

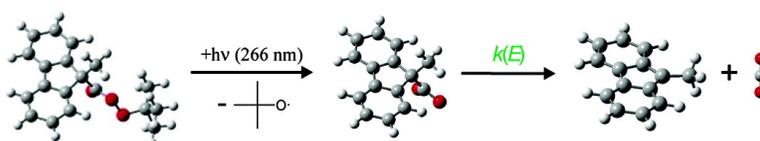
Article

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J. Am. Chem. Soc., **2003**, 125 (43), 13274-13278 • DOI: 10.1021/ja036304d • Publication Date (Web): 04 October 2003

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A Seemingly Well Understood Light-Induced Peroxide Decarboxylation Reaction Reinvestigated with Femtosecond Time Resolution

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Abstract: The photoinduced (266 nm) ultrafast decarboxylation of the peroxyester *tert*-butyl 9-methylfluorene-9-percarboxylate (TBFC) in solution has been studied with femtosecond time resolution. While the photodissociation of TBFC occurs too fast to be resolved, the intermediate 9-methylfluorenylcarbonyloxy radical (MeFl-CO₂) decarboxylates on a picosecond time scale. The latter process is monitored by pump-probe absorption spectroscopy at wavelengths between 400 and 883 nm. The measured transient absorbance signals reveal a dominant fast decay with a lifetime of a few picoseconds and, to a minor extent, a slow component with a lifetime of about 55 ps. Statistical modeling of MeFl-CO₂ decarboxylation employing molecular parameters calculated by density functional theory suggests that the fast component is associated with the decarboxylation of vibrationally hot radicals, whereas the 55 ps decay reflects the dissociation of thermally equilibrated MeFl-CO₂ at ambient temperature. The vast majority of MeFl-CO₂ radicals thus decarboxylate on a time scale about an order of magnitude faster than expected from the time constant of 55 ps reported by Falvey and Schuster for this reference reaction. This literature value turns out to refer to decarboxylation rate of MeFl-CO₂ at ambient temperature.

I. Introduction

Decomposition mechanisms of organic peroxyesters have attracted considerable interest which is partly due to their widespread use as initiators in free-radical polymerizations.^{1–5} Fragmentation kinetics of the peroxide and of intermediate species may affect polymerization rate, initiator efficiency, and also polymer microstructure. Detailed insight into the mechanism has been derived from experiments in which dissociation has been induced photochemically.^{6–15}

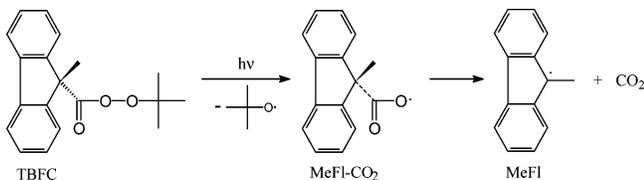
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Falvey and Schuster were the first to study the photoinduced decomposition of *tert*-butyl 9-methylfluorene-9-percarboxylate (TBFC) with picosecond (ps) time resolution.¹¹ TBFC was selected for these studies because of the stability of the 9-methylfluorenyl product radical. Falvey and Schuster¹¹ argued that the high stability of the 9-methylfluorenyl radical (MeFl) indicates a very short (ps) lifetime of the intermediate 9-methylfluorenyl carbonyloxy radical (MeFl-CO₂). UV-induced (266 nm) experiments on the decarboxylation of TBFC in acetonitrile and cyclohexane indeed showed a transient absorbance rise with a time constant of 55 ± 15 ps which was attributed to the formation of MeFl.¹¹ This photodissociation reaction became the textbook example for a very fast photoinduced sequential peroxide dissociation^{16–18} and, more importantly, served as a reference system for determination of rate constants and reaction yields of related reactions that were not studied with high time resolution.¹⁹ Recently, in our group the UV-induced (308 nm) decarboxylation of TBFC in CCl₄ solution was investigated by picosecond IR spectroscopy.⁷ The formation of CO₂ was monitored via absorption of the asymmetric stretching vibrational mode (ν_3) at around 4.3 μm . In contrast to the results reported in ref 11, it was found that more than 80% of the

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Scheme 1. Sequential Dissociation in the UV Photoinduced Decomposition of *tert*-Butyl 9-Methylfluorenyl-9-percarboxylate (TBFC)



CO₂ was produced within the experimental time resolution of about 2 ps. An analysis of the temporal spectral evolution of the ν_3 -band after TBFC excitation showed that CO₂ is released with high initial vibrational energy. Recent UV photoexcitation studies of our group on various aromatic peroxyesters, diacyl peroxides, and peroxy carbonates also indicate that intermediate carbonyloxy radicals may contain considerable vibrational excess energy and undergo extremely rapid decarboxylation.^{8–10}

To clarify this apparent discrepancy about decomposition rate of MeFl-CO₂ radicals from photodissociation of TBFC, we carried out femtosecond (fs) time-resolved experiments on UV-induced (266 nm) decomposition of TBFC in propylene carbonate (PC) solution. The decomposition of TBFC yields a *tert*-butoxy radical and an intermediate MeFl-CO₂ radical. The latter decarboxylates producing a MeFl radical (see Scheme 1). As we have shown recently,^{8–10} investigation of this type of reactions with femtosecond time resolution in conjunction with modeling via statistical unimolecular rate theory based on data obtained from quantum-chemical calculations is highly advantageous. The modeling helps to identify a priori unknown reaction pathways.

II. Experimental Techniques and Theoretical Methods

The Ti:sapphire laser amplifier system employed in the present study has already been described in detail elsewhere.²⁰ Of the pulse energy at 800 nm, 30% was used for third-harmonic generation at 266 nm, while the remaining part of the regenerative amplifier output was used to pump an optical parametric amplifier (TOPAS, Light Conversion). The TOPAS output was frequency mixed to provide the probe wavelengths. The two laser pulses were mildly focused ($f = 200$ mm) and overlapped in time in a fast-flow cell (0.1–0.2 mm path length), containing peroxide solutions of optical density (OD) close to 1 at the pump wavelength. To avoid two-photon absorption, the pump pulses were attenuated to 1 μ J in energy. Pump and probe pulses with relative polarization at the magic angle (54.7°) in a nearly collinear pump–probe geometry (5°) were chosen for the experiments. Transient difference absorbance (optical density), Δ OD, was recorded at a 1 kHz repetition rate. A time resolution of typically 100 to 200 fs was achieved. TBFC was kindly provided by AKZO Nobel (Research Center Deventer, The Netherlands) in high purity (>99%). Propylene carbonate of high purity ($\geq 99\%$, Fluka) was used as supplied.

As in our previous work on the 1-naphthoyloxy,⁸ benzoyloxy,⁹ phenyloxycarbonyloxy,²¹ benzylcarbonyloxy,²¹ and 2-naphthylloxycarbonyloxy²¹ radicals, density functional theory (DFT) calculations were performed employing the variant UB3LYP^{22,23} as implemented into the GAUSSIAN98 package²⁴ in conjunction with the 6-31G(d), 6-311+G(2d,p), and 6-311+G(2df,2pd) basis sets. At three stationary points (reactants, products, and first-order saddle points pertinent to decar-

boxylation) on the potential energy surface (PES) that were optimized using the 6-31G(d) basis set, single-point calculations with the two larger basis sets were performed. The stationary points were characterized by the Hessian matrices, and transition state geometries were confirmed using the intrinsic reaction coordinate (IRC) method.^{25,26} The energies were corrected for zero-point vibrational energy effects (at the harmonic level with the imaginary frequency excluded). The saddle point structure turns out to be very close to the reactant geometry with the breaking bond being only slightly elongated. Thus, nondynamical electron correlation effects should play only a minor role. After refining the UB3LYP/6-31G(d) geometries employing additional diffuse basis functions (6-31+G(d)) to account for the “loose” structure at the saddle point, we found only a vanishingly small effect on the geometries and energies.

III. Results and Discussion

In previous studies, the formation of CO₂⁷ and MeFl¹¹ after photolysis of TBFC was probed with time resolutions of about 2 ps⁷ and 20 ps,¹¹ respectively, which, as we found recently, is insufficient for monitoring the extremely rapid decarboxylation of vibrationally hot intermediate radicals.

As band overlap of intermediate and product radical species in a condensed phase may pose problems for an unambiguous assignment of transient absorbance traces,^{8,27} suitable wavelengths for measuring the concentrations of the various species need to be carefully selected.

After photolysis of TBFC in PC solution at 266 nm, the transient absorbance, Δ OD, was recorded at various probe wavelengths between 400 and 883 nm in order to identify a suitable spectral window for monitoring MeFl–CO₂ concentration. Typical experimental traces are shown in Figure 1. For the entire series of detection wavelengths, an initial peak is seen around $t = 0$ ps. Although nonlinear artifacts generated in the solvent by pump and probe pulses may contribute to a minor extent, the instantaneous rise is predominantly due to the formation of carbonyloxy radicals within the pump–probe cross correlation time of 100 to 200 fs. A pronounced decay of absorbance occurs within the first few picoseconds, while at delay times greater than 5 ps, the absorbance is almost constant. The absorbance plateau is relatively high at and below 594 nm and small at 766 and 883 nm. A UV–VIS absorption spectrum (recorded with a VARIAN Cary5E spectrometer) of the parent peroxide (TBFC) in propylene carbonate solution did not show any significant absorbance at wavelengths above 320 nm. While it seems unlikely that the *tert*-butoxy product radical contributes to the transient absorbance in our detection range between 400 and 883 nm,²⁸ it is known that the 9-methylfluorenyl radical absorbs in the VIS region.¹¹ This absorbance should, however,

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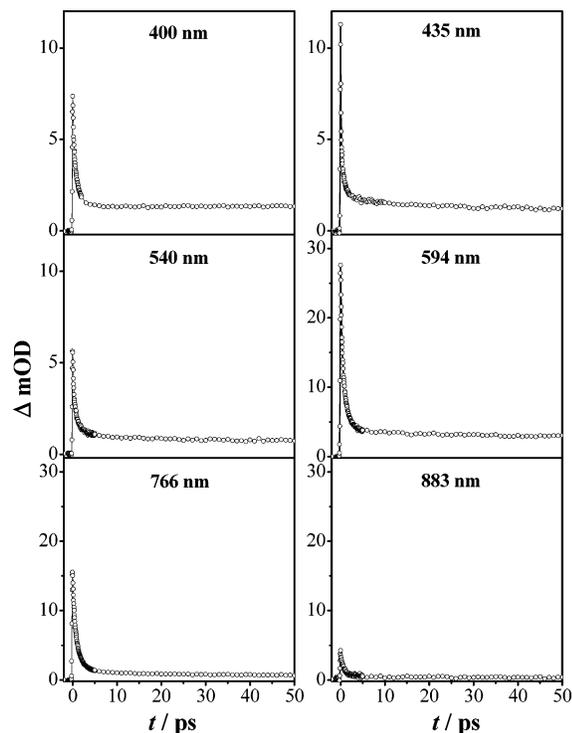


Figure 1. Transient absorbance after photolysis of TBFC in propylene carbonate solution at 266 nm monitored at different wavelengths as indicated. Note the different ordinate scales.

be negligible at the largest probe wavelengths of our experiments (766 and 883 nm). A comparison of the transient absorbance recorded at these two wavelengths shows virtually identical kinetics, which strongly suggests that absorbance is mostly due to MeFl-CO₂. In contrast, the pronounced “off-set” in absorbance at larger delay times, seen at shorter probe wavelengths, indicates significant contributions of the 9-methylfluorenyl radical. Therefore, the transient absorbance traces at 766 and 883 nm appear to be very suitable for spectroscopic observation of the intermediate carbonyloxy radical. Because of the better signal-to-noise ratio, the decay recorded at 766 nm is selected for quantitative analysis of decarboxylation kinetics of the MeFl-CO₂ radical.

TBFC decarboxylation has previously been investigated in our group by picosecond time-resolved UV pump-IR probe spectroscopy.⁷ The time evolution of CO₂ concentration has been monitored via the integrated absorbance of the ν_3 IR-absorption band. The comparison of the so-obtained time dependence of CO₂ concentration with the inverted transient absorbance of the MeFl-CO₂ radical measured at 766 nm is shown in Figure 2. Both curves exhibit a rather similar, steplike rise within the first few picoseconds followed by almost no further change. Unfortunately, the dynamic range of the IR experiment did not allow to precisely measure CO₂ formation at long time scales.²⁹ However, in contrast to the time constant of 55 ps reported by Falvey and Schuster,¹¹ the data indicate that only a small fraction of the almost instantaneously produced intermediate MeFl-CO₂ radicals survives the first few picoseconds.

(29) A small decrease in the signal at delay times above 10 ps most likely originates from a small temperature dependence of the integrated absorption coefficient (vibrational intensity) of the ν_3 mode of CO₂ and did not allow for an observation of minor contributions in this time window in the IR experiment. See ref 7 for more details.

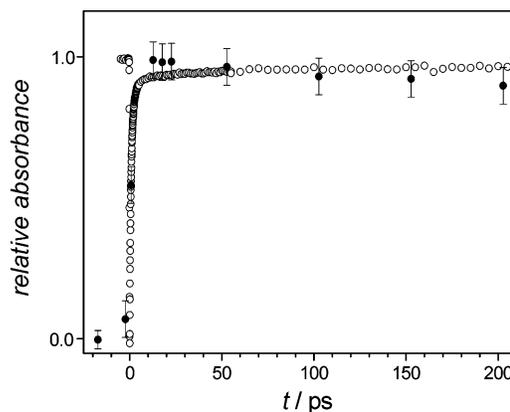


Figure 2. Change in relative absorbance measured after photolysis of TBFC. Open symbols: inverted decay of MeFl-CO₂ radical absorbance measured at 766 nm (solvent propylene carbonate; photolysis at 266 nm). Solid symbols: CO₂ product absorbance deduced from the integrated absorption at 4.3 μm (solvent CCl₄; photolysis at 308 nm).⁷

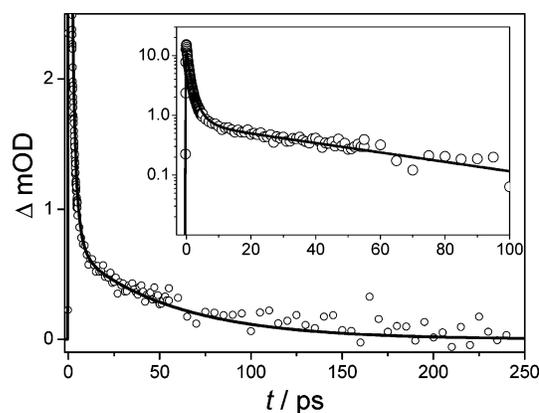


Figure 3. Transient absorbance of MeFl-CO₂ radicals (○) at 766 nm during photoinduced (266 nm) decomposition of TBFC in propylene carbonate. Solid line: simulation of MeFl-CO₂ decarboxylation using the parameters $\langle E_{\text{vib}} \rangle = 19\,500\text{ cm}^{-1}$, $E_0 = 3.1\text{ kcal mol}^{-1}$, and $\tau_{\text{VET}} = 4\text{ ps}$. Given in the inset is a log $\Delta m\text{OD}$ vs time plot. For further details see text.

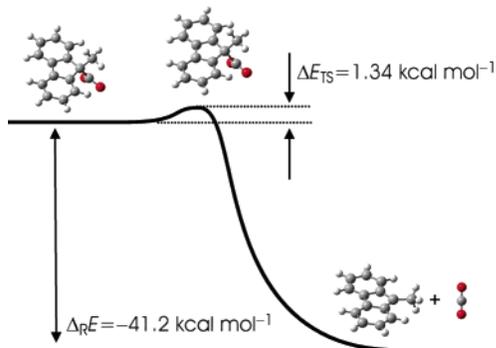
The rapid decay of MeFl-CO₂ concentration in the early picoseconds region is shown in Figure 3 on both a linear and a logarithmic absorbance scale. Surprisingly, at delay times above 10 ps, the absorbance versus time trace shows an almost single-exponential decay of the remaining small fraction of MeFl-CO₂ radicals with a time constant of $55 \pm 5\text{ ps}$. This number is in close agreement with the value reported for formation of the 9-methylfluorenyl product radical in ref 11. We assume that this larger time constant for the reaction of a minor fraction of the initially generated MeFl-CO₂ radicals reflects the decarboxylation of thermally equilibrated radicals at ambient temperature. The fast initial decay, on the other hand, represents the decarboxylation reaction of vibrationally excited MeFl-CO₂ radicals. To verify this interpretation, overall decarboxylation was modeled via statistical unimolecular rate theory.

Recently, we presented an analysis of the photoinduced decarboxylation reaction of di(1-naphthoyl)peroxide⁸ and of di-(4-methoxybenzoyl)peroxide.³⁰ These reactions could adequately be described by a model based on statistical unimolecular rate theory and by assuming decarboxylation to occur across a potential barrier on the ground state potential energy surface

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Table 1. Harmonic Vibrational Frequencies (in cm^{-1}) of the normal Modes of the Reactant ($\text{MeFl}-\text{CO}_2$) and at the Saddle Point (TS) Geometry Pertinent to Decarboxylation; Results from UB3LYP/6-31G(d) Calculations

MeFl-CO ₂	TS
44, 64, 94, 105, 150, 184, 214, 229, 248, 287, 312, 374, 404, 426, 443, 492, 519, 545, 573, 590, 630, 638, 709, 723, 751, 769, 774, 778, 803, 865, 883, 892, 908, 946, 947, 985, 988, 1025, 1051, 1054, 1062, 1102, 1132, 1143, 1155, 1193, 1194, 1219, 1226, 1245, 1267, 1327, 1336, 1358, 1394, 1429, 1478, 1495, 1514, 1517, 1523, 1526, 1544, 1628, 1636, 1657, 1658, 3062, 3135, 3148, 3186, 3188, 3196, 3198, 3205, 3206, 3215, 3215	618i (reaction coordinate), 60, 67, 105, 110, 167, 193, 218, 242, 246, 302, 311, 371, 419, 428, 451, 501, 521, 549, 566, 623, 635, 673, 723, 740, 756, 771, 779, 803, 820, 856, 883, 890, 947, 956, 987, 992, 1020, 1036, 1044, 1053, 1055, 1104, 1136, 1141, 1153, 1194, 1195, 1229, 1246, 1270, 1327, 1341, 1363, 1390, 1422, 1475, 1493, 1507, 1518, 1522, 1526, 1617, 1623, 1645, 1653, 1712, 3061, 3130, 3157, 3187, 3190, 3196, 3201, 3205, 3211, 3215, 3225

**Figure 4.** Energetics of $\text{MeFl}-\text{CO}_2$ radical decarboxylation obtained from DFT calculations (UB3LYP/6-311+G(2df,2pd)//6-31G(d)). Δ_{RE} and ΔE_{TS} denote the reaction energy and the barrier height toward decarboxylation, respectively. Correction for zero-point vibrational energy effects (UB3LYP/6-31G(d)) results in $\Delta_{\text{RE}0} = -42.1 \text{ kcal mol}^{-1}$ and $E_0 = 0.38 \text{ kcal mol}^{-1}$, respectively.

(PES).^{8–10,30} Electronically excited states of carbonyloxy radicals, which may give rise to ultrafast direct decarboxylation,^{9,10} are not accessible with these particular peroxides if photoexcitation is carried out at 266 nm. The simple model described in detail in refs 8 and 9 will now be applied toward the decarboxylation of $\text{MeFl}-\text{CO}_2$ radicals.

Microcanonical reaction rate constants were calculated using eq 1³¹

$$k(E) = \frac{W^\ddagger(E - E_0)}{h \cdot \rho(E)} \quad (1)$$

with $W^\ddagger(E - E_0)$ and $\rho(E)$ being the number of transition state levels and the density of reactant states, respectively. Energies of the reactant, the transition state, and the products of $\text{MeFl}-\text{CO}_2$ decarboxylation as well as the ground and transition state vibrational frequencies (see Table 1) of $\text{MeFl}-\text{CO}_2$ were obtained from DFT calculations.

The UB3LYP/6-31G(d) calculations reveal that the geometry at the saddle point pertinent to decarboxylation on the ground state PES is very close to that of the reactant species (Figure 4). In the transition state, the C–CO₂ bond distance is elongated by 0.07 Å to 1.59 Å while the O–C–O angle is widened by 14.6° to 129.4°. The classical barrier height ΔE_{TS} is obtained from single-point calculations to be 1.51 kcal mol^{-1} and 1.34 kcal mol^{-1} with the 6-311+G(2d,p) and 6-311+G(2df,2pd) basis sets, respectively. The reaction coordinate is described as

C–CO₂ bond fission accompanied by the CO₂ unit attaining a linear geometry and the carbon atom of the exocyclic methyl group becoming coplanar with the ring system. The reaction energy obtained from single-point calculations to be $\Delta_{\text{RE}} = -40.0 \text{ kcal mol}^{-1}$ (UB3LYP/6-311+G(2d,p)) or $\Delta_{\text{RE}} = -41.2 \text{ kcal mol}^{-1}$ (UB3LYP/6-311+G(2df,2pd)) is particularly large because of the formation of CO₂ and of a very stable product radical, in which the singly occupied p orbital at the 1-carbon atom is part of molecular orbitals that are delocalized over the entire tricyclic system.

The time-resolved traces of $\text{MeFl}-\text{CO}_2$ concentration, to be compared with the measured transient absorbance at 766 nm, are simulated with a simple master equation (or stepladder) model.^{8,9} Intermolecular vibrational energy transfer was globally taken into account by assuming first-order relaxation of the internal energy distribution $f(E)$ of $\text{MeFl}-\text{CO}_2$ radicals with an overall phenomenological relaxation time, τ_{VET} . The zero-point energy corrected barrier height E_0 for decarboxylation was adjusted to 3.1 kcal mol^{-1} to fit decarboxylation at ambient temperature. This number is close to the value from the DFT calculations. The accurate value for E_0 determined the short-time behavior at delays below 10 ps. The initial ($t = 0$) internal energy of the $\text{MeFl}-\text{CO}_2$ radical after photoinduced dissociation of TBFC is estimated from the pump energy at 266 nm and from the dissociation energy of TBFC (calculated via UB3LYP/6-311+G(2df,2pd)//6-31G(d) to be 22.5 kcal mol^{-1}) under the assumption, that the initial excess energy is statistically distributed among all vibrational degrees of freedom of the two ground state radicals, $\text{MeFl}-\text{CO}_2$ and *tert*-butoxy. The resulting mean energy $\langle E \rangle$ of nascent $\text{MeFl}-\text{CO}_2$ radicals is 19 500 cm^{-1} , which was converted to a vibrational temperature of 870 K according to

$$\langle E \rangle = \sum_{i=1}^{78} \frac{\hbar \omega_i}{\exp(\hbar \omega_i / k_{\text{B}} T) - 1} \quad (2)$$

where ω_i are the corresponding normal-mode frequencies from Table 1 and k_{B} is Boltzmann's constant.

With this initial excess energy and with a relaxation time of $\tau_{\text{VET}} = 4 \text{ ps}$ for intermolecular energy transfer, the modeling via eq 1 gives an excellent representation (full line in Figure 3) of the measured transient absorbance over the entire range of delay times. As the barrier height is determined by the long-time kinetics, the only parameter in our modeling is the energy transfer time. Assuming that the dissociation of the intermediate proceeds exclusively on the electronic ground state PES, we

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found τ_{VET} to be about a factor of 2 below the one found for energy relaxation of several smaller carbonyloxy radicals in the same solvent.¹⁰

In view of our recent results on the decomposition of *tert*-butyl peroxyesters involving electronically excited states of intermediate carbonyloxy radicals,^{9,10} a participation of excited states of MeFl-CO₂ radicals in the photolysis of TBFC at 266 nm cannot be ruled out. If we assume that τ_{VET} is closer to the value used with other carbonyloxy radicals ($\tau_{\text{VET}} = 7.5$ ps),⁸⁻¹⁰ kinetic modeling suggests that decarboxylation of MeFl-CO₂ radicals via low-lying electronically excited states contributes to the rapid initial decay. Modeling of MeFl-CO₂ radical decarboxylation via electronically excited states¹⁰ requires accurate PESs of electronically excited states, which presently are out of reach for MeFl-CO₂. The potential contribution of an additional very fast reaction channel does not, however, affect the conclusion of the paper, that rapid (around 2 ps or below) and slow (around 55 ps) decarboxylation processes are occurring after photoexcitation of TBFC at 266 nm.

The findings of the present paper have implications on studies in which the photochemical decarboxylation of MeFl-CO₂ radicals is used as a reference reaction. For example, Hilborn and Pincock investigated the decarboxylation of a series of carbonyloxy radicals, which are formed upon light-induced (Pyrex-filtered mercury lamp) decomposition of substituted 1-naphthylmethyl alkanates.¹⁹ Rate constant determination was based on measured product yields, on a suggested reaction mechanism, and on the reference rate constant given by Falvey and Schuster for the decarboxylation of the MeFl-CO₂ radical.¹¹ According to our analysis, the reported value represents the decarboxylation time constant of MeFl-CO₂ radicals at ambient temperature. In situations, where carbonyloxy radicals are generated via photoexcitation of molecular precursors, these radicals may be produced with high excess energies. If this is the case, a rate constant describing the main decarboxylation channel deduced from a time-resolved experiment may be significantly above the value referring to ambient temperature. With the MeFl-CO₂ radical, photoexcitation of TBFC at 266 nm results in a decarboxylation rate which is by more than one order of magnitude above the value for decarboxylation of thermally equilibrated MeFl-CO₂ radicals at ambient temperature. Hilborn and Pincock may have underestimated the rate constants of carbonyloxy radical decomposition. This conclusion was supported by our recent investigation of the decarboxylation of benzylcarbonyloxy radicals, PhCH₂-CO₂, where we found a rate constant of $k = 1.3 \times 10^{10} \text{ s}^{-1}$ in PC solution¹⁰ and Hilborn and Pincock report

$k = 5 \times 10^9 \text{ s}^{-1}$ for decarboxylation in methanol.¹⁹ It appears unlikely that solvent effects give rise to this difference.

In summary, the laser light-induced decarboxylation of TBFC in propylene carbonate solution has been studied with femtosecond time resolution. An initial very fast decarboxylation of the intermediate MeFl-CO₂ radical is observed followed by a slower decomposition with a time constant of about 55 ps. In an earlier experiment by Falvey and Schuster¹¹ the *ultrafast component*, which is the main reaction channel in the decarboxylation of MeFl-CO₂ radicals *after* photolysis of TBFC, could not be resolved. The authors attributed their measured decarboxylation time constant of 55 ps to the characteristic reaction time of the decomposition of MeFl-CO₂ radicals after photoexcitation of the parent peroxide. In light of the present findings, this assignment is incomplete and may be misleading as this time constant refers only to the decarboxylation channel of the minor fraction of MeFl-CO₂ radicals that has relaxed to ambient temperature.

The fast decomposition of MeFl-CO₂ radicals may be satisfactorily explained by the small barrier E_0 for the ground state reaction in conjunction with high excess energy available after photoexcitation of the parent peroxide. Neglecting electronically excited states of MeFl-CO₂ radicals, photodissociation of TBFC at 266 nm produces MeFl-CO₂ radicals with considerable internal energy, corresponding to initial vibrational temperatures up to 870 K. The reaction of MeFl-CO₂ radicals at such high temperatures is expected to be more than one order of magnitude faster than the one of the equilibrated species. Another possible reason for the experimental findings may be (at least in part) a fast and direct dissociation via electronically excited states, such as found for other peroxides.¹⁰ As in our previous studies, femtosecond time resolution and statistical unimolecular rate theory based upon DFT calculations have been the key to understand the seemingly simple but obviously complicated decarboxylation dynamics of intermediate MeFl-CO₂ radicals.

Acknowledgment. The authors acknowledge generous financial support by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 357 (*“Molekulare Mechanismen Unimolekularer Reaktionen”*). We are grateful to AKZO Nobel for providing the peroxide sample, to Dr. J. A β mann and Dipl.-Chem. T. Witte for their experimental support, and to Professors P. Botschwina and J. Troe for stimulating discussions on various aspects of this work.

JA036304D