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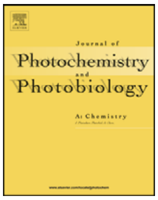

Laser flash photolysis of new water-soluble peroxyl radical precursor

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ABSTRACT

Laser flash photolysis (LFP) of commercially available water-soluble 4-acetyl-4-phenylpiperidine hydrochloride (APP) in the presence of oxygen gives rise to acetylperoxyl radical (ACP). The formation of ACP during LFP of APP has been established by determining their rate constants with $ABTS^{2-}$ in methanolic and aqueous solutions (0.15 ± 0.02 and $2.0 \pm 0.2 \times 10^9\ M^{-1}\ s^{-1}$, respectively). These rate constants are in agreement with those reported in the literature.

The reactivity of ACP was investigated with crocin in aqueous and methanolic solutions. Moreover, the rate constant for the reaction of ACP with nitrite anion (NO_2^-) in aqueous solution was determined to be $4.45 \pm 0.4 \times 10^6\ M^{-1}\ s^{-1}$.Overall, APP can be used as ACP precursor in aqueous and organic solutions using the more accessible LFP technique than the normally used (especially in aqueous solutions) pulse radiolysis technique.

1. Introduction

Peroxyl radicals are important intermediates in chemistry and biology. They are involved in atmospheric chemistry, combustion and many oxidation reactions. Also, they are the main radicals responsible for lipid peroxidation, which can lead to oxidative stress. For example, the hepatotoxicity of CCl_4 has been attributed to the formation of trichloromethylperoxyl radical ($CCl_3O_2^{\bullet}$) which triggers lipid peroxidation processes [1,2].

Pulse radiolysis (PR) and laser flash photolysis (LFP) are two of the most important techniques to investigate fast reactions between peroxyl radicals and different compounds in aqueous and organic solutions [3]. Most of the reported peroxyl radical reactions in aqueous solutions have been investigated using pulse radiolysis. However, this technique is not easily accessible to many laboratories [4]. Peroxyl radical generation using pulse radiolysis has been described previously [4].

Laser flash photolysis is a far more available than pulse radiolysis. However, its use to investigate peroxyl radical reactions in aqueous solution is rare because of the poor solubility of most peroxyl radical precursors in water. Using laser flash photolysis technique, there are few examples for the reactions of peroxyl radicals with different substrates, using commercially unavailable cobalt or nickel complexes as precursors, in aqueous solutions [5–8]. For example [5,6], the generation of acetylperoxyl radicals using organo-cobalt complexes is shown in Scheme 1.

The use of water-soluble azo compounds as peroxyl radical precursors is not possible due to the very low quantum yield of the cleavage process in aqueous solutions [8,9].

In this study, LFP of water-soluble and commercially available 4-acetyl-4-phenylpiperidine hydrochloride (APP), which has an analgesic activity [10], is reported in methanolic and aqueous solutions (see ground state spectra in supplementary material). In air-saturated solution, acetylperoxyl radicals, generated from photolysis of APP, are the main reactive peroxyl radicals. In addition, the reactivity of acetylperoxyl radical toward 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt ($ABTS^{2-}$), crocin and nitrite anion in aqueous solutions is reported (Fig. 1).

2. Materials and methods

2.1. Materials

Methanol (Fisher Scientific, HPLC grade), sodium nitrite (Fisher Scientific), 4-acetyl-4-phenylpiperidine hydrochloride (Aldrich), and 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt ($ABTS^{2-}$) (Sigma) were used as received. Purified crocin was kindly supplied by Dr. V. Partali and Dr. H.R. Sliwka (NTNU, Inst. Kjemi, Trondheim, N-7491 Norway) and was used as received. Argon was supplied by the British Oxygen Company (BOC). For aqueous solutions, ultra pure water (conductivity <0.067 μS/cm, Elga UK) was used.

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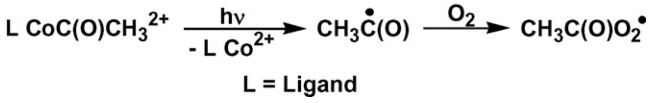

$$\mathrm{L\,CoC(O)CH_3^{2+}} \xrightarrow[\mathrm{-\,L\,Co^{2+}}]{h\nu} \mathrm{CH_3\overset{\bullet}{C}(O)} \xrightarrow{\mathrm{O_2}} \mathrm{CH_3C(O)O_2^{\bullet}}$$

L = Ligand

Scheme 1.

2.2. Experimental methods

The LFP system was constructed in-house at Keele University using a variety of components from various suppliers, including Applied Photophysics.

The fourth harmonic (266 nm) of a Spectron Q-switched Nd:YAG laser was used to excite the samples in this work. Changes in absorbance of the sample are monitored using a 275 W Xenon arc Lamp (Kratos) at 90° to the laser path. For UV–vis measurements, an Applied Photophysics *f*/3.4 grating monochromator (260–820 nm) coupled to a Hamamatsu R928 photomultiplier tube (PMT) was used. For the detection of short-lived transients (100's ns timescale), a time delay pulse generator and lamp pulsing unit were used.

The PMT analog output is converted into the digital form using a Tektronix TDS 320 digital oscilloscope. The data recorded consists of 512 data points and the vertical resolution is 8-bit. Finally, the digital signal is transferred to an IBM-compatible PC via a GPIB interface where it can be stored and analyzed. The time resolution of the Laser flash photolysis system is 50 ns.

All transients are recorded from single irradiation except those at short timescales ($\leq$1 μs/division), which were averaged four times to improve S/N ratio. Oxygen-free solutions were prepared by saturating the solutions with argon and this was examined by measuring the triplet lifetime of benzophenone and it was in agreement with the literature. In addition, flow system was used for argon-saturated samples to avoid any interference due to sample degradation.

All the experiments were carried out at ~20 °C. More detailed LFP description is included in supplementary material.

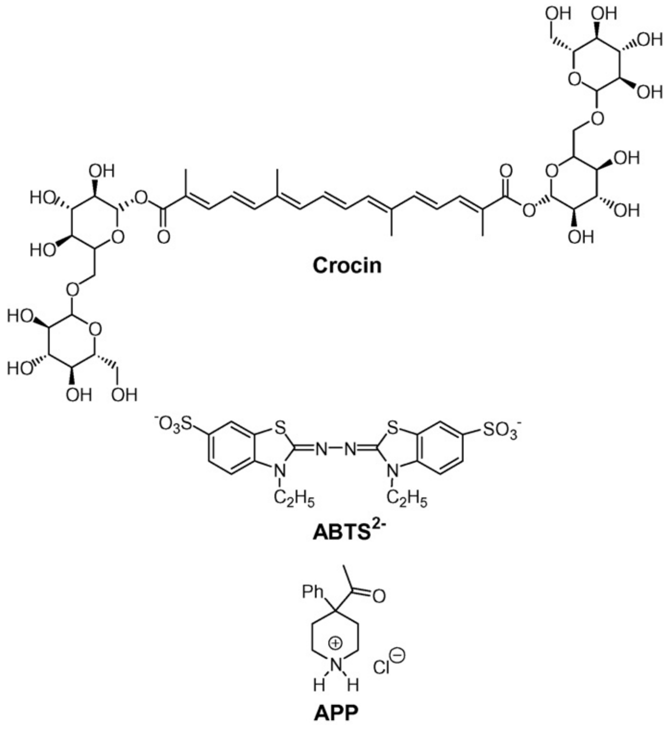

Fig. 1. Structures of crocin, ABTS^{2-} and APP.

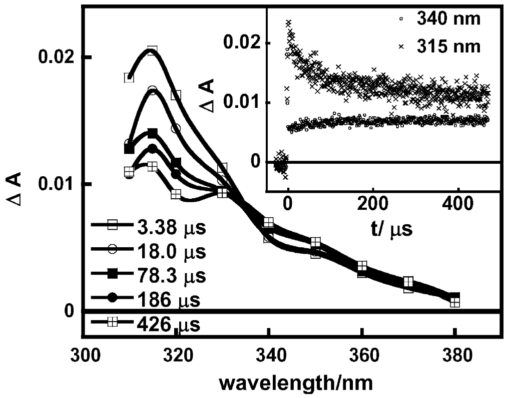

Fig. 2. Transient absorption spectra obtained following LFP (266 nm) of APP (1.5×10^{-3} M) in argon-saturated aqueous solution (Laser energy = 12.8 mJ/pulse). The inset shows kinetic traces at 315 and 340 nm.

3. Results and discussion

3.1. Laser (266 nm) flash photolysis of 4-acetyl-4-phenylpiperidine hydrochloride (APP)

Laser flash photolysis of APP in oxygen-free aqueous solution gives a transient spectrum with λ_{max} = 315 nm (Fig. 2).

The second-order decay of the 315 nm transient is accompanied by a transient growth at 340 nm. In addition, no other transient was observed at longer wavelengths (between 400 and 650 nm) in oxygen-free aqueous solutions. Moreover, no information about the triplet absorption spectrum and triplet lifetime of APP was previously reported. However, the very short triplet lifetime of some structurally related ketones (e.g. τ_T (pinacolone) <1 ns [11]), compared to the lifetime of the transient observed at 315 nm, excludes the possibility of attributing the transient spectrum (Fig. 2) to the triplet APP (^{3}APP). In addition, at short timescales (1–2.5 μs), the formation of the transient is instantaneous (see Fig. S2 in supplementary material), which indicates that the lifetime of the excited state responsible for transient formation is less than 100 ns.

APP has an alkyl-substituted benzyl moiety in the α-position of carbonyl group. Moreover, the transient spectrum (Fig. 2) is similar to the benzyl radical spectrum reported by Maouf et al. [12] and its λ_{max} is close to literature values (314–318 nm) [12–16]. Therefore, from the structure of APP and the observation of a transient spectrum similar to that of benzyl radical, it can be suggested that APP undergoes α-cleavage from a very short-lived triplet state (or excited singlet state) to give acetyl radical and a substituted benzyl radical. In the presence of oxygen, both radicals form the corresponding acetylperoxyl radical (ACP) and benzylperoxyl radical derivative, respectively (Scheme 2). As a further evidence, in air-saturated aqueous solution, there is a rapid decay ($k = 1.0 \pm 0.2 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$) for the transient at 320 nm, which is in support for its identification as carbon-centered radical (substituted benzyl radical).

The second-order transient decay at 315 nm, ascribed to benzyl radical derivative, can be attributed to radical–radical reaction. Moreover, the formation of stable transient at 340 nm can be ascribed to products formed from dimerization and/or disproportionation reactions of the radicals generated from α-cleavage of APP (Fig. 2). Also, the initial fast step of 340 nm transient is due to the absorption of benzyl radical derivative, generated from α-cleavage of APP, at this wavelength (see Fig. 2).

LFP of APP in methanolic solution gives similar transient spectra (see Fig. S3 in supplementary material).

The system was further examined by studying the reactions of the peroxyl radicals, formed from the α-cleavage of APP in