Characterization of Alkoxycarbonyl Radicals by Step-Scan Time-Resolved Infrared Spectroscopy

Götz Bucher,*[a] Martin Halupka,[a] Christoph Kolano,[a] Olaf Schade,[a] and Wolfram Sander*[a]

A series of alkoxycarbonyl radicals has been generated by laser flash photolysis (355 nm) of fluorenone oxime alkyl oxalates in carbon tetrachloride and characterized by time-resolved infrared spectroscopy using the step-scan technique. The alkoxycarbonyl radicals ($\tilde{\nu}_{C=O}$ = 1802 cm^{-1} for R = ethyl) generally have a lifetime of several microseconds, decaying by reaction with the solvent to yield esters of chloroformic acid. In some cases, decarboxylation yielding alkyl radicals has also been observed. Thus, photolysis of fluorenone oxime *tert*-butyl oxalate results in the formation of *tert*-butoxycarbonyl radicals, which subsequently decay, mainly yielding CO_2 and *tert*-butyl radicals. The benzyloxycarbonyl radical and the acetoneiminoxycarbonyl radical both decarboxylate too rapidly to be detected with our spectrometer (25 ns risetime). Upon purging the solution with oxygen, the alkoxycarbonyl radicals were efficiently quenched, to yield alkoxycarbonylperoxy radicals ($\tilde{\nu}_{C=O}$ = 1845 cm^{-1} for R = ethyl), which again had a lifetime of the order of several microseconds. A short-lived transient ($\tilde{\nu}$ = 1768 cm^{-1}, $\tau \approx$ 200 ns) is assigned as the carbonyloxy radical **4a** on the basis of comparison with time-resolved UV/Vis data. A further product of the photolysis of fluorenone oxime oxalates can be tentatively assigned as the 9-fluorenylideneiminoxy radical **3** ($\tilde{\nu}$ = 1670 cm^{-1}), which according to our DFT calculations should show a very intense $\tilde{\nu}_{C=N-O,as.}$ = 1665 cm^{-1}. Fluorenone oxime oxalates are compounds well suited as precursors for alkoxycarbonyl radicals, since they are easily synthesized as crystalline solids, show a convenient absorption at λ = 355 nm, and exhibit a high degree of thermal stability.

Introduction

Acyl radicals represent an important class of reactive intermediates, which has been the focus of research for a long time. Typical reactions of acyl radicals include additions to double bonds, C−H and C−X (X = halogen) abstraction, and decarbonylation.[1] Alkoxycarbonyl radicals ROCO˙ represent an interesting subset of acyl radicals, which, apart from the decay pathways just mentioned, may also decay by decarboxylation. Decarboxylation can generally compete with other reactions if R is either a tertiary alkyl substituent or is stabilized electronically (e.g. R = benzyl).[2,3] Thus, the rate constant for the decarboxylation of the benzyloxycarbonyl radical has been determined by laser flash photolysis (LFP) to be 5·10^8 M^{-1} s^{-1} in THF,[4] while the *tert*-butoxycarbonyl radical decarboxylates with k = 3.6·10^6 M^{-1} s^{-1} (80 °C, in cyclohexane).[3,4] The reaction is an important step in a process for the deoxygenation of alcohols. Alkyloxyacyl radicals bearing primary or secondary alkyl substituents decarboxylate much less readily, but this limitation can be circumvented by raising the temperature.

Time-resolved studies on acyl radicals are difficult if using the well established technique of LFP with UV/Vis detection, because acyl radicals are usually poor chromophores, absorbing mainly in the poorly characteristic UV region of the spectrum, while bands in the Vis region of the spectrum are weak.[5] Some work has been performed on the detection of acyl radicals with time-resolved infrared spectroscopy. Acyl radicals generally exhibit highly characteristic and intense C=O stretching bands (e.g., $\tilde{\nu}_{C=O}$ (acetyl) = 1864 cm^{-1}, $\tilde{\nu}_{C=O}$ (benzoyl) = 1828 cm^{-1} [6a,6b]). Thus, time-resolved infrared spectroscopy is well suited to the detection of acyl radicals in solution. For this reason, we have undertaken a study aimed at characterizing a variety of alkoxycarbonyl radicals using time-resolved infrared spectroscopy. The precursors used are derivatives of 9-fluorenone oxime, as previous work[7] has shown that compounds of this type may undergo efficient N−O scission upon photolysis. The results of this study are presented here.
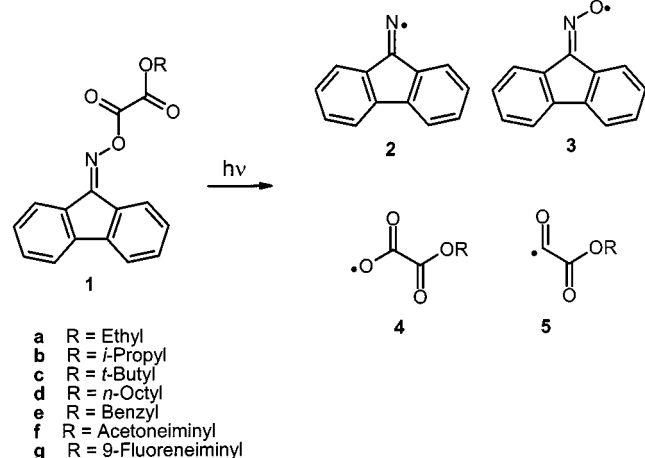
Results

Ethoxycarbonyl Radical

LFP of ethyl oxalate **1a** (4.06 mM in CCl$_4$, Ar purged) resulted in formation of CO_2 ($\nu_{C=O,as.}$ = 2336 cm^{-1}) and a transient with $\tilde{\nu}$ = 1802 cm^{-1} with a lifetime τ = 2.4 µs. Both CO_2 and the transient at 1802 cm^{-1} were formed during the rise-time of our instrument. Concomitantly with the decay at 1802 cm^{-1}, a growth at $\tilde{\nu}$ = 1722 cm^{-1} and another at $\tilde{\nu}$ = 1768 cm^{-1} were observed. A further product showed a band at $\tilde{\nu}$ = 1670 cm^{-1}. In addition, we observed a very short-lived decaying transient ($\tilde{\nu}$ = 1768 cm^{-1}, $\tau \approx$
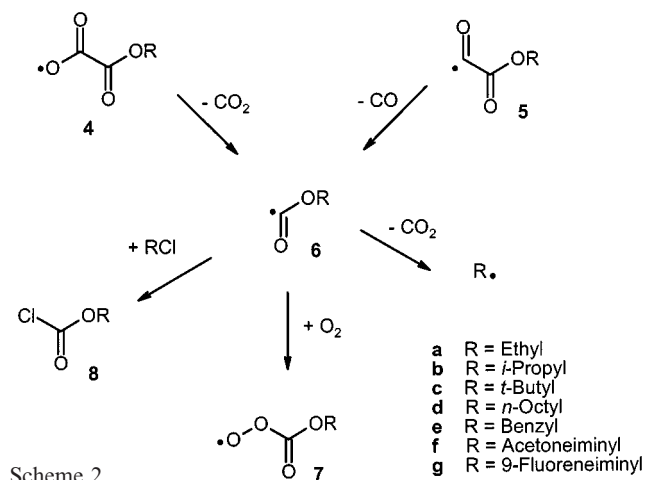
[a] Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum
Universitätsstrasse 150, 44801 Bochum, Germany
Fax: (internat.) + 49-(0)234/3214353
E-mail: goetz.bucher@orch.ruhr-uni-bochum.de
E-mail: sander@xenon.orch.ruhr-uni-bochum.de

200 ns). When the solution was purged with oxygen, the immediate formation of CO_2 was again detected. However, the 1802 cm^{-1} transient was no longer observed. Instead, we found a transient with $\tilde{\nu}$ = 1845 cm^{-1} being formed within the rise-time of our detector. This transient decayed with a lifetime τ = 4.9 µs.

Infrared bands at ca. 1800 cm^{-1} are characteristic of acyl radicals. A probable fragmentation pathway for oxalate **1a** consists of primary photochemical cleavage of the N−O bond of the fluorenone oxime moiety, followed by rapid decarboxylation of the resulting acylcarbonyloxy radical **4a**

a R = Ethyl
b R = *i*-Propyl
c R = *t*-Butyl
d R = *n*-Octyl
e R = Benzyl
f R = Acetoneiminyl
g R = 9-Fluoreneiminyl

Scheme 1

a R = Ethyl
b R = *i*-Propyl
c R = *t*-Butyl
d R = *n*-Octyl
e R = Benzyl
f R = Acetoneiminyl
g R = 9-Fluoreneiminyl

Scheme 2

(Scheme 1, Scheme 2). Alternatively, **1a** could also yield the 9-fluorenoneiminoxy radical **3** and the oxalyl radical **5a**, which could subsequently decarbonylate.

Carbonyloxy radicals are known to be particularly prone to decarboxylation. For instance, the phenylcarbonyloxy radical decarboxylates within 500 ns, yielding the highly reactive phenyl radical,[8] while the 9-methylfluorenylcarbonyloxy radical has a lifetime considerably shorter than 1 ns.[9] In our case, the resulting radical should be the ethoxycarbonyl radical **6a**. In order to confirm this assignment, the infrared spectrum of the ethoxycarbonyl radical was calculated using density functional theory (UBPW91/cc-pVDZ; UB3LYP/6-311G(d,p) gave similar results). The calcula-

tions gave a $\tilde{\nu}_{C=O}$ = 1781 cm^{-1} for the ethoxycarbonyl radical **6a**, in good agreement with the data (1802 cm^{-1}) obtained for the transient observed upon LFP of **1a** (Figure 1). We thus feel confident in assigning the 1802 cm^{-1}-transient to the ethoxycarbonyl radical.
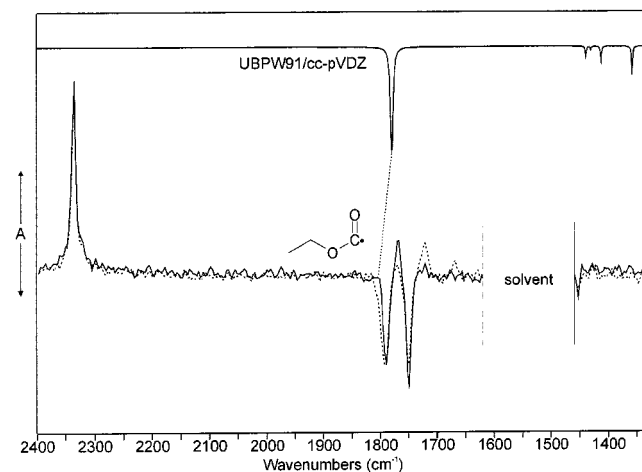

Figure 1. Top: calculated vibrational spectrum of **6a** (UBPW91/cc-pVDZ). Bottom: time-resolved IR difference spectra (time resolution 500 ns, spectral resolution 6 cm^{-1}) showing the photochemistry of **1a** in argon-purged CCl$_4$. Bands appearing on irradiation (λ = 355 nm) are pointing upwards, bands disappearing are pointing downwards. Black: spectrum 500 ns after irradiation. Dotted: spectrum after 20 µs.

In order to generate this radical from an independent precursor, we synthesized the pyridinethione oxalate **9** and investigated its photochemistry by step-scan FTIR. In our hands, compound **9** proved to be difficult to handle. As reported in the literature,[4] it is very difficult to purify and decomposes readily upon exposure to heat or light. Furthermore, dilute solutions of **9** are unstable towards oxygen, which made it impossible for us to study the oxidation of radicals derived from **9**. LFP (355 nm) of a solution of **9** in carbon tetrachloride (7.05 mM) under Ar atmosphere gave results that were very similar to the results obtained with **1a**. Because of rapid precipitation of a polymeric film on the cell windows, we were forced to reduce the laser intensity to ca. 4 mJ/pulse. The signal-to-noise ratio was thus significantly reduced, in comparison with the experiments performed with **1a**. Nevertheless, we were able to obtain transient spectra, which are shown in Figure 2. As in the case of LFP with **1a**, we observed a transient with $\tilde{\nu}_{C=O}$ around 1800 cm^{-1}. Compared to **1**, the band position is slightly shifted. All transient spectra presented in this contribution represent difference spectra (product minus precursor), and slight shifts in product band positions are due to changes in precursor band positions. An attempt to generate **1a** from diethyl *trans*-azodicarboxylate **10** failed (Scheme 3). No transient was detected, most probably because of efficient *trans-cis* isomerization of the azo chromophore.

The reaction of acyl radicals with oxygen, yielding acylperoxy radicals, has been studied previously by time-resolved infrared spectroscopy. The benzoyl radical reacts with $^{3}O_2$ with a rate constant of k = 1.8·10^9 M^{-1} s^{-1} (in hexane),[6b] which is essentially diffusion controlled. This reaction yields
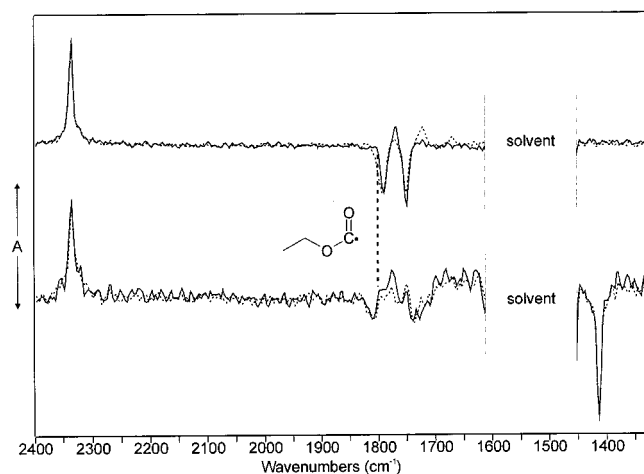
Figure 2. Top: time-resolved IR difference spectra (time resolution 500 ns, spectral resolution 6 cm^{-1}) showing the photochemistry of **1a** in argon-purged CCl$_4$. Black: spectrum 500 ns after irradiation. Dotted: spectrum after 20 µs. Bottom: time-resolved IR difference spectra (time resolution 1.5 µs, spectral resolution 6 cm^{-1}) showing the photochemistry of **9** in argon-purged CCl$_4$. Black: spectrum 1.5 µs after irradiation. Dotted: spectrum after 20 µs. Bands appearing on irradiation (λ = 355 nm) are pointing upwards, bands disappearing are pointing downwards.
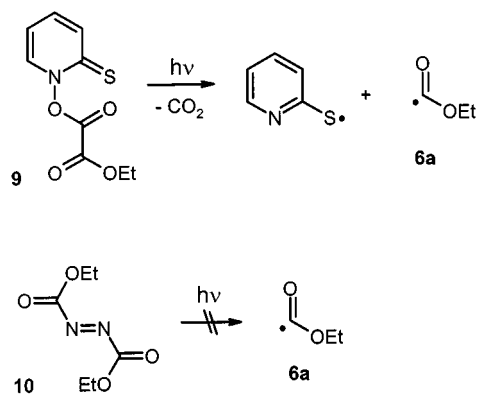
Scheme 3

the benzoylperoxy radical ($\tilde{\nu}_{C=O}$ = 1820 cm^{-1}). The expected reaction pathway in our system is therefore oxidation of the ethoxycarbonyl radical **6a**, yielding the ethoxycarbonylperoxy radical **7a**. Comparison of a calculated (UBPW91/cc-pVDZ) infrared spectrum of the ethoxycarbonylperoxy radical **7a** ($\tilde{\nu}_{C=O}$ = 1854 cm^{-1}) with the data for the transient observed upon LFP of **1a** under 1 atm. oxygen ($\tilde{\nu}$ = 1845 cm^{-1}) shows excellent agreement (Figure 3). Thus, we feel confident in assigning this transient as the ethoxycarbonylperoxy radical **7a**.

The product expected for the reaction of **6a** with carbon tetrachloride solvent is ethyl chloroformate **8a**. One of the products formed concomitantly with the decay of **6a** could indeed be identified as **8a** ($\tilde{\nu}_{C=O}$ = 1777 cm^{-1}).

The identification of the remaining product and transient signals, however, proved a difficult task. The very short-lived transient ($\tilde{\nu}$ = 1768 cm^{-1}, τ ≈ 200 ns) observed upon LFP of **1a** could in principle be assigned variously as the carbonyloxy radical **4a**, the oxalyl radical **5a**, or the acyl radical **6g** that would result from cleavage of the α-dicar-
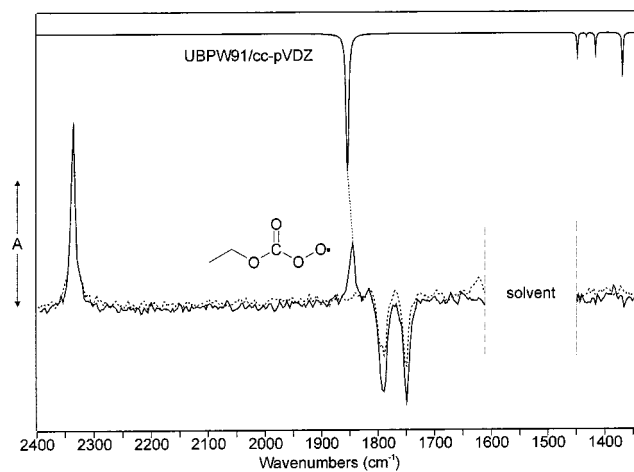

Figure 3. Top: calculated vibrational spectrum of **7a** (UBPW91/cc-pVDZ). Bottom: time-resolved IR difference spectra (time resolution 500 ns, spectral resolution 6 cm^{-1}) showing the photochemistry of **1a** in oxygen-purged CCl$_4$. Bands appearing on irradiation (λ = 355 nm) are pointing upwards, bands disappearing are pointing downwards. Black: spectrum 500 ns after irradiation. Dotted: spectrum after 20 µs.

bonyl moiety. Neither **6g** nor **5a** seem promising candidates. According to our calculations (UBPW91/cc-pVDZ), the oxalyl radical **5a** should display two intense carbonyl vibrations at $\tilde{\nu}_{C=O}$ = 1705 (ester) and 1898 (acyl radical) cm^{-1}. Neither of these is consistent with the experimental data. For the iminoxycarbonyl radical **6g**, the same method gave a calculated $\tilde{\nu}_{C=O}$ = 1811 cm^{-1}, which also makes it unlikely that this radical was observed.

As far as the carbonyloxy radical **4a** is concerned, a short lifetime is to be expected. Alkylcarbonyloxy radicals have a lifetime in the ps range,[9] while carbonyloxy radicals bound to sp^2 centers have been reported to be longer lived, such as the phenylcarbonyloxy radical with τ ≈ 500 ns.[8] Carbonyloxy radicals have been shown to exhibit a characteristic λ_{max} in the red to near-IR range of the spectrum. They are highly reactive species, rapidly quenched by hydrogen donors.[8] This means that, should a carbonyloxy radical of measurable lifetime (τ > 25 ns) be formed in our step-scan IR experiments, it should also be detectable by time-resolved UV/Vis spectroscopy. For that reason, we conducted laser flash photolysis experiments with **1a** in cyclohexane solution, using λ_{exc} = 266 nm. We monitored a very short-lived transient (τ = 10 ns, weak λ_{max} ≈ 700 nm, trace see Figure 4), that was completely quenched upon addition of 1% 1,4-cyclohexadiene. In tetrachloromethane solution (λ_{exc} = 355 nm), the transient lifetime, monitored at λ = 330 nm, was 200 ns, while the signal was also weak at λ = 670 nm. On the basis of these observations, we assign the 1768 cm^{-1} transient to the carbonyloxy radical **4a**. As a caveat it has to be noted that our calculations (UBPW91/cc-pVDZ) gave a $\tilde{\nu}_{C=O}$ (ester) = 1726 cm^{-1} for **4a** ($\nu_{C=O}$ of the carbonyl group of the carbonyloxy radical moiety appears at much smaller wavenumbers and has a much lower intensity), which is considerably lower than the experimental value of $\tilde{\nu}$ = 1768 cm^{-1}.

The additional product formed in the photolysis of **1a**, showing a band at $\tilde{\nu}$ = 1670 cm^{-1}, is unlikely to be any
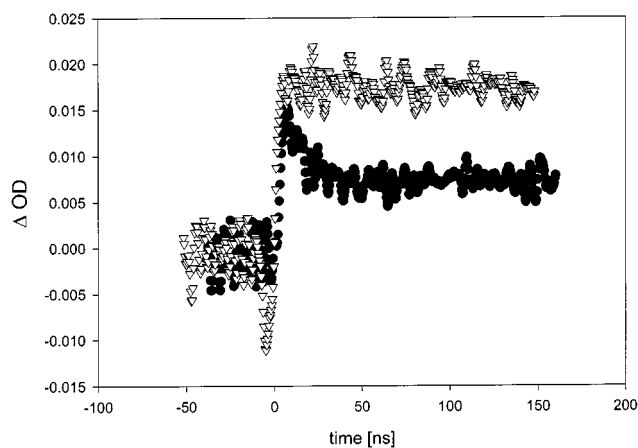
Figure 4. Black dots: transient decay trace, recorded at $\lambda = 700$ nm upon laser flash photolysis ($\lambda_{exc} = 266$ nm) of **1a** in cyclohexane at ambient temperature. Light triangles: transient decay trace ($\lambda = 700$ nm), recorded after LFP ($\lambda_{exc} = 266$ nm) of **1a** in cyclohexane containing 1% 1,4-cyclohexadiene.

kind of ester, because of the low frequency of the band. A possible candidate for this product, however, is the iminoxy radical **3**. According to DFT calculations (UBPW91/cc-pVDZ), this radical should have an intense $\tilde{\nu}_{C=N-O} = 1665$ cm^{-1}: in excellent agreement with our experiment. However, in a study on an oxime carbamate related to **1a**, no evidence could be gained for C−O scission competing with N−O cleavage.[7] The assignment of **3** should therefore be regarded as tentative.

These experiments clearly show that LFP of fluorenone oxime oxalate **1a** leads to efficient formation of ethoxycarbonyl radicals **6a**, which undergo chlorine abstraction from the carbon tetrachloride solvent to yield ethyl chloroformate **8a**. They can be trapped with oxygen to yield ethoxycarbonylperoxy radicals **7a**. Other species include a very short-lived transient − which, on the basis of experi-

ments performed using time-resolved UV/Vis spectroscopy, can tentatively be identified as carbonyloxy radical **4a** − and also possibly the iminoxy radical **3**, which is stable on the time scale of our experiments.

In order to characterize alkoxycarbonyl radicals more prone to decarboxylation, we extended our study to the isopropyloxy-, *tert*-butoxy-, benzyloxy-, and acetoneiminoxycarbonyl radicals. All these radicals were generated photochemically from the corresponding 9-fluorenone oxime oxalates. Additionally, the chemistry of the *n*-octyloxycarbonyl radical was investigated by product analysis.

Other Alkoxycarbonyl Radicals

LFP of isopropyl oxalate **1b** (5.17 mM in CCl$_4$, Ar purged) again resulted in observations very similar to those made with **1a**. The observed transient ($\tilde{\nu} = 1799$ cm^{-1}, $\tau = 4.4$ μs) was efficiently quenched by ^{3}O$_2$, yielding a second transient ($\tilde{\nu} = 1842$ cm^{-1}, $\tau = 10.9$ μs). Because of their similarity with those observed upon LFP of **1a**, these two transients can be assigned as the isopropyloxycarbonyl radical (**6b**, $\tilde{\nu} = 1799$ cm^{-1}) and the isopropyloxycarbonylperoxy radical (**7b**, $\tilde{\nu} = 1842$ cm^{-1}). Concomitantly with the decay of **6b** (under Ar atmosphere), we detected the formation of products showing bands at $\tilde{\nu} = 1713$ cm^{-1} (not identified) and $\tilde{\nu} = 1778$ cm^{-1} (assigned to isopropyl chloroformate **8b**). In this system, however, we also noted a secondary growth in the CO$_2$ absorption at 2336 cm^{-1} when the photolysis was performed under Ar atmosphere. This secondary increase amounted to ca. 20% of the "instantaneous" primary CO$_2$ absorption (Figure 5). Again, under argon atmosphere, a very short-lived transient ($\tilde{\nu} = 1765$ cm^{-1}, $\tau \approx 200$ ns) was observed.

In the case of LFP of *tert*-butyl oxalate **1c** (4.95 mM in CCl$_4$, Ar purged), this secondary growth in CO$_2$ absorption was even more pronounced, amounting to 60% of the "in-
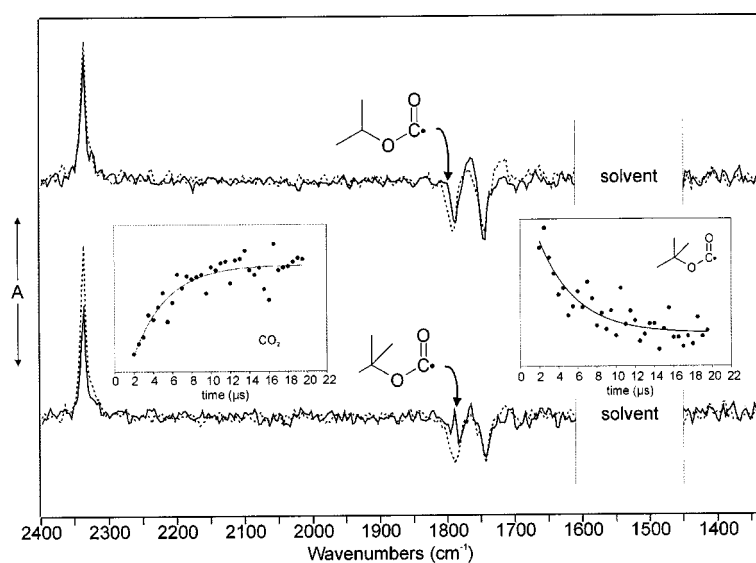

Figure 5. Top: time-resolved IR difference spectra showing the photochemistry of **1b** in argon-purged CCl$_4$. Bottom: time-resolved IR difference spectra showing the photochemistry of **1c** in argon-purged CCl$_4$. Time resolution 500 ns, spectral resolution 6 cm^{-1}. Bands appearing on irradiation ($\lambda = 355$ nm) are pointing upwards, bands disappearing are pointing downwards. Black: spectrum 500 ns after irradiation. Dotted: spectrum after 20 μs. Inset: left: kinetic trace of the increase of CO$_2$; right: kinetic trace of the decay of the *tert*-butoxycarbonyl radical.

stantaneous" primary absorption. The lifetime of the increase in CO_2 absorption was $\tau = 2.0$ µs. There is a certain discrepancy in the decay rate constant of transient **6c** ($\tilde{\nu} = 1790$ cm^{-1}, $\tau = 3.6$ µs) (Figure 5). The quality of the trace obtained for the 1790 cm^{-1} transient was limited by the fact that the corresponding band is located on a large negative absorption due to bleaching of **1c**. To us, therefore, 1.9 µs seems more trustworthy than 3.6 µs as a value for the lifetime of **6c**. As in the case of **1b**, LFP of **1c** under oxygen atmosphere gave no secondary CO_2 evolution, but resulted in the formation of transient **7c** ($\tilde{\nu} = 1846$ cm^{-1}, $\tau = 10.6$ µs) instead. A very short-lived transient ($\tilde{\nu} = 1765$ cm^{-1}, $\tau \approx 200$ ns) was again observed under Ar atmosphere.

LFP of benzyl oxalate **1e** (4.47 mM in CCl$_4$) gave results very different from those obtained with **1a**−**c**. Neither under Ar, nor under oxygen atmosphere could any transient be detected. Instead, twice the amount of carbon dioxide, relative to with **1a**, was formed within the rise-time of our detector (Figure 6).
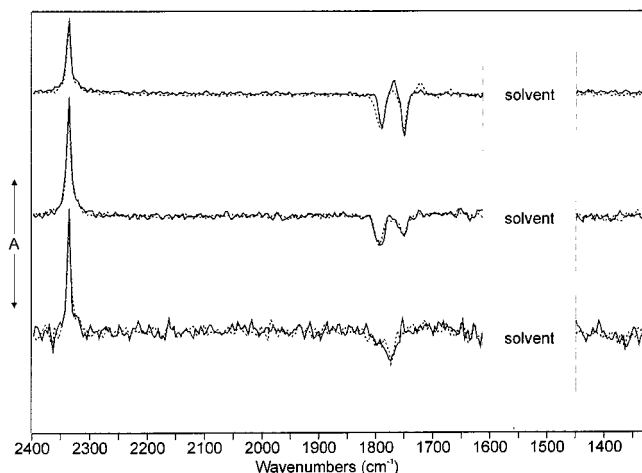

Figure 6. Top: time-resolved IR difference spectra showing the photochemistry of **1a** in argon-purged CCl$_4$. Middle: time-resolved IR difference spectra showing the photochemistry of **1e** in argon-purged CCl$_4$. Bottom: time-resolved IR difference spectra showing the photochemistry of **1f** in argon-purged CCl$_4$. Bands appearing on irradiation ($\lambda = 355$ nm) are pointing upwards, bands disappearing are pointing downwards. Time resolution 500 ns, spectral resolution 6 cm^{-1}. Black: spectrum 500 ns after irradiation. Dotted: spectrum after 20 µs.

In an attempt to characterize the iminoxyacyl radical **6g**, which also represents a probable radical product after LFP of fluorenone oxime oxalates, we synthesized bis(9-fluorenoneoxime)oxalate **1g**. Unfortunately, we were unable to find a solvent suitable for time-resolved infrared spectroscopy (transparent in the mid IR range) and in which this compound is sufficiently soluble. We therefore synthesized the mixed fluorenone oxime / acetone oxime oxalate **1f** and investigated it using step-scan TRIR (3.62 mM in CCl$_4$). The results of these experiments were virtually identical to those obtained using benzyl oxalate **1e**. Again, twice the amount of CO_2, relative to the experiments done with **1a**, was liberated within the rise-time of our detector (Figure 6). Neither under Ar atmosphere, nor under oxygen could any transient

be detected. Experimental data and calculated IR modes of the transients **6** and **7** are summarized in Table 1.

Table 1. Lifetime, and experimental and calculated C=O stretching vibrations of the alkoxycarbonyl **6** and alkoxycarbonylperoxy radicals **7**

radical	lifetime τ [µs][a]	$\nu_{C=O}$ exp. [cm^{-1}][a]	$\nu_{C=O}$ calcd. [cm^{-1}][b]
6a	2.4	1802	1781
7a	4.9	1845	1854
6b	4.4	1799	1803
7b	10.9	1842	1846
6c	2.0[c] 3.6[d]	1790	1800
7c	10.6	1846	1845
6e	−	−	1784
7e	−	−	1850
6f	−	−	1804
7f	−	−	1890
6g	−	−	1811

[a] In CCl$_4$, ambient temperature. − [b] UBPW91/cc-pVDZ, unscaled. − [c] Value based on the growth kinetics of CO_2. − [d] Value measured directly.

The photochemistry of *n*-octyl oxalate **1d** was investigated by GC-MS analysis. Steady-state photolysis ($\lambda = 320$ nm) of a 0.6 mM solution of oxalate **1d** in CCl$_4$ yielded the following products (by GC-MS analysis, in brackets: relative yield; the relative yield of *N*-chloro-9-fluorenoneimine was set to 1.0, average of seven determinations): 1-chlorooctane (0.06), hexachloroethane (2.0), *n*-octyl chloroformate **8d** (2.0), 9-fluorenone (1.5), *N*-chloro-9-fluorenoneimine (1.0), 9-fluorenoneimine (0.3). Additionally, a range of further, unidentified products containing trichloromethyl and alkyl (presumably octyl- or fragments thereof) functionalities was formed. This product distribution is consistent with the formation of the radicals **2** and **6d** as the major products and their subsequent trapping by the solvent.

Discussion

Our failure to detect the benzyloxycarbonyl radical upon LFP of **1e** and the observation of secondary CO_2 formation upon LFP of **1b** and **1c** are in agreement with the expected properties of the benzyloxycarbonyl, the *tert*-butoxycarbonyl, and related radicals.[3,4] The rate of decarboxylation of the benzyloxycarbonyl radical has been determined by Simakov et al.[4] as $k = 5 \cdot 10^8$ s^{-1} (in THF), corresponding to a lifetime of $\tau = 2$ ns, which is much shorter than the rise-time of our detection system. The rate law for decarboxylation of the *tert*-butoxycarbonyl radical has been determined by Rüegge and Fischer[3] as $\log (k/\text{s}^{-1}) = 13.8 - 49.0/\theta$ (with $\theta = 2.303$ RT/kJ mol^{-1}), which would correspond to a lifetime $\tau = 6.1$ µs at 298 K, provided no other pathway for decay existed. In our hands, **6c** showed a lifetime $\tau = 1.9$ µs, which is somewhat faster than the value expected for decarboxylation alone. This observation is consistent with the fact that the yield of secondary CO_2 amounts to only 60% of the yield liberated instantaneously, which suggests that 40% of **6c** is consumed by an alternative pathway. In

LFP experiments with **1a**, no secondary formation of CO_2 was detected; this is in agreement with the product studies with **1d**, in which 1-chlorooctane (formed via the octyl radical by abstraction of a chlorine atom from the solvent) was only a very minor product. Our observation of relatively efficient decarboxylation of the *tert*-butoxycarbonyl radical, a lesser degree of decarboxylation in the case of the isopropyloxycarbonyl radical, and practically no cleavage of the ethoxycarbonyl or *n*-octyloxycarbonyl radical is consistent with recent calculations [CCSD(T)/6-311G(d,p)//MP2/6-311G(d,p)] by Schiesser and co-workers, which give energy barriers of 72.8, 67.0, and 60.3 kJ/mol for the decarboxylation of the ethoxycarbonyl, isopropyloxycarbonyl, and *tert*-butoxycarbonyl radicals, respectively.[10]

The benzoyl radical is quenched by CCl_4 with a rate constant $k = 5.6\cdot10^4$ M^{-1} s^{-1};[6b] given a molarity of 10.36 for pure CCl_4, this corresponds to a lifetime $\tau = 1.7$ µs. Obviously, alkoxyacyl radicals react less efficiently with CCl_4 than the benzoyl radical does.

Bromotrichloromethane is known to be an efficient scavenger for acyl radicals. Its rate constant for reaction with the benzoyl radical has been determined as $k = 2.2\cdot10^8$ M^{-1} s^{-1},[6b] which is 4000 times more rapid than the reaction of PhCO with CCl_4. We measured the rate constant for the reaction of **6a** with $BrCCl_3$ by determining the decay rate for **6a** in the presence of three different concentrations of $BrCCl_3$ (Figure 7). The rate constant thus obtained is $k = 2.7 \pm 0.5\cdot10^7$ M^{-1} s^{-1}, which is considerably slower than the reaction of the benzoyl radical.
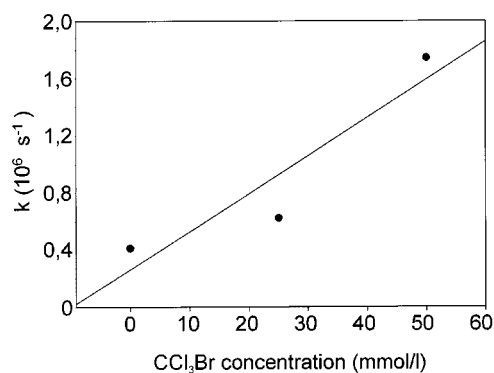
Figure 7. Decay rate of **6a** in the presence of three different concentrations of $BrCCl_3$

Conclusion

Photolysis of fluorenone oxime alkyl oxalates results in the formation of alkoxycarbonyl radicals, which can be trapped by oxygen to yield alkoxycarbonylperoxy radicals. Both types of transients were characterized by time-resolved step-scan FTIR spectroscopy and exhibit lifetimes of the order of several microseconds in carbon tetrachloride. Alkoxycarbonyl radicals decay by chlorine abstraction from the solvent and by decarboxylation. The relative quantum yields of the two decay channels strongly depend on the substituent. The benzyloxy and acetoneiminoxycarbonyl radicals decarboxylate too rapidly to be detectable by our

equipment. In the case of the *tert*-butoxycarbonyl and isopropyloxycarbonyl radicals, decarboxylation competes with chlorine abstraction, while the decarboxylation of the ethoxycarbonyl radical could not be detected with our equipment. The ethoxycarbonyl radical is quenched by bromotrichloromethane, albeit much less efficiently than the benzoyl radical.

Experimental Section

Step-Scan FTIR: For time-resolved measurements, we have built an apparatus consisting of a modified Bruker IFS 66v/S FTIR spectrometer with step/scan option, a Nd-YAG laser (Spectra Physics Quanta Ray Lab 130) and a sample cell connected to a continuous flow system. The sample cell is positioned outside the spectrometer. The IR beam is reflected out of the spectrometer through a KBr window onto the sample cell and reflected back by an IR mirror positioned behind the cell. We use a photovoltaic MCT detector (KMPV11-1-LJ2/239 Kolmar Technologies, rise-time 25 ns) with internal preamplifier. The AC-coupled output of the preamplifier is fed directly into a second amplifier and then read out by a 40 MHz, 12 bit transient recorder (Spectrum, PAD 1232) connected to a PC. The second amplifier has no effect on the signal-to-noise ratio, but amplifies the entire signal by a factor of four to make use of the full dynamic range of the transient recorder. Positioning of the interferometer mirror and data acquisition is performed using OPUS software package (Bruker). The solution is pumped through the sample cell (two CaF_2 windows, 0.25 mm Teflon spacer) by a peristaltic pump with low pulsation (Ismatec IPC-N-4, flow 1.7 mL/min) and transferred back into the tank. Experiments in which the flow was maintained by gravity showed that the low pulsation of the peristaltic pump had no effect on the signal-to-noise ratio. The sample is excited by the 3rd harmonic (355 nm) of the Nd-YAG laser. The repetition rate is 10 Hz. To avoid thermal effects and shockwaves, the laser energy is attenuated to between 9 and 14 mJ/pulse by an external attenuator. During measurements, the spectrometer is evacuated to 1 mbar pressure. In order to eliminate external vibrations, the whole system is placed on a vibrationally insulated table (Melles Griot). The fluctuations of the interferometer mirror amount to an estimated ±1.3 nm.

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 could be improved by averaging a smaller number of spectra. The sample was dissolved (1 g L^{-1}) in carbon tetrachloride (Riedel-de Haën, spectroscopic grade) and purged with argon for at least 45 min. In experiments involving oxygen trapping, the solution was purged with oxygen for 15 min.

Laser Flash Photolysis: A standard LFP set-up was used, consisting of a Spectra-Physics Quanta-Ray LAB 130 Nd-YAG laser, operated at 1 Hz and 266 nm (50 mJ/pulse, 8 ns pulse duration) or 355 nm (130 mJ/pulse, 8 ns pulse duration), a pulsed Xe arc lamp (Müller, Germany), a SPEX Minimate monochromator coupled to a photoelectron multiplier tube, and a LeCroy 9361 digital oscilloscope. The entire set-up was controlled from a personal computer using LabView software. Data evaluation was performed using

SigmaPlot software. In order to avoid depletion of the precursor and product build-up, a flow cell was used. The concentration of **1a** was adjusted so that an optical density of 0.3 was achieved at the laser wavelength used.

Calculations: Calculations were performed with a standard density functional method (UBPW91)[11,12] using a cc-pVDZ or 6-311G(d,p) basis set. The calculated vibrational frequencies given are unscaled. The Gaussian 98 suite of programs[13] was employed for all calculations.

Product Studies: Photolyses were performed using CCl_4 and $\lambda_{exc} =$ 320 nm (Hg low-pressure lamp, Gräntzel, Germany, filtered). Samples (0.6 mM) were purged with Ar for 20 minutes prior to photolysis. After 30 min photolysis, the solvent was evaporated and the mixture analyzed by GC-MS (Hewlett-Packard 5890 series II GC, HP 5972 mass detector, column MDN-5 S, 30 m × 0.25 mm, 0.1 μm film, poly (5% phenyl/95% methylsiloxane). Products were identified by MS analysis and/or by coinjection with authentic samples.

Synthesis and Characterization of the Precursors: The precursor molecules were synthesized from 9-fluorenone oxime and oxalic acid monochloride monoesters, which were partly commercially available, and partly synthesized from the corresponding alcohol (or acetone oxime) and an excess of oxalyl dichloride. The oxalate **8** was prepared according to a literature procedure.[4,14]

General Procedure for the Conversion of Alcohols to Oxalic Acid Monoester Monochlorides: The alcohol (10 mmol) was added dropwise over 15 min to an excess of oxalyl chloride (20 mmol) at 0 °C. When the addition was complete, the mixture was allowed to warm to room temperature. Excess oxalyl chloride was removed by vacuum distillation. The product was distilled and kept at 0 °C in the dark.

General Procedure for the Conversion of Oxalic Acid Monoester Monochlorides into Alkyl-[(9-fluorenylidenamino)oxycarbonyl]formates: 9-Fluorenone oxime (10 mmol) was suspended in CCl_4 (50 mL) at room temperature. To this suspension was added dropwise over 15 min a solution of oxalic acid monoester monochloride (10 mmol) in CCl_4 (10 mL). The solution was stirred for 12 h and filtered, and the solvent was removed. The alkyl-[(9-fluorenylidenamino)oxycarbonyl]formates were recrystallized from *n*-hexane. Yield: typically ca. 90% (60% for **1f**).

Synthesis of 1g: 9-Fluorenone oxime (4.1 g, 21 mmol) was suspended in CCl_4 (350 mL) at room temperature. To this suspension was added dropwise a solution of oxalyl dichloride (1 mL, 10 mmol) in CCl_4 (10 mL). The solution was stirred for 12 h and filtered, and the solvent was removed. The product was recrystallized from toluene (1700 mL). Yield: 4.0 g (86%), dec. 221 °C.

Ethyl [(9-Fluorenylideneamino)oxycarbonyl]formate (1a): ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 8.43 (d, 1 H), 7.88 (d, 1 H), 7.57 (d, 1 H), 7.55 (d, 1 H), 7.46 (t, 1 H), 7.42 (t, 1 H), 7.31 (t, 1 H), 7.26 (t, 1 H), 4.48 (q, 2 H), 1.47 (t, 3 H). − ^{13}C NMR (CDCl$_3$): δ = 160.76, 156.84, 154.89, 142.72, 141.58, 133.66, 133 16, 132.27, 131.08, 129.92, 128.88, 128.51, 123.72, 120.32, 120.24, 63.65, 13.98. − IR (KBr) ṽ = 3400, 2990, 1785, 1749, 1612, 1597, 1497, 1367, 1324, 1291, 1207, 1164, 1152, 1109, 1039, 1017, 985, 945, 912, 874, 814, 786, 733, 647 cm^{-1}. − MS; *m/z*: 295, 232, 195, 178, 164, 151, 29. − HRMS: found 295.084458, calcd. 295.085100. − C$_{17}$H$_{13}$NO$_4$ (295.3): calcd. C 69.15, H 4.44, N 4.74; found C 69.25, H 4.54, N 4.66. − M.p. 116 °C.

Isopropyl [(9-Fluorenylideneamino)oxycarbonyl]formate (1b): ^{1}H NMR ([D$_6$]DMSO, 200 MHz): δ = 1.38 (d, 6 H), 5.16 (m, 1 H), 7.37 (t, 1 H), 7.42 (t, 1 H), 7.55 (t, 1 H), 7.61 (t, 1 H), 7.77 (d, 1 H), 7.85 (d, 1 H), 7.88 (d, 1 H), 8.47 (d, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 50 MHz): δ = 21.39, 71.72, 121.28, 123.01, 129.00, 130.66, 132.83, 133.87, 141.17, 142.13, 154.09, 155.58, 159.81. − IR (KBr) ṽ = 2987, 1787, 1631, 1609, 1596, 1453, 1388, 1375, 1357, 1323, 1294, 1229, 1206, 1154, 1095, 1041, 991, 922, 894, 878, 830, 790, 754, 732, 646 cm^{-1}. − MS; *m/z*: 309, 195, 179, 164, 151, 43. − C$_{18}$H$_{15}$NO$_4$ (309.3): calcd. C 69.89, H 4.89, N 4.53; found C 69.01, H 5.03, N 4.32. − M.p. 99° C.

***tert*-Butyl [(9-Fluorenylideneamino)oxycarbonyl]formate (1c):** ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 1.65 (s, 9 H), 7.27 (t, 1 H), 7.30 (t, 1 H), 7.42 (t, 1 H), 7.46 (t, 1 H), 7.56 (d, 1 H), 7.59 (d, 1 H), 7.88 (d, 1 H), 8.46 (d, 1 H). − ^{13}C NMR (CDCl$_3$, 50 MHz) δ = 27.86, 85.77, 120.24, 120.32, 123.70, 128.51, 128.72, 130.02, 131.00, 132.20, 133.09, 133.80, 141.56, 142.70. − IR (KBr) ṽ = 3059, 2986, 2936, 1784, 1749, 1633, 1611, 1598, 1452, 1370, 1306, 1260, 1176, 1158, 1130, 1038, 987, 927, 905, 870, 836, 810, 788, 752, 730, 645 cm^{-1}. − MS; *m/z*: 323, 195, 179, 164, 151, 76, 57. − C$_{19}$H$_{17}$NO$_4$ (323.3): calcd. C 70.58, H 5.30 N 4.33; found C 70.60, H 5.79, N 4.31. − M.p. 86 °C.

***n*-Octyl [(9-Fluorenylideneamino)oxycarbonyl]formate (1d):** ^{1}H NMR (CDCl$_3$): δ = 0.86 (t, 2 H), 1.28 (m, 10 H), 1.82 (m, 2 H), 4.41 (t, 2 H), 7.28 (dt, 1 H), 7.31 (dt, 1 H), 7.43 (dt, 1 H), 7.47 (dt, 1 H), 7.57 (dt, 1 H), 7.60 (dt, 1 H), 7.90 (d, 1 H), 8.45 (d, 1 H). − ^{13}C NMR (CDCl$_3$): δ = 14.04, 22.59, 25.78, 28.37, 29.12, 31.73, 67.75, 120.26, 120.34, 123.74, 128.53, 128.82, 129.94, 131.06, 132.29, 133.18, 133.70, 141.58, 142.74, 154.93, 156.97, 160.72. − IR (KBr): ṽ = 3451, 3060, 2952, 2927, 2860, 1809, 1793, 1758, 1609, 1595, 1471, 1377, 1292, 1228, 1204, 1139, 1126, 1038, 989, 955, 900, 877, 817, 788, 733, 661, 647 cm^{-1}. − MS: m/z: 379, 206, 195, 179, 164, 151, 71, 57, 43, 29. − C$_{23}$H$_{25}$NO$_4$ (379.5): calcd. C 72.8, H 6.64, N 3.69; found C 72.8, H 7.08, N 3.65. − M.p. 62 °C.

Benzyl [(9-Fluorenylideneamino)oxycarbonyl]formate (1e): ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 5.42 (s, 2 H), 7.10 (t, 1 H), 7.25 (t, 1 H), 7.43 (m, 7 H), 7.54 (d, 1 H), 7.58(d, 1 H), 7.84 (d, 1 H), 8.31(d, 1 H). − ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 69.18, 120.24, 123.76, 128.53, 128.88, 128.97, 129.11, 129.84, 131.08, 132.29, 133.14, 133.67, 133.97, 141.58, 142.70, 156.67, 160.74. − IR (KBr): ṽ = 1800, 1752, 1609, 1595, 1452, 1320, 1286, 1219, 1205, 1136, 1039, 980, 941, 924, 902, 874, 791, 753, 732, 698, 646 cm^{-1}. − MS; *m/z*: 357, 179, 151, 91, 77, 65, 44. − C$_{22}$H$_{15}$NO$_4$ (357.4): calcd. C 73.94 H 4.23, N 3.92; found C 73.32 H 3.87 N 4.32. − M.p. 143 °C.

2-Propylideneamino [(9-Fluorenylideneamino)oxycarbonyl]formate (1f): ^{1}H NMR (CDCl$_3$): δ = 2.09 (s, 3 H), 2.14 (s, 3 H), 7.27(td, 1 H), 7.29 (td, 1 H), 7.42 (td, 1 H), 7.46(td, 1 H), 7.55 (d, 1 H), 7.59 (d, 1 H), 7.84 (d, 1 H) 8.40 (d, 1 H). − ^{13}C NMR (CDCl$_3$): δ = 17.44, 21.80, 120.30, 120.34, 123.62, 128.51, 128.88, 129.80, 131.08, 132.31, 133.24, 133.66, 141.58, 142.70, 160.39, 166.81. − IR (KBr): ṽ = 1787, 1732, 1637, 1610, 1597, 1452, 1370, 1321, 1277, 1249, 1204, 1157, 1129, 1038, 983, 915, 866, 840, 792, 783, 755, 730, 644 cm^{-1}. − MS; *m/z*: 322, 179, 164, 151, 76, 56, 44. − HRMS: found 322.096000, calcd. 322.095357. − M.p. 215 °C (dec.).

9-Fluorenylideneamino [(9-Fluorenoneamino)oxycarbonyl]formate (1g): IR (KBr): ṽ = 1770, 1631, 1593, 1452, 1319, 1207, 1158, 1121, 1101, 1039): 989, 969, 880, 858, 827, 788, 730, 648 cm^{-1}. − MS: *m/z*: 444, 372, 356, 327, 206, 195, 179, 164, 151, 91, 76, 63, 44. − HRMS: found 444.111200, calcd. 444.111007. − M.p. 221 °C (dec.).

[1] C. Chatgilialoglu, D. Crich, M. Komatsu, I. Ryu, *Chem. Rev.* **1999**, *99*, 1991−2069.

[2] A. L. Beckwith, V. W. Bowry, *J. Am. Chem. Soc.* **1994**, *116*, 2710−2716.

[3] D. Rüegge, H. Fischer, *Int. J. Chem. Kin.* **1986**, *18*, 145−158.

[4] P. A. Simakov, F. N. Martinez, J. H. Horner, M. Newcomb, *J. Org. Chem.* **1998**, *63*, 1226−1232.

[5] C. Huggenberger, J. Lipscher, H. Fischer, *J. Phys. Chem.* **1980**, *84*, 3467−3474.

[6] [6a] C. E. Brown, A. G. Neville, D. M. Rayner, K. U. Ingold, J. Lusztyk, *Aust. J. Chem.* **1995**, *48*, 363−379. − [6b] A. G. Neville, C. E. Brown, D. M. Rayner, J. Lusztyk, K. U. Ingold, *J. Am. Chem. Soc.* **1991**, *113*, 1869−1870.

[7] G. Bucher, J. C. Scaiano, R. Sinta, G. Barclay, J. Cameron, *J. Am. Chem. Soc.* **1995**, *117*, 3848−3855.

[8] J. Chateauneuf, J. Lusztyk, K. U. Ingold, *J. Am. Chem. Soc.* **1988**, *110*, 2886−2893.

[9] D. E. Falvey, G. B. Schuster, *J. Am. Chem. Soc.* **1986**, *108*, 7419−7420.

[10] T. Morihovitis, C. H. Schiesser, M. A. Skidmore, *J. Chem. Soc., Perkin Trans. 2* **1999**, 2041−2047.

[11] K. Burke, J. P. Perdew, Y. Wang, *Electronic Density Functional Theory: Recent Progress and New Directions* (Eds.: J. F. Dobson, G. Vignale, M. P. Das); Plenum, 1998.

[12] J. P. Perdew, K. Burke, Y. Wang, *Phys. Rev. B* **1996**, *54*, 16533.

[13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, R. Cammi, B. Menucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Ciolowski, J. V. Ortiz, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaroni, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.6*; Gaussian Inc.: Pittsburgh, PA., 1998.

[14] H. Togo, M. Fujii, M. Yokoyama, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 57−67.