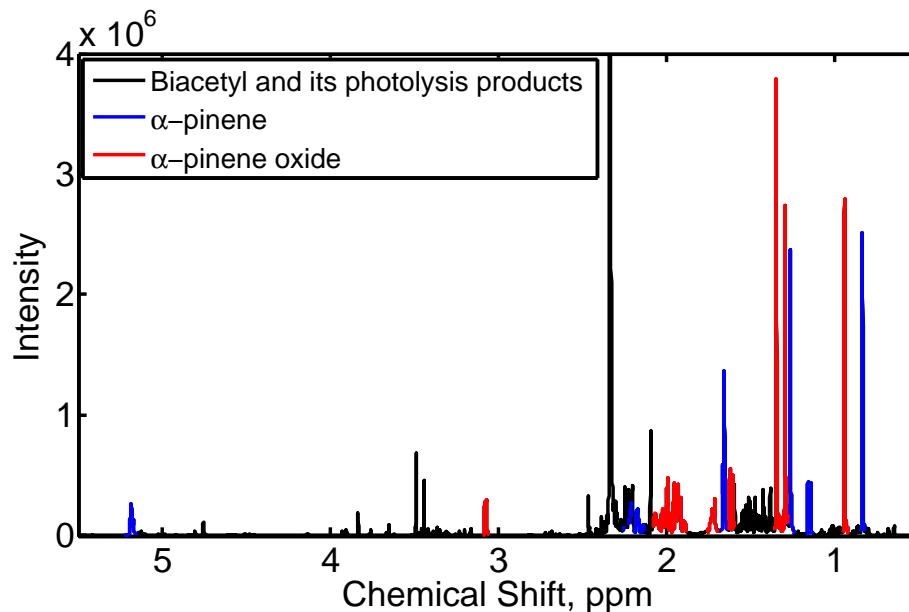
Fig. 1. Sample NMR spectra of 0.055 M α-pinene and 0.18 M biacetyl in CDCl$_3$ after 30 min irradiation with a solar simulator operating at 39.5 % power. The epoxide yield was 53.4 %. Note the biacetyl peak at 2.34 ppm is off-scale (peak intensity 5.8 × 10^7).
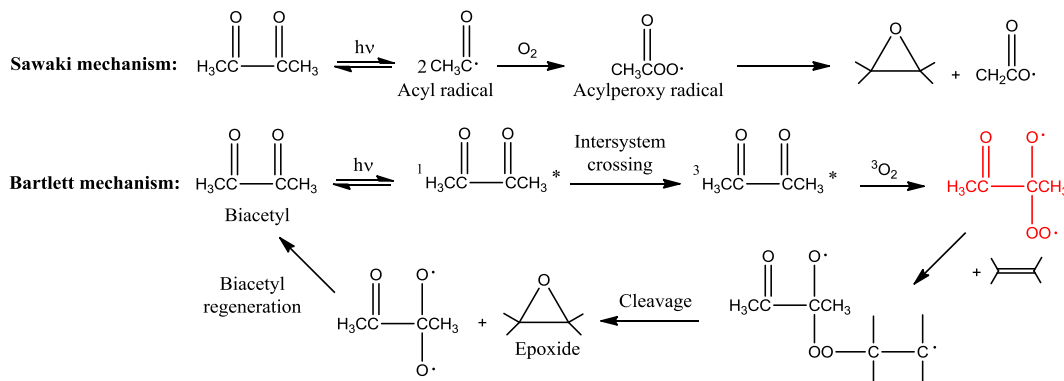
Fig. 2. Comparison of the mechanism suggested by Sawaki and Foote (1983) and Bartle (Shimizu and Bartlett, 1976; Bartlett and Becherer, 1978). The red structure is the key oxyperoxy biradical (see text).
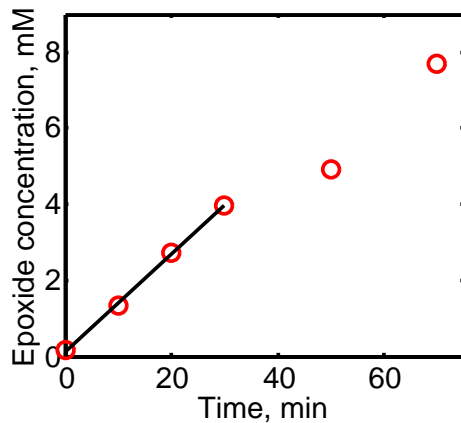
Fig. 3. The concentration of α-pinene oxide as a function of UV exposure time. Initial concentrations of α-pinene and biacetyl were 0.1 M each.
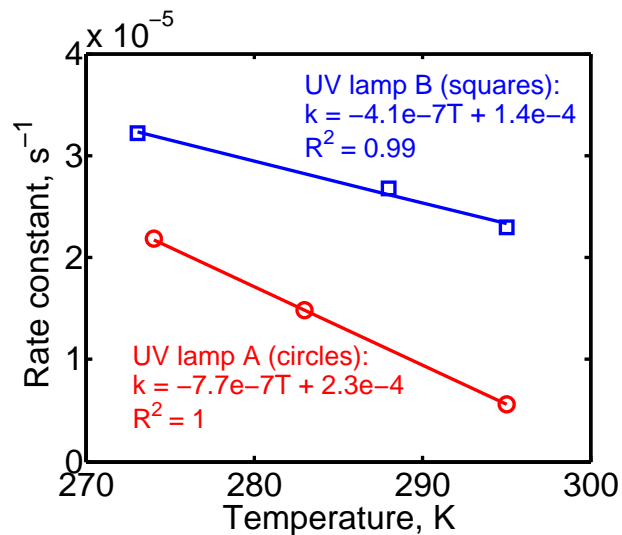
Fig. 4. Temperature dependence of the rate constant of α-pinene epoxidation using the UV lamp.
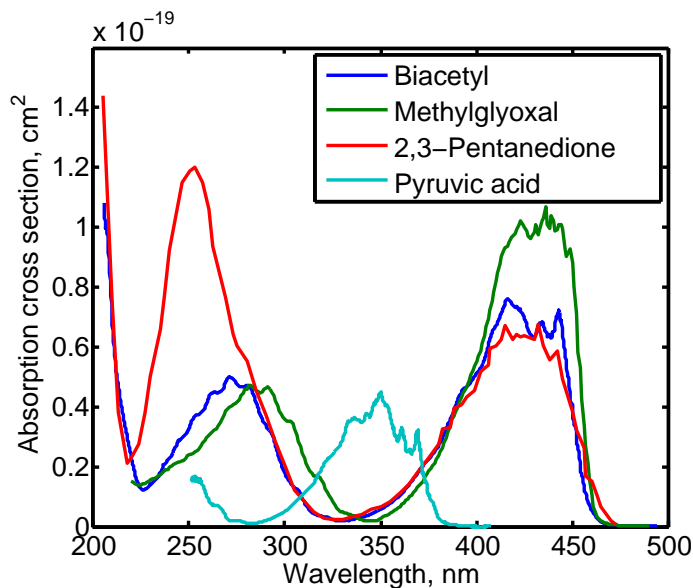
Fig. 5. Absorption cross sections of different α-dicarbonyls and pyruvic acid. The absorption cross section data are obtained from: Horowitz et al. (2001) for biacetyl and pyruvic acid, Calvert et al. (2000) for methylglyoxal, and Jackson and Yarwood (1972) for 2,3-pentanedione.