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Photochemistry of 9-fluorenone oxime phenylglyoxylate: a combined TRIR, TREPR and *ab initio* study

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ABSTRACT: The photochemistry of 9-fluorenone oxime phenylglyoxylate (**1**) in tetrachloromethane was investigated by a variety of time-resolved methods [STEP-SCAN TRIR and time-resolved EPR (TREPR)]. Photolysis of **1** yields the benzoyl radical, carbon dioxide and the fluorene-9-iminyl radical on pulsed irradiation ($\lambda = 355$ nm). All radicals have a lifetime in the range of microseconds and can be detected within the rise time of our time-resolved equipment before undergoing recombination or reactions with the solvent. The benzoyl radical shows a strong absorption ($\tilde{\nu}_{C=O} = 1824\,\text{cm}^{-1}$) in the IR spectrum. Upon purging the solution with oxygen, the benzoyl radical is quenched to yield the benzoylperoxy radical ($\tilde{\nu}_{C=O} = 1814\,\text{cm}^{-1}$), which has a lifetime that is several microseconds longer than that of the benzoyl radical. Owing to the lack of a good IR chromophore, the fluorene-9-iminyl radical is not detected by IR spectroscopy. It can, however, be detected by TREPR spectroscopy, which allows the detection of a 1 : 1 : 1 triplet of the fluorene-9-iminyl radical at 3456 G and a 1 : 2 : 1 triplet of the benzoyl radical at 3460 G. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: infrared spectroscopy; STEP-SCAN; TREPR; laser flash photolysis; radicals; peroxides; density functional theory

INTRODUCTION

It has recently been shown by our group[1] that fluorenone oxime oxalates are suitable precursors for the generation of alkoxycarbonyl radicals. They are synthesized easily and show excellent thermal stability. Irradiation with $\lambda = 355$ nm yields carbon dioxide, the fluorene-9-iminyl radical and an alkoxycarbonyl radical in a clean reaction. We were able to show that the STEP-SCAN technique is a powerful tool for the investigation of this photoreaction. The technique allows the detection of a variety of different reactive acyl type intermediates with different stabilities depending on the substituents. One of the most interesting acyl radicals is the benzoyl radical, which plays an important role in the initiation process of polymerizations [e.g. photopolymerization of methyl methacrylate (MMA)].[2,3] A variety of precursors have been synthesized and checked by laser flash photolysis to be suitable sources for benzoyl radicals.[4,5] The most common method to generate benzoyl radicals photochemically consists of the irradiation of ketones, which undergo α-cleavage (Norrish type I reaction). Such reactions have been monitored by time-resolved IR spectroscopy using a dispersive IR spectrometer.[4,6a] The reaction of the benzoyl radical with molecular oxygen has been reported to yield the benzoylperoxy radical, PhC(O)OO.[4] Peroxy radicals, and possibly their tetroxide dimers, play an important role in atmospheric chemistry.[6b] The self-reaction of gas-phase acylperoxy radicals, such as the acetylperoxy radical,[6c] has been reported to lead to alkyl radicals via acyloxy radicals. We have undertaken a study using different time-resolved methods and a variety of theoretical methods to investigate the photochemistry of 9-fluorenone oxime phenylglyoxylate (**1**) and to demonstrate the potential of this compound to serve as a source for the generation of acyl radicals, especially the benzoyl radical and the benzoylperoxy radical.

RESULTS AND DISCUSSION

Laser flash photolysis (LFP) of **1** in tetrachloromethane (4.0 mM, Ar purge) at $\lambda_{ex} = 355$ nm resulted in bleaching of the precursor bands at $\tilde{\nu}_{C=O} = 1768$ and $1691\,\text{cm}^{-1}$ and the formation of a transient at $\tilde{\nu}_{C=O} = 1824\,\text{cm}^{-1}$ (Fig. 1). Additionally, the strong ν_{as} of CO_2 at $\tilde{\nu}_{C=O} = 2336\,\text{cm}^{-1}$ was observed. Both the $1824\,\text{cm}^{-1}$ transient and ν_{as} (CO_2) built up during the rise time (25 ns) of the STEP-SCAN set-up. Furthermore, an IR band growing in at $\tilde{\nu}_{C=O} = 1779\,\text{cm}^{-1}$ was detected. When the solution was purged with oxygen prior to LFP, again the disappearance

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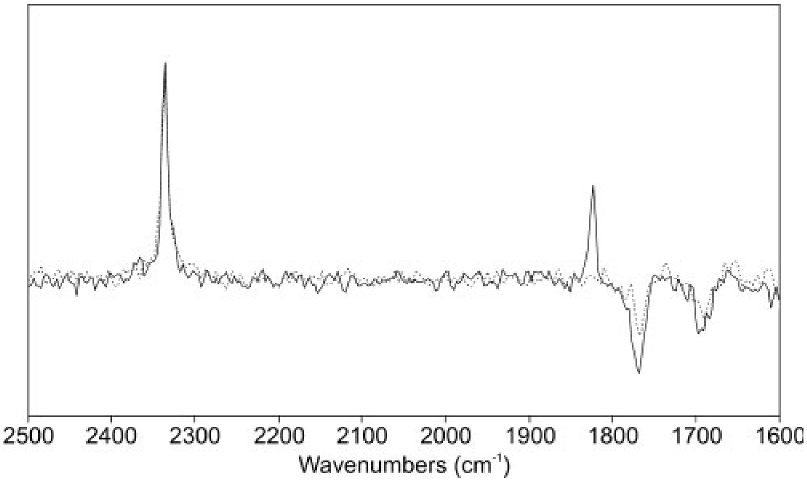


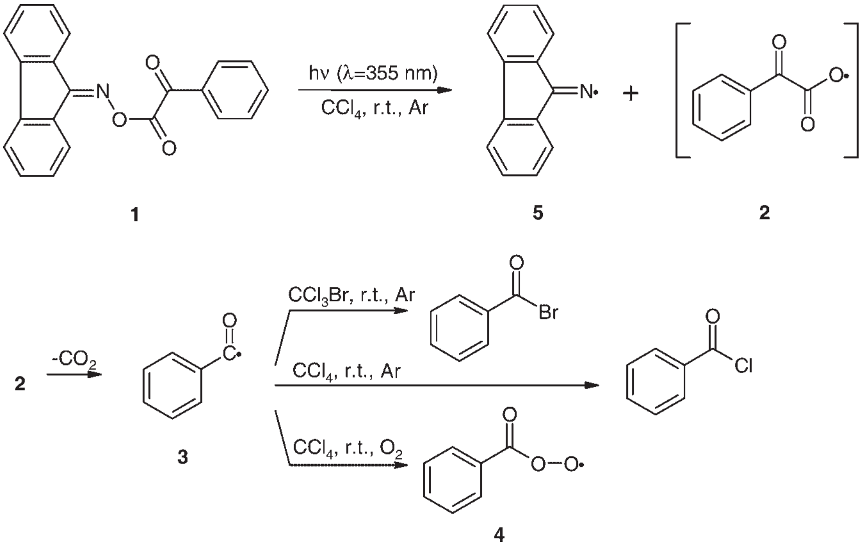
Figure 1. Time-resolved IR difference spectra (time resolution 100 ns, spectral resolution 6 cm^{-1}) showing the photochemistry of **1** in CCl_4 purged with argon. Bands appearing on irradiation ($\lambda = 355$ nm) are pointing upwards; bands disappearing are pointing downwards. Solid line, spectrum 100 ns after irradiation; dotted line, spectrum after 20 μs

of two precursor bands and the immediate formation of the CO_2 absorption at $\tilde{\nu}_{C=O} = 2335.8\,cm^{-1}$ were noted. A transient species was observed at $\tilde{\nu}_{C=O} = 1814\,cm^{-1}$ decaying with a lifetime of 5.2 ± 0.2 μs. With oxygen purge, the IR absorption due to CO_2 at $\tilde{\nu}_{C=O} = 2336\,cm^{-1}$ undergoes a secondary growth. The lifetime of this secondary growth ($\tau = 6.1 \pm 0.5$ μs) does not change when the oxygen concentration is varied.

Strong IR absorptions near $1800\,cm^{-1}$ are characteristic of acyl radicals.[4,6a] Thus, the benzoyl radical **3** is a likely assignment for the $\tilde{\nu}_{C=O} = 1824\,cm^{-1}$ transient. The first step in the reaction sequence would be cleavage of the N—O bond of the fluorenone oxime part of the molecule, followed by rapid decarboxylation of the benzoylcarbonyloxy radical **2**. In presence of $^3O_2$ the benzoyl radical **3** is effectively trapped and the benzoylperoxy radical **4** is formed (Scheme 1).

The position of $\nu_{C=O}$ of the benzoyl radical had been reported before.[4,5] A calculated vibrational spectrum [UB3LYP/6–311 + G(d,p)] and the literature value are in good agreement with our experimental data. Decarboxylation of the intermediate benzoylcarbonyloxy radical **2** causes the intense initial absorption at $\tilde{\nu}_{C=O}$ $(CO_2)_{as} = 2335.8\,cm^{-1}$ The benzoylcarbonyloxy radical **2** itself has such a short lifetime that it cannot be monitored with our set-up.

A plot of the band integrals versus the time yields the lifetime of **3** in CCl_4. The measured lifetime of $\tau = 1.0 \pm 0.05$ μs is in good agreement with published experimental data.[6a] Quenching of the benzoyl radical **3** with $^3O_2$ leads to the formation of the benzoylperoxy radical **4**, which has a characteristic absorption at $\tilde{\nu}_{C=O} = 1814\,cm^{-1}$, decaying with a measured lifetime of $\tau = 5.2 \pm 0.2$ μs (Fig. 2).



Scheme 1

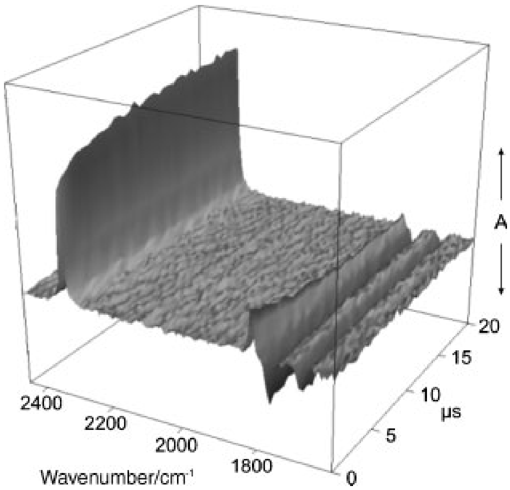


Figure 2. A three-dimensional representation of the time-resolved difference STEP-SCAN FTIR spectrum of **1** in oxygen-saturated CCl_4. The transient absorption is observed at 1814 cm^{-1}. Carbon dioxide is observed at 2336 cm^{-1}, whereas the two disappearing bands at 1768 and 1691 cm^{-1} belong to the starting material

In a further quenching experiment we used bromotrichloromethane as an effective scavenger for the benzoyl radical **3**. The lifetime of **3** in the presence of 3 mM CCl_3Br is $\tau = 460 \pm 50$ ns. From this value and the lifetime of **3** in neat CCl_4, the rate constant for the reaction of **3** with $BrCCl_3$ can be estimated to be $k = 3.7 \times 10^8\,l\,mol^{-1}\,s^{-1}$, which is higher than the published value of $k = (2.2 \pm 0.1) \times 10^8\,l\,mol^{-1}\,s^{-1}$.[4] Concomitant with the decay of **3**, we observed a growth at $\tilde{\nu}_{C=O} = 1780\,cm^{-1}$ ($\tau = 450 \pm 50$ ns), which is assigned to the product, benzoyl bromide. Evaluation of the growth kinetics of benzoyl bromide gave a similar value of $k = 3.8 \times 10^8\,l\,mol^{-1}\,s^{-1}$. Experimental data and calculated IR modes are summarized in Table 1.

The photochemistry of **1** was also investigated by time-resolved EPR (TREPR) spectroscopy. LFP ($\lambda_{ex} = 355$ nm) of a 5 mM solution of **1** in CCl_4 (1 atm Ar) led to the detection of two sets of transient signals, both of which evolve during the laser pulse. The 1:2:1 triplet centred at 3460.3 G ($J_{meta} = 1.3$ G) is attributed to the benzoyl radical,[7–12] whereas the 1:1:1 triplet centred at 3455.7 G ($J_N = 9.7$ G) is assigned to the 9-fluorenoneiminyl radical **5** (Fig. 3).[13] Hence TREPR clearly demonstrates that both the benzoyl radical **3** and the iminyl radical **5** are formed very rapidly upon LFP of **1**.

Our results presented so far agree well with what has previously been known about the chemistry of the benzoyl radical. Noteworthy, however, is the secondary build-up of IR absorption due to carbon dioxide. The formation of CO_2 from benzoylperoxy radicals **4** had been observed before by Hancock-Chen and Scaiano, who could follow this reaction only indirectly by monitoring the formation of phenylperoxy radicals.[14] Their reaction mechanism involves the dimerization of **4** to a highly labile dibenzoyl tetroxide (**6**), which subsequently decays yielding 2 equiv. of benzoyloxy radicals (**7**). The latter rapidly decarboxylate, yielding phenyl radicals (**8**), which in turn react with oxygen to yield phenylperoxy radicals (**9**) as observed by Hancock-Chen and Scaiano. The reaction mechanism is shown in Scheme 2.

Calculations [B3LYP/6–311 + G(d,p)] on dibenzoyl tetroxide (**6**) predict two similarly intense C═O bands at $\tilde{\nu}_{C=O} = 1792$ and 1823 cm^{-1}. In our TRIR experiments, no transient double peak was observed in this region of the spectrum. Hence our experiments do not allow us to conclude whether **6** is indeed involved in the decay of **4**.

Molecules containing several heteroatoms connected in a chain are notoriously difficult to describe by theoretical methods.[15a,b] Owing to the size of the molecule, calculations on **6** and its reactions were limited to standard density functional theory (DFT). In order to check for the reliability of the method chosen, we also studied the model system diformyl tetroxide (**10**), using both DFT and MP4(SDQ) *ab initio* theory. The structure of **10**, optimized at the MP4(SDQ)/6–31 + G(d) level of theory, consists of a chain of four oxygen atoms with an O—O—O—O dihedral angle of 82.2°. The formyl groups are oriented such that the vectors of the carbonyl dipole moments point in nearly opposite directions. As a result the two formyloxy groups show opposing conformations of the C—O bonds (one *Z* and one *E*).

The results of our calculations on the formation and reactions of **10** are summarized in Scheme 3. Formation of **10** from (*Z*)-formylperoxy [(*Z*)-**11**] and (*E*)-formylperoxy [(*E*)-**11**] is calculated to be exothermic by 16–19 kcal mol^{-1} (1 kcal = 4.184 kJ). The reaction is

Table 1. Lifetime, experimental and calculated C═O stretching vibrations of the transient species

Species	Lifetime τ^a (μs)	Lifetime τ(μs)	$\nu_{C=O}$ exp^a (cm^{-1})	$\nu_{C=O}$ exp (cm^{-1})	$\nu_{C=O}$ calcd^b
2	—	—	—	—	1733
3	1.0 ± 0.02	1.7[6]	1824	1828[6] 1818[5]	1882
4	5.2 ± 0.2	—	1814	1820[6]	1870
CO_2	—	—	2336	—	—

[a] In CCl_4, ambient temperature.
[b] UB3LYP/6–311+g(d,p), unscaled.

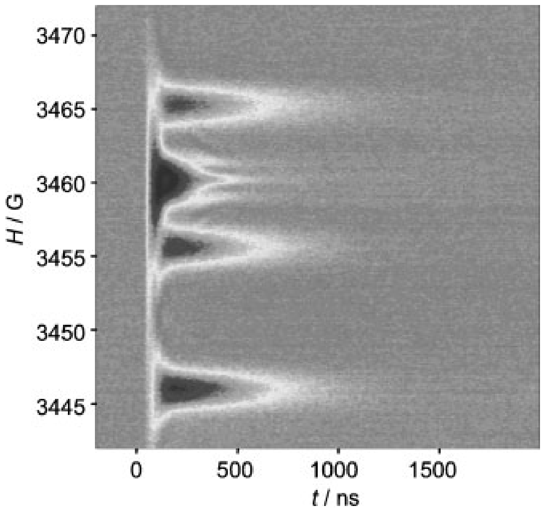
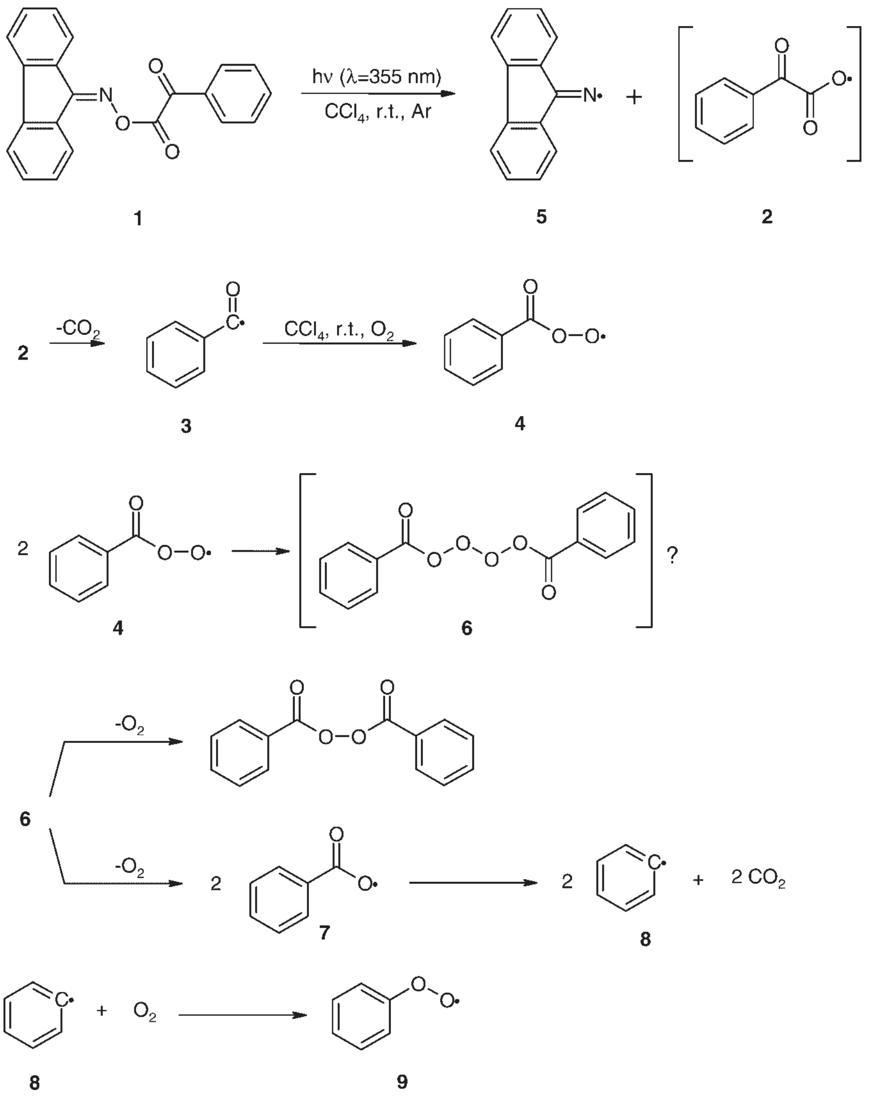


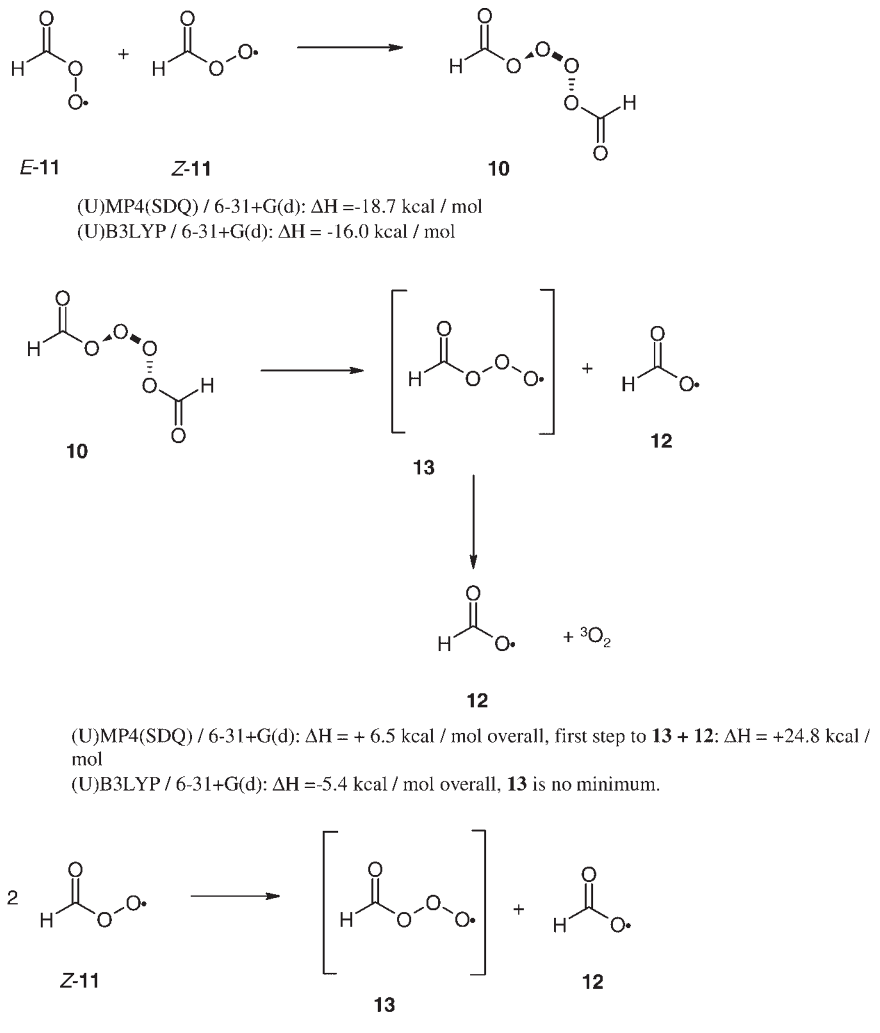
Figure 3. Time-resolved EPR spectrum of the doublet transient species formed upon LFP ($\lambda_{ex} = 355$ nm) of **1** in CCl_4

thus predicted to be more exothermic than the dimerization of alkylperoxy radicals such as methylperoxy, for which ΔH of the dimerization reaction had been calculated by DFT (B3LYP/6–31G**) to be -9.34 kcal mol^{-1}.[15c] Cleavage of **10** can also occur at the O1—O2 bond, which yields the formyloxy radical **12** and the formyltrioxy radical **13**. Trioxy radical **13** is only found to be a minimum when MP4(SDQ) theory is used, whereas attempted optimization using B3LYP theory results in fragmentation into **12** and oxygen. Overall, the fragmentation of **10** into 2 equiv. of **12** + O_2 ($^3\Sigma_g-$) is predicted to be weakly endothermic [MP4(SDQ)] or exothermic (B3LYP). Direct oxygen transfer from (*Z*)-**11** to another molecule of (*Z*)-**11**, yielding a (**13** + **12**) triplet radical pair, can also possibly occur. On the triplet surface, this reaction is predicted to have a significant activation enthalpy of $\Delta H^{\#} = 35.1$ kcal mol^{-1} (B3LYP).

The results of our calculations on **6** and its formation and fragmentation reactions are summarized in Scheme 4.



Scheme 2



(U)MP4(SDQ) / 6-31+G(d): $\Delta H = -18.7$ kcal / mol
(U)B3LYP / 6-31+G(d): $\Delta H = -16.0$ kcal / mol

(U)MP4(SDQ) / 6-31+G(d): $\Delta H = +6.5$ kcal / mol overall, first step to **13** + **12**: $\Delta H = +24.8$ kcal / mol
(U)B3LYP / 6-31+G(d): $\Delta H = -5.4$ kcal / mol overall, **13** is no minimum.

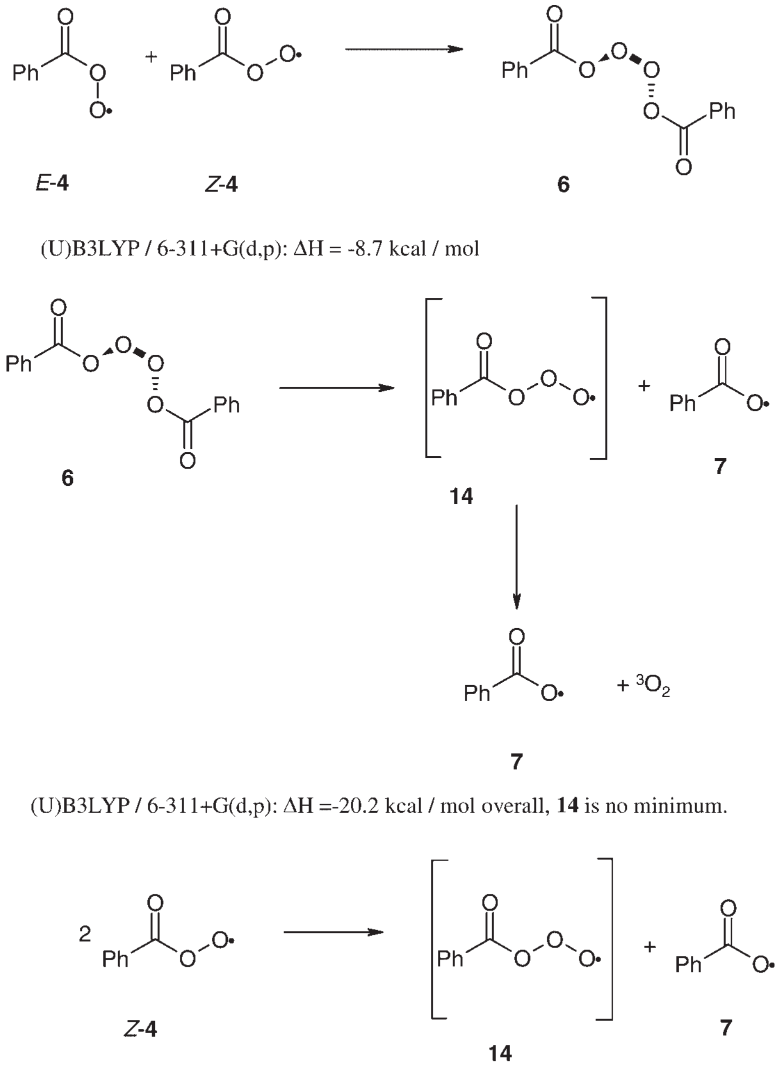
(U)B3LYP / 6-31+G(d): $\Delta H^{\#} = 35.1$ kcal / mol

Scheme 3

Owing to the size of the molecule, MP4(SDQ) *ab initio* theory could no longer be applied here, and the calculations are limited to DFT (B3LYP).

Dibenzoyl tetroxide (**6**) shows a helical structure, as does diformyl tetroxide (**10**). Unlike in **10**, the dihedral angle $D_{\mathrm{OC}\cdots\mathrm{CO}}$ which is defined by the two C=O bonds is no longer close to 180° {**6**, $D_{\mathrm{OC}\cdots\mathrm{CO}} = 40.2°$; **10**, $D_{\mathrm{OC}\cdots\mathrm{CO}} = 167.3°$ [MP4(SDQ)]}. Hence, in **6**, the orientation of the vectors of the dipole moments of the two carbonyl moieties is closer to parallel than to antiparallel. The chemistry of **6** should be similar to that of **10**. The fragmentation of **6** into 2 equiv. of benzoyloxy radical **7** plus O_2 ($^3\Sigma_g-$) is predicted to be more exothermic [B3LYP/6–311 + G(d,p): $\Delta H = -20.2\,\mathrm{kcal\,mol^{-1}}$] than the corresponding fragmentation of **10**. This is probably due to stabilization of **7** by the phenyl substituent. However, the oxygen transfer reaction from (*Z*)-**4** to another molecule of (*Z*)-**4**, yielding **7** plus **14**, which should then decay into O_2 ($^3\Sigma_g-$) plus a second molecule of **7**, is predicted to have a significant activation enthalpy of $\Delta H^{\#} = 34.6\,\mathrm{kcal\,mol^{-1}}$. The TS for O-transfer from (*Z*)-**4** to (*Z*)-**4** is calculated to have an $r_{\mathrm{O2—O3}}$ of the newly formed benzoyltrioxy fragment of 137 pm, which is shorter than $r_{\mathrm{O2—O3}}$ of **6**. This indicates that along the reaction coordinate of the O-transfer reaction the dissociation of **14** does not proceed to any significant degree. Hence the TS for O-transfer from (*Z*)-**4** to (*Z*)-**4** is not able to profit from the energy gain connected with the fragmentation of **14** into **7** plus O_2 ($^3\Sigma_g-$). As the same argument probably applies for the fragmentation of **6** into **7** plus **14**, this reaction can also be expected to have a significant activation enthalpy of the order of $25\,\mathrm{kcal\,mol^{-1}}$ (cf. Scheme 3, MP4 results). It is noted that we have been unable to locate a transition structure for a direct fragmentation of **6** (**10**) into 2 equiv. of **7** (**12**) plus O_2 ($^3\Sigma_g-$), in which both O—O bonds would be broken simultaneously. The results of our calculations on the system **6**–**4** are summarized in Fig. 4.

Bimolecular self-quenching of two molecules of benzoylperoxy radicals **4** could thus give rise to tetroxide **6** in



(U)B3LYP / 6-311+G(d,p): ΔH = -8.7 kcal / mol

(U)B3LYP / 6-311+G(d,p): ΔH =-20.2 kcal / mol overall, **14** is no minimum.

(U)B3LYP / 6-31+G(d): $\Delta H^{\#}$ = 34.0kcal / mol
(U)B3LYP / 6-311+G(d,p): $\Delta H^{\#}$ =34.6 kcal / mol

Scheme 4

a mildly exothermic, yet entropically unfavourable reaction. For the dissociation of the related di-*tert*-butyl tetroxide into two molecules of *tert*-butylperoxyl, Honeywill and Mile[16] recently reported $\Delta H = 7.9\,\text{kcal mol}^{-1}$ and $\Delta S = 33.3\,\text{cal mol}^{-1}\,\text{K}^{-1}$. If we assume a similar reaction entropy for the cleavage of **6**, a ΔG of around $0\,\text{kcal mol}^{-1}$ results for the dissociation of **6** at ambient temperature. Hence the room temperature dimerization of **4** could (but does not have to) play a role in the chemistry of **4**. If the reaction pathway leading from **4** to **7** is to run via tetroxide **6**, the reaction of **6** leading to **7** has to compete with the re-dissociation of **6** into 2 equiv. of **4**. In our calculations, however, we have been unable to find such a monomolecular reaction of **6**. Bimolecular reactions of **6** therefore cannot be excluded. Direct oxygen transfer from **4** to **4**, yielding 2 equiv. of **7** plus O_2 ($^3\Sigma_g-$), represents an alternative mechanism, which does not involve **6**. This reaction, however, is predicted to be impeded by a significant activation enthalpy.

CONCLUSION

We have shown by two independent time-resolved methods that 9-fluorenone oxime phenylglyoxylate is a very good precursor for the generation of benzoyl radicals. Photolysis of **1** leads in good yields and in a clean photoreaction to the benzoyl radical **3**, which plays an important role in a variety of synthetic applications, such as photochemical-initiated polymerization reactions. By the combined use of time-resolved FTIR spectroscopy, DFT and *ab initio* calculations we were able to gain new insights into the reaction of **3** in the presence of $^3O_2$ leading to secondary growth of carbon dioxide.

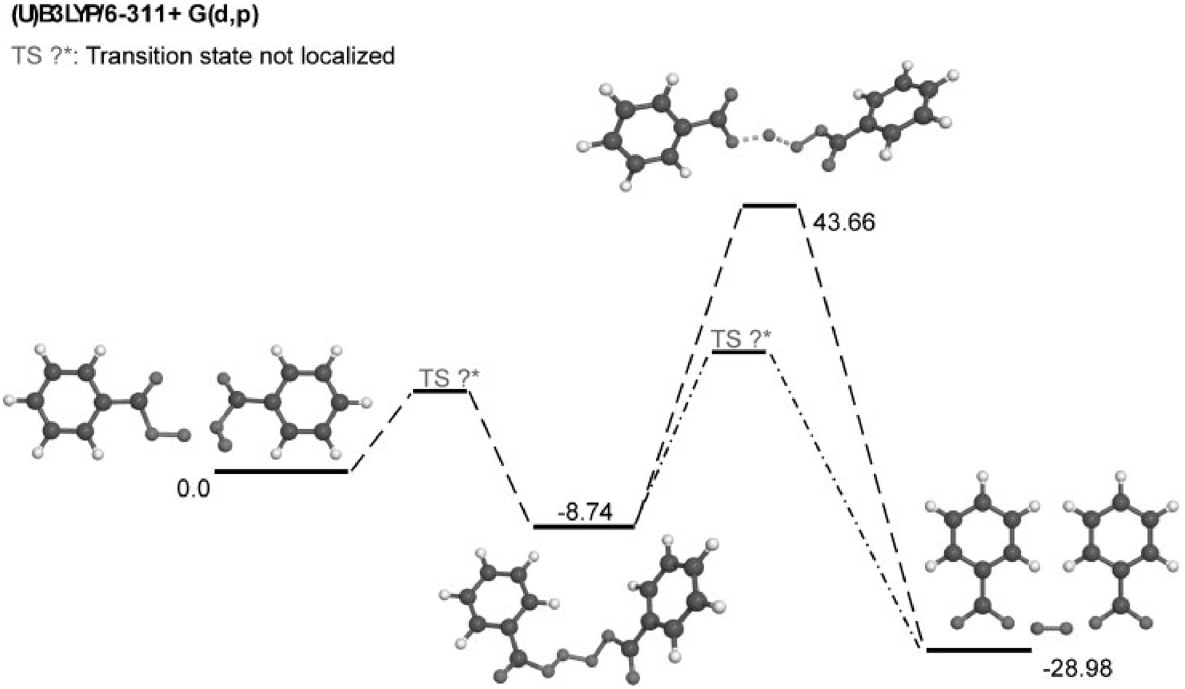


Figure 4. Graphic representation of relevant stationary points on the $C_{14}H_{10}O_6$ surface

EXPERIMENTAL

STEP-SCAN FTIR. For time-resolved measurements we used the set-up described previously.[1,17] Excitation of the sample was carried out by the third harmonic (355 nm) of an Nd:YAG laser (Spectra-Physics Quanta-Ray LAB 130) with a repetition rate of 10 Hz. To avoid thermal effects and shockwaves, the laser energy was attenuated to between 10 and 18 mJ per pulse by an external attenuator.

All measurements were carried out with 6 cm^{-1} resolution in a spectral range between 0 and 3160 cm^{-1}, resulting in an interferogram containing 1060 points. The signal was averaged 20 times per sampling position. In all experiments a time range of 20 µs was recorded with a resolution of 25 ns. After FT, the average of 20 successive spectra was calculated to achieve a better signal-to-noise ratio, resulting in an effective time resolution of 500 ns. If necessary, this figure can be improved by averaging a smaller number of spectra. The sample was dissolved (between 1.0 and 1.5 $g\,l^{-1}$, depending on the layer thickness of the cell) in carbon tetrachloride (Riedel-de Haën, spectroscopic grade) and purged with argon for at least 45 min.

TREPR. The TREPR spectra were measured with a Bruker Elexsys E500 spectrometer at 9.66 GHz microwave frequency and 0.002 W microwave power. The ER4118 split ring resonator was equipped with a 1 mm inner diameter quartz tube connected to an Ismatec IPC dispensing pump with PTFE tubing. An argon-purged 5 mM solution of **1** in CCl_4 was pumped through the quartz tube at a flow-rate of 50 ml min^{-1} The photoreaction was initiated by the third harmonic (355 nm) of an Nd:YAG laser (Spectra-Physics Quanta-Ray LAB 130) with a repetition rate of 10 Hz. The laser beam was widened by an $f = 50$ mm Suprasil lens. Three hundred time traces (10 µs, 1000 points; averaged over 50 laser pulses) between 3442 and 3442 G (0.1 G resolution) were recorded with a LeCroy 9450 digital oscilloscope triggered by a Thorlabs DET210 photodetector (1 ns rise time, 200–1100 nm spectral range).

Calculations. Calculations were performed with the Gaussian 98 suite of programs.[18] Vibrational spectra were calculated using the B3LYP[19] functional or MP4(SDQ)[20,21] with 6–311 + G(d,p) or 6–31 + G(d,p) basis sets. The calculated vibrational frequencies given are unscaled.

9-Fluorenone oxime phenylglyoxylate (1). 9-Fluorenone oxime (3.5 g, 17.9 mmol) was suspended in dry dichloromethane (170 ml). A solution of phenylglyoxylyl chloride (3.9 g, 23.1 mmol) in dry dichloromethane (10 ml) was added dropwise. After a few minutes, the colour of the solution changed and after an additional 1 h of stirring the solution became clear. The solution was stirred for a further 12 h at room temperature. Removal of the solvent yielded a residue, which was recrystallized from hexane (~1500 ml). This yielded 5.1 g (87%) of pure **1**. IR (KBr): $\tilde{\nu}_{C=O} = 1753$, 1676, 1597, 1579, 1453, 1320, 1228, 1204, 1150, 1105, 1002, 950, 880, 843, 816, 785, 750, 729, 687, 677, 646 cm^{-1} ^1H NMR (200 MHz, DMSO-d_6): δ 7.35 (td, 1H), 7.41 (td, 1H), 7.62 (m, 5H), 7.79 (d, 1H), 7.88 (t, 2H), 8.12 (d, 2H), 8.25 (d, 1H) ppm. ^{13}C NMR (50 MHz, DMSO-d_6): δ 121.20, 122.75, 128.86, 128.91, 129.19, 129.32, 129.94, 130.46, 132.23, 132.77, 132.83, 133.85, 135.53, 141.05, 142.15, 159.37, 161.24, 185.03 ppm. EI MS: *m/z* 327, 179, 151, 105, 77, 51, 44, 28. $C_{21}H_{13}NO_3$ (327.339): calcd C 77.06, H 4.00, N 4.28; found C 76.17, H 4.22, N 4.08%.

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REFERENCES

1. Bucher G, Halupka M, Kolano C, Schade O, Sander W. *Eur. J. Org. Chem.* 2001; 545–552.
2. Ajayaghosh A, Das S, George MV. *J. Polym. Sci., Polym. Chem.* 1993; **31**: 653–659.
3. Allen NS, Marin MC, Edge M, Davies DW, Garrett J, Jones F, Navaratnam S, Parsons BJ. *J. Photochem. Photobiol. A Chem.* 1999; **126**: 135–149.
4. Brown CE, Neville AG, Rayner DM, Ingold KU, Lusztyk J. *Aust. J. Chem.* 1995; **48**: 363–379.
5. Colley CS, Grills DC, Besley NA, Jockusch S, Matousek P, Parker AW, Towrie M, Turro NJ, Gill PMW, George MW. *J. Am. Chem. Soc.* 2002; **124**: 14952–14958.
6. (a) Neville AG, Brown CE, Rayner DM, Lusztyk J, Ingold KU. *J. Am. Chem. Soc.* 1991; **113**: 1869–1870; (b) Wallington TJ, Dagaut P, Kurylo MJ. *Chem. Rev.* 1992; **92**: 667–710; (c) Moortgat G, Veyret B, Lesclaux R. *J. Phys. Chem.* 1989; **93**: 2362–2368.
7. Davies AG, Sutcliffe R. *J. Chem. Soc., Perkin Trans. 2*, 1980; 819–824.
8. Huggenberger C, Lipscher J, Fischer H. *J. Phys. Chem.* 1980; **84**: 3467–3474.
9. Krusic PJ, Rettig TA. *J. Am. Chem. Soc.* 1970; **92**: 722–724.
10. Paul H, Fischer H. *Helv. Chim. Acta* 1973; **56**: 1575–1594.
11. Bennett JE, Mile B. *Trans. Faraday Soc.* 1971; **67**: 1587–1597.
12. Atkins PW, Dobbs AJ, McLauchlan KA. *J. Chem. Soc., Faraday Trans. 2*, 1975; **71**: 1269–1274.
13. Forrester AR, Gill M, Meyer CJ, Sadd JS, Thomson RH. *J. Chem. Soc., Perkin Trans. 1*, 1979; 606–611.
14. Hancock-Chen T, Scaiano JC. *Photochem. Photobiol.* 1998; **67**: 174–178.
15. (a) Kraka E, He Y, Cremer D. *J. Phys. Chem. A* 2001; **105**: 3269–3276; (b) Kraka E, Cremer D, Koller J, Plesnicar B. *J. Am. Chem. Soc.* 2002; **124**: 8462–8470; (c) Bohr F, Henon E, García I, Castro M. *Int. J. Quantum Chem.* 1999; **75**: 671–682.
16. Honeywill JD, Mile B. *J. Chem. Soc., Perkin Trans. 2*, 2002; 569–575.
17. Kolano C, Sander W. *Eur. J. Org. Chem.* 2003; 1074–1079.
18. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Salvador P, Dannenberg JJ, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98, Revision A.11.1.* Gaussian: Pittsburgh, PA, 2001.
19. Becke AD. *J. Chem. Phys.* 1993; **98**: 5648–5652.
20. Trucks GW, Watts JD, Salter EA, Bartlett RJ. *Chem. Phys. Lett.* 1988; **153**: 490–495.
21. Trucks GW, Salter EA, Sosa C, Bartlett RJ. *Chem. Phys. Lett.* 1988; **147**: 359–366.