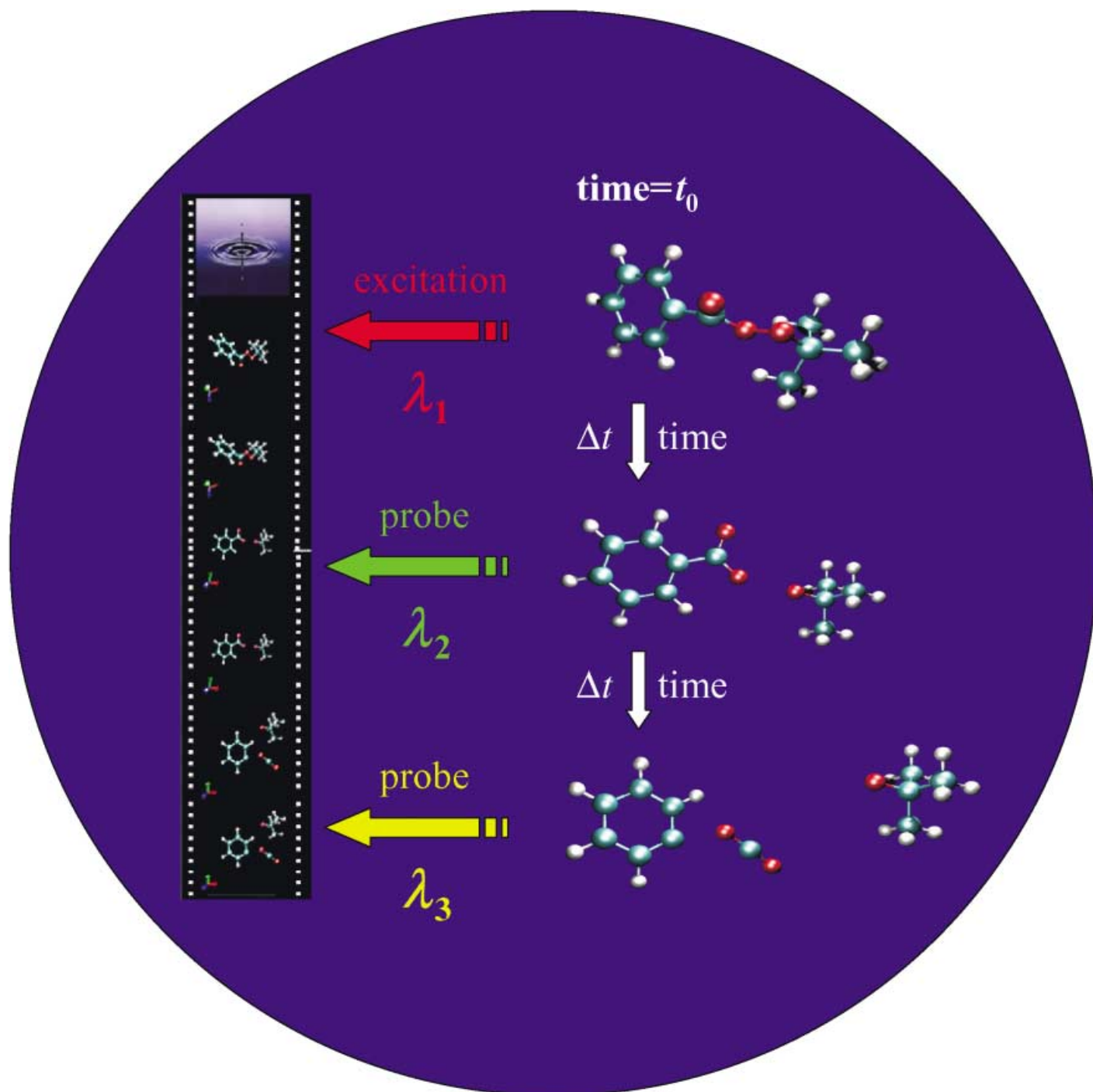


Communications



Watching photoinduced chemical reactions in solution in real time by femtosecond spectroscopy. For more information, see the Communication by B. Abel and S. Schmatz et al. on the following pages.



Ultrafast Decarboxylation of Organic Peroxides in Solution: Interplay of Different Spectroscopic Techniques, Quantum Chemistry, and Theoretical Modeling**

Bernd Abel,* Jens Aßmann, Michael Buback, Matthias Kling, Stefan Schmatz,* and Jörg Schroeder

Dedicated to Professor Dr. Lutz F. Tietze on the occasion of his 60th birthday

Studies of the decomposition of organic peroxides are of fundamental interest and importance for application-oriented polymer chemistry. The time scales of the formation of free-radical intermediates and of subsequent processes, including unimolecular decomposition of intermediates, ultimately determine the initiator efficiency in radical polymerizations.^[1–4] A large body of literature on thermal peroxide decomposition has accumulated.^[5,6] Photochemical decomposition has almost exclusively been investigated in the nanosecond to microsecond time domain by means of visible absorption and EPR spectroscopy.^[7–10] As a result of the poor time resolution, a complete mechanistic understanding of the elementary reactions of peroxide decomposition has not been possible. Even subsequent experiments with picosecond (ps) time resolution did not provide detailed unambiguous mechanistic insight,^[1–3,11,12] mostly because of insufficient time resolution and spectral overlap of transient absorption bands. More recently, the formation of CO₂ and its subsequent vibrational cooling after peroxide decomposition could be monitored with about 2–5-ps time resolution by transient IR spectroscopy.^[1–3] These studies clearly indicate that femtosecond (fs) time resolution is required for a detailed understanding of the mechanisms.^[1–3] While a recent paper focuses on experimental studies of peroxide decomposition on the femtosecond (fs) timescale,^[13] we describe herein time-resolved

monitoring of transient intermediates and products in peroxide decarboxylation with ultrafast fs spectroscopy in combination with high-level quantum chemistry and theoretical modeling. Although we have investigated a considerable number of different peroxides, we only discuss di-1-naphthoyl peroxide (DNPO) as an example of our strategy (Figure 1).

DNPO photodissociation yields 1-naphthoyloxy free-radical intermediates and, as products, naphthyl radicals and CO₂. As shown for the photodecomposition of DNPO in Figure 1, the decay of transient 1-naphthoyloxy radicals and the formation of products can be probed directly by ultrafast transient absorption spectroscopy in different spectral regions: 1-naphthoyloxy radicals can conveniently be detected in the visible region,^[14] whereas CO₂ is detected through the IR absorption of ν_3 fundamental.^[1] Competing processes such as vibrational cooling of hot intermediates^[15–18] may also produce overlapping spectral absorptions on a similar time scale to that of photoinduced peroxide decarboxylation

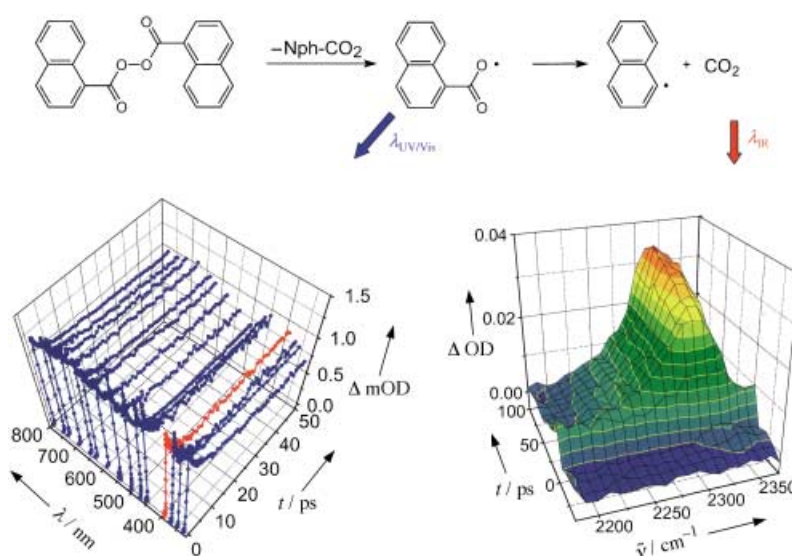


Figure 1. Decarboxylation of dinaphthoyl peroxide (DNPO). Left: transient decays at probe wavelengths in the visible spectral region; right: complementary transient spectra of nascent “hot” CO₂ with an absorption at around 2340 cm⁻¹.

kinetics in solution. It was thus necessary to scan the probe wavelength over broad wavelength ranges (UV to IR) to identify suitable spectral observation windows.

Transient absorption profiles after excitation of DNPO in a solution of propylene carbonate (PC) at 266 nm and probing the subsequent transient absorption in the 300–800-nm spectral range are shown on the left-hand side of Figure 1. A characteristic feature of these traces is the rapid rise in absorbance within 1 ps, which is attributed to the extremely fast formation of “hot” 1-naphthoyloxy radicals. Whereas the hot radicals in turn dissociate on a ps time scale (as is indicated by the fast absorbance decay), the relaxed radicals decompose on a much longer timescale, which manifests itself in the “offset” of the decay traces. At long delay times, two broad absorption bands of 1-naphthoyloxy radicals can be identified, which agree with the transient spectra reported by Tateno et al.^[14] From an analysis of several absorption signals,

[*] Prof. Dr. B. Abel, Priv.-Doz. Dr. S. Schmatz, Dr. J. Aßmann, Prof. Dr. M. Buback, Dr. M. Kling, Prof. Dr. J. Schroeder
Institut für Physikalische Chemie, Universität Göttingen
Tammannstrasse 6, 37077 Göttingen (Germany)
Fax: (+49) 551-39-3150
E-mail: babel@gwdg.de
sschmat@gwdg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 357) and AKZO Nobel. The authors gratefully acknowledge interesting discussions of several aspects of this work with Prof. P. Botschwina and Prof. J. Troe.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

we found two nearly optimal spectral windows at 390 and 620 nm for the sensitive and unperturbed quantitative observation of the intermediate radical. The diagram on the right-hand side of Figure 1 shows a 3D plot of the time-resolved IR absorbance of the asymmetric stretch of CO₂. The nascent CO₂ product is vibrationally excited as indicated by the initially broad spectrum, which subsequently shifts and narrows as the molecule cools to ambient temperature. These spectra provide information about the rate of CO₂ formation, the initial CO₂ energy content after decarboxylation, and the vibrational cooling dynamics in the particular solvent. In Figure 2 we compare the rise of the ν_3 band integral

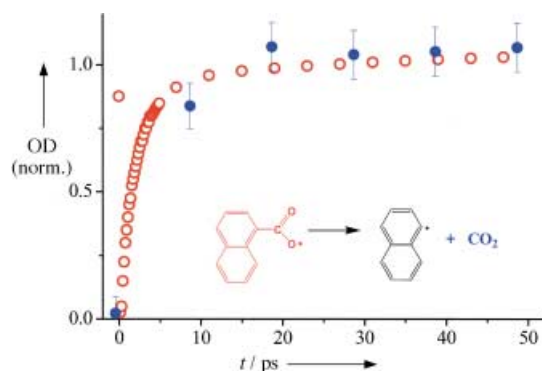


Figure 2. Comparison of the decay of the intermediate naphthoyloxy radical and formation of CO₂ from different experiments. ○: inverted (normalized) transient absorption of the 1-naphthoyloxy radical monitored at 390 nm after excitation of DNPO at 266 nm; ●: integrated absorption of the nascent CO₂ molecule at around 4.3 μm after photodissociation of DNPO at 308 nm^[1] (see also Figure 1).

absorption of nascent CO₂ from Figure 1 with the inverted and normalized transient absorption decay of naphthoyloxy radicals at 390 nm. The good agreement between the two traces demonstrates that the observed transient decay of the intermediate radical in the visible spectral region correlates with the formation of CO₂.

The rigorous theoretical treatment of chemical transformations in solution is still a difficult task. Our analysis of peroxide decomposition is based upon the following approximations and assumptions: We assume that absorption at 266 nm excites the peroxide into the electronically excited (repulsive) S₁ state from which the molecule decomposes within one vibrational period and produces intermediate species in their respective electronic ground states. It is reasonable to assume that elimination of CO₂ occurs through a fast sequential mechanism (which appears to be the rule rather than the exception in the decomposition of organic peroxides).^[19] The vibrationally hot intermediate radicals on the ground-state potential-energy surface (PES) rapidly dissociate in a statistical unimolecular barrier reaction to the products or cool down to ambient temperature and subsequently react in a much slower thermal reaction. Both cases can be treated quantitatively by unimolecular rate theory. The energetics for the intermediate 1-naphthoyloxy radical from DNPO dissociation is depicted in Figure 3. The rate constants of the fragmentation of the 1-naphthoyloxy

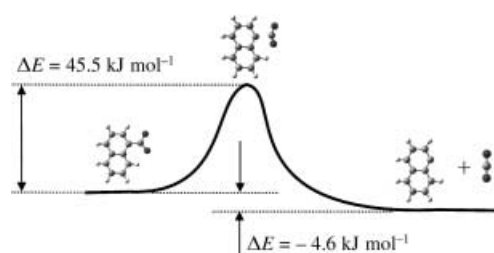


Figure 3. Energetics of 1-naphthoyloxy radical decomposition from DFT calculations. $\Delta_r H^\circ$ (298 K) = -9.4 kJ mol^{-1} (B3LYP/6-311 + G(2d,p), zero-point energy corrected barrier height $E_0 = 39.0 \text{ kJ mol}^{-1}$ (B3LYP/6-311 + G(2d,p)//6-31G(d)).

radical can be calculated by statistical unimolecular rate theory if the barrier height and the vibrational frequencies of the radical in its equilibrium and transition-state geometry are available from high-level quantum-chemical calculations. The underlying assumption of this approach is that the initial excess energy is statistically distributed among the radical fragments such that a temperature may be assigned to the intermediates and to the end products.

Our approach is actually a predictive modeling of experimental curves without parameter fitting, which—as shown below—works well for diaryl peroxides in nonpolar and/or weakly interacting solvents. In fact, DNPO appears to be a prototype system because the corresponding intermediate naphthoyloxy radical reaction proceeds exclusively on the ground-state PES. Density-functional theory (DFT) was used to calculate the barrier height, energies of all species, and the frequencies of the normal modes on the ground-state PES.^[20] The hybrid functionals B3LYP and B3PW91 were used in conjunction with basis sets of up to 393 contracted Gaussian orbitals. Kieninger et al. have reported extensive B3LYP and B3PW91 calculations for HCOO and CH₃COO radicals.^[21] Furthermore, these authors report B3PW91 calculations of the energetics of the benzoyloxy radical. A comparison of their DFT calculations with results obtained on the CASPT2/ANO and MP2 level indicated that DFT calculations can provide reasonable data for free-radical species such as those used in our studies.

The microcanonical (statistical) specific rate constant for a molecule that overcomes a distinct barrier of height E_0 in a reaction to form products is given by [Eq. (1)].

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

The terms $W(E-E_0)$ and $\rho(E)$ describe the number of energetically accessible transition-state energy levels and the density of states of the reactant molecules at energy E , respectively. The barrier was calculated to be $E_0 = 39.0 \text{ kJ mol}^{-1}$. The calculated frequencies of the reactant and the transition state are given in the Supporting Information. The normal mode Q_{TS} , which corresponds to the reaction coordinate ($\omega_{\text{TS}} = 313i \text{ cm}^{-1}$), is characterized by a simultaneous stretching of the nph-CO₂ bond and widening of the O-C-O angle toward linear CO₂ (Figure 3). From the excess energy $h\nu - E_0$ ($h\nu$ = photon energy at the excitation wavelength), the initial internal energy $\langle E \rangle_{\text{ini}}$ of the intermediate

radical was estimated based on the assumption that the excess energy was statistically distributed among all vibrational degrees of freedom of the two fragments. For the nascent 1-naphthoyloxy radical, we found $\langle E \rangle_{\text{ini}} = 172 \text{ kJ mol}^{-1}$, which corresponds to an initial vibrational temperature $T_{\text{ini}} = 910 \text{ K}$. The subsequent time evolution of energy level populations $n(i, t)$ as a result of cooling and fragmentation of hot radicals was calculated with a stepladder model, which includes the rates of stepwise energy transfer to the solvent and the energy-dependent rates of the fragmentation. Energy transfer was globally taken into account by a simple model that mimics a first-order energy relaxation with an overall phenomenological vibrational energy transfer (VET) relaxation time constant of $\tau_{\text{VET}} = (7.5 \pm 1.5) \text{ ps}$. Strictly speaking, τ_{VET} is a parameter in our calculation that was taken from experimental relaxation studies in solution (propylene carbonate) for molecules of comparable complexity and with a similar number of vibrational degrees of freedom.^[17,22] Normalized concentration–time profiles, $S(t)_{\text{norm}}$, of the hot 1-naphthoyloxy radical were calculated according to Eq. (2) and convolution with the cross-correlation function of the two laser pulses.

$$S(t)_{\text{norm}} = \frac{\sum_i n(i, t)}{\sum_i n(i, t=0)} \quad (2)$$

An experimental 1-naphthoyloxy radical transient absorbance trace (○) recorded at 390 nm (compare to red curve in Figure 1) is presented in Figure 4 together with the result of a model calculation based on energies, barrier heights, and vibrational frequencies from our DFT computations (full red line). To illustrate the effective time resolution of the experiment, the cross-correlation function between pump and probe pulses is given together with the experimental signal in the insert of Figure 4. The agreement between the experiment and the theoretical model in this particular case is very satisfactory. Notably, the long-time behavior of the

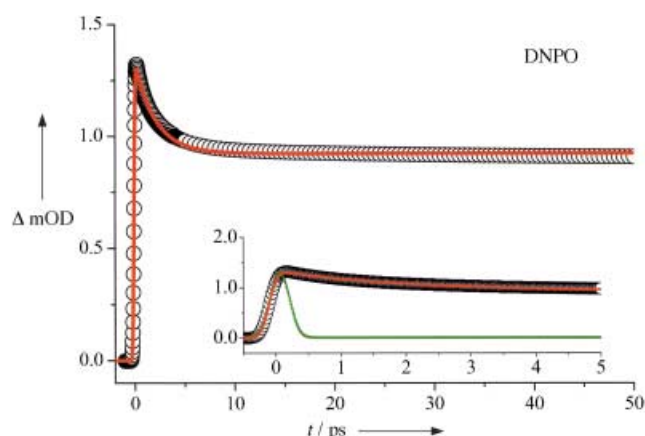


Figure 4. Experiment (○) and simulation (red solid line) of the formation and decay of the 1-naphthoyloxy radical in photoinduced DNPO decomposition in propylene carbonate. The cross-correlation of the pump and probe pulses at 266 nm and 390 nm (green line) in the insert indicates the time resolution of the experiment.

transients is a result of the slow thermal fragmentation of the intermediate radical at ambient temperature which is accounted for in the modeling. The excellent representation of the measured signal indicates that the rate constants as well as the calculated barriers adequately describe the ultrafast as well as the long-time kinetics (i.e., about $1/3$ and $2/3$, respectively, of the overall decarboxylation) beyond the ps timescale.

The successful modeling of the photodissociation dynamics of DNPO is probably a result of the fact that DNPO is an almost ideal system because the reaction of the intermediate proceeds exclusively on the ground-state PES. Although DFT calculations were not expected to yield barrier heights to an accuracy much better than a few kcal mol^{-1} , our calculated barrier for DNPO agrees with the experimentally determined value to within 1–2 kcal mol^{-1} .^[14] However, some favorable error compensation in the calculation cannot be ruled out. Furthermore, τ_{VET} is a parameter rather than a precisely known energy-transfer coefficient, which may be significantly different for other solvents such as CCl_4 .^[23] Recently, the model was also used successfully for the analysis of the dissociation dynamics of other peroxides. It was found that in some cases the model needs to be extended to include direct dissociation from electronically excited states of the intermediates.^[23]

In summary, we have demonstrated that ultrafast spectroscopy in the UV/Vis and in the IR spectral range in combination with quantum-chemical calculations is a powerful tool for probing and understanding photoinduced “femtochemistry” (of DNPO) in solution. A high time resolution and broad spectral tunability are indispensable to identify species unambiguously and to monitor their kinetics, whereas quantum theory and theoretical modeling provide the key to decode the experimental data.

Experimental Section

In the experiments a commercial Ti:sapphire laser system with regenerative amplification (Clark CPA-2001) and 150-fs time resolution pumped two tunable optical parametric amplifiers (NOPA, Clark and TOPAS, Light Conversion). λ_{pump} was tuned to a broad electronic absorption band of the peroxides at 266 nm, and λ_{probe} was varied between 300 and 800 nm. The two laser pulses with relative polarizations at the magic angle (54.7°) were weakly focused ($f = 200 \text{ mm}$) and overlapped in a nearly collinear pump/probe geometry (5°) in a fast-flow cell (path length: 0.1–0.2 mm). Transient absorption differences were recorded at a repetition rate of 1 kHz. The experimental setup for transient IR absorption spectroscopy with ps time resolution was described elsewhere.^[24] The peroxides were synthesized and kindly provided by AKZO Nobel (Research Center Deventer, The Netherlands) and used without further purification.

Received: June 6, 2002

Revised: September 19, 2002 [Z19490]

- [1] J. Aschenbrücker, M. Buback, N. P. Ernstring, J. Schroeder, U. Steegmüller, *Ber. Bunsen-Ges.* **1998**, *102*, 965.
- [2] J. Aschenbrücker, M. Buback, N. P. Ernstring, J. Schroeder, U. Steegmüller, *J. Phys. Chem. B* **1998**, *102*, 5552.

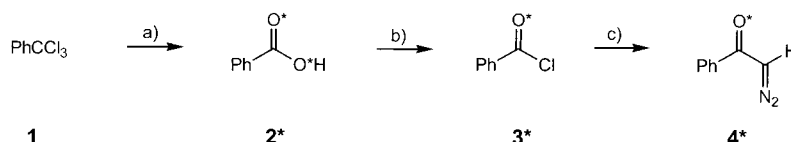
- [3] M. Buback, M. Kling, M. T. Seidel, F.-D. Schott, J. Schroeder, U. Steegmüller, *Z. Phys. Chem.* **2001**, *215*, 717.
- [4] C. A. Barson, J. C. Bevington, *J. Polym. Sci. Part A* **1997**, *35*, 2955.
- [5] M. Buback, J. Sandmann, *Z. Phys. Chem.* **2000**, *214*, 583.
- [6] Y. Sawaki in *Organic Peroxides* (Ed.: W. Ando), Wiley, New York, **1992**, p. 425.
- [7] J. Hashimoto, K. Segawa, H. Sakuragi, *Chem. Phys. Lett.* **1999**, *314*, 261.
- [8] J. Wang, T. Tateno, H. Sakuragi, K. Tokumaru, *J. Photochem. Photobiol. A* **1995**, *92*, 53.
- [9] J. Chateaufneuf, J. Luszytk, K. U. Ingold, *J. Am. Chem. Soc.* **1988**, *110*, 2877.
- [10] S. Yamauchi, N. Hirota, S. Takahara, H. Misama, K. Sawabe, H. Sakuragi, K. Tokumaru, *J. Am. Chem. Soc.* **1989**, *111*, 4402.
- [11] D. E. Falvey, G. B. Schuster, *J. Am. Chem. Soc.* **1986**, *108*, 7419.
- [12] E. A. Morlino, M. D. Bohorquez, D. C. Neckers, A. A. J. Rodgers, *J. Am. Chem. Soc.* **1991**, *113*, 3599.
- [13] T. M. Brockman, S. M. Hubig, J. K. Kochi, *J. Org. Chem.* **1997**, *62*, 2210.
- [14] T. Tateno, H. Sakuragi, K. Tokumaru, *Chem. Lett.* **1992**, *20*, 1883.
- [15] A. Charvat, J. Aßmann, B. Abel, D. Schwarzer, *J. Phys. Chem. A* **2001**, *105*, 5071.
- [16] A. Charvat, J. Aßmann, B. Abel, D. Schwarzer, K. Henning, K. Luther, J. Troe, *Phys. Chem. Chem. Phys.* **2001**, *3*, 2230.
- [17] J. C. Owrutsky, D. Raftery, R. M. Hochstrasser, *Annu. Rev. Phys. Chem.* **1994**, *45*, 519.
- [18] R. M. Stratt, M. Maroncelli, *J. Phys. Chem.* **1996**, *100*, 12981.
- [19] C. Maul, K.-H. Gericke, *Int. Rev. Phys. Chem.* **1997**, *16*, 1.
- [20] Gaussian98 (Revision A.7), 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, M. Cossi, R. Cammi, B. Mennucci, 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. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
- [21] M. Kieninger, O. N. Ventura, S. Suhai, *Int. J. Quantum Chem.* **1998**, *70*, 253.
- [22] D. Schwarzer, J. Troe, M. Zerezke, *J. Chem. Phys.* **1997**, *107*, 8380.
- [23] B. Abel, J. Aßmann, P. Botschwina, M. Buback, M. Kling, R. Oswald, S. Schmatz, J. Schroeder, T. Witte, unpublished results.
- [24] J. Aschenbrücker, M. Buback, N. P. Ernstring, J. Jasny, J. Schroeder, U. Stegmüller, *Appl. Phys. B* **1997**, *65*, 441.

Oxygen Labeling and Exchange

Loss of Isotope Labeling in the Conversion of [¹⁸O]₂Benzoic Acid into [¹⁸O]Benzoyl Chloride with Oxalyl Chloride**

Peter Haiss and Klaus-Peter Zeller*

In the course of a study on reaction mechanisms, we needed [¹⁸O]-2-phenyl-2-oxodiazoethane (**4***), which was prepared following the reactions given in Scheme 1. [¹⁸O]Water with an enrichment of 95% ¹⁸O was used as labeling source in the reactions. Based on this, benzoic acid (**2***) formed by the hydrolysis of benzotrichloride (**1**) should have a composition of 90.25% ¹⁸O₂, 9.5% ¹⁶O¹⁸O, and 0.25% ¹⁶O₂. The experimental verification with the help of EI- (positive mode) and ESI-mass spectrometry (negative mode) confirms this isotope distribution (90% ¹⁸O₂, 10% ¹⁶O¹⁸O, < 1% ¹⁶O₂). Dissolution of the labeled benzoic acid in water/acetonitrile does not result in any decrease in the ¹⁸O content.



Scheme 1. Synthesis of α -diazoketone **4***, * = ¹⁸O: a) H₂¹⁸O/110 °C/48 h, ampoule; b) 3 equivalents of (COCl)₂/77 °C/1 h; c) CH₂N₂/Et₂O/0 °C.

For the derivatization of the marked benzoic acid (**2***) to [¹⁸O]benzoyl chloride (**3***), we chose oxalyl chloride on account of its preparative advantage, a decision which led to unexpected consequences. The reaction of benzoyl chloride (**3***) with diazomethane gives the diazoketone **4***, the carbonyl group of which unexpectedly shows two resonance signals with marginally different shifts ($\Delta\delta = 0.03$ ppm) in the ¹³C NMR spectrum (Figure 1 a).

Risley and Van Etten have also reported a similar isotope effect for the ¹³C resonances of [¹⁶O]- and [¹⁸O]-carbonyl groups, in approximately the same range as ours,^[2] in which the signal at a somewhat higher field strength can be assigned to the ¹⁸O isotopomer. It can be seen from the intensities of the resonance signals of **4*** that the required ¹⁸O-isotopomer is formed in only 40%.

At first we thought that a hydration–dehydration sequence involving the formed α diazoketone **4***, because of adventitious moisture present in ethereal diazomethane, could be responsible for the drastic loss of ¹⁸O. This inference

[*] Prof. Dr. K.-P. Zeller, Dipl.-Chem. P. Haiss
 Institut für Organische Chemie
 Universität Tübingen
 Auf der Morgenstelle 18, 72076 Tübingen (Germany)
 Fax: (+49) 7071-29-5076
 E-mail: kpz@uni-tuebingen.de

[**] We thank Prof. Dr. H.-J. Machulla, Sektion für Radiopharmazie, Universitätsklinikum Tübingen, for a generous gift of [¹⁸O]water.