Damped Oscillations in UV−Vis Spectra of Pentazadiene Monomers and Polymers after Laser Photolysis

Th. Kunz,[†] Ch. Hahn,[†] A. Baindl,[‡] O. Nuyken,[‡] Th. Lippert,[†] F. Gassmann,[†] and A. Wokaun*,[†],[§]

General Energy Research, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland, Institute for Makromolekulare Stoffe, TU Munich, D-85747 Garching, Germany, and Department of Industrial Chemistry and Chemical Engineering, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092 Zürich, Switzerland

The photochemical decomposition of substituted 1,5-diaryl-3-alkyl-pentazadiene monomers and polymers induced by UV irradiation with a pulsed excimer laser was monitored by UV−vis spectroscopy. The net photochemical reaction proceeds in an overall one-step pathway A→B. Quantum yields for the laser decomposition are determined to be ≤10%. An oscillating behavior of the absorption was found during the dark period following the irradiation. The temperature dependence of this dark reaction has been studied. The oscillatory behavior is discussed in the light of current theories concerning instabilities in photochemical systems.

Introduction

Due to their photosensitive properties and their thermal stability, azo compounds have a widespread field of interests in research and technology. Compounds containing azo groups are used as photosensitive materials in photolithography and laser ablation.[1] These compounds may be applied, e.g., in nonsilver photographic processes. The photochemistry[2] and microstructuring[3,4] of several classes of azo compounds have been investigated in earlier studies. Their photosensitivity and the superior structuring properties are mainly due to the lability of substituents binding to the N=N groups. During the ablation process these bonds are broken, and nitrogen as well as other small organic fragments are released without leaving any residuals on the surface.

Pentazadiene compounds, in particular, contain five nitrogen atoms in a row. In view of the lability of this arrangement, they appear to be predestined for utilization in photochemical experiments. The first representative of these aromatic 1,4-pentazadienes was synthesized 1866 by P. Griess[5] in the reaction of diazotized aniline with ammonia. Since then, a wide variety of aromatic 1,4-pentazadiene model compounds and polymers have been synthesized to investigate the influence of the substituents on the photolability. CW photolysis with a HgXe high-pressure lamp and thermolysis behavior have been investigated.[6] It was found that electron donating aromatic substituents increase the photosensitivity and decrease the thermostability.

In a semiempirical study,[7] the calculated bond lengths and the quantum yields for the photolysis were compared to experimental data of several compounds. In general the quantum yield of photolysis is quite high compared to triazenes, which is attributed to the sterical hindrance of the competitive reaction channel, i.e., isomerization.

The decomposition pathway was investigated with different methods. Electron paramagnetic resonance (EPR) experiments of the model compounds were performed to decide whether an ionic or radical reaction is taking place during the UV photolysis.[6] In the presence of nitrosodural (ND), used as spin trap, aryl and alkyl radicals have been detected for all model compounds.

The thermolysis in solution was followed with NMR spectroscopy.[6] In nonprotic solvents, a homolytic bond fission was suggested since the typical emission signals due to the radicals, caused by the CIDNP effect, were found in the NMR spectra. In contrast, heterolytic fission was favored for the thermolysis in protic solvents. A heterolytic fission was found in electron impact mass spectra.[8]

Since some hints on a dark reaction were found in the CW photolysis[9] but could not be quantified with the CW setup, it was decided to use a pulsed laser. The highly energetic pulses of the XeCl* excimer laser operating at 308 nm with a length of only about 20 ns give the opportunity for a comprehensive investigation of a time-dependent dark reaction. The oscillatory behavior of the absorption spectra was discussed in the framework of current theories about thermokinetic instabilities in photochemical systems.

Experimental Section

Photolysis and Spectroscopy. Solutions of the pentazadiene monomers and polymers in THF (Merck spectroscopic grade), CH_3Cl (Fluka spectroscopic grade), and dioxane (spectroscopic grade) were irradiated in quartz cuvettes of 10 mm path length. The concentrations were adjusted in the 10^{-5} M range such that UV−vis spectra could be recorded with an optical density of 1−1.5. The photolysis experiments were carried out with a XeCl* excimer laser (Lambda Physik, model Compex 205) as the irradiation source; the cuvettes were placed into the beam path of the laser. The pulse energy delivered to the sample was adjusted to 190 mJ. The spectrometer was triggered by the laser. In a direction perpendicular to the laser beam, glass fibers were attached to the spectrometer housing for coupling the signal

SCHEME 1. Structural Formulas of the Investigated Compounds

model compounds M1-M7

polymer compounds P1-P5
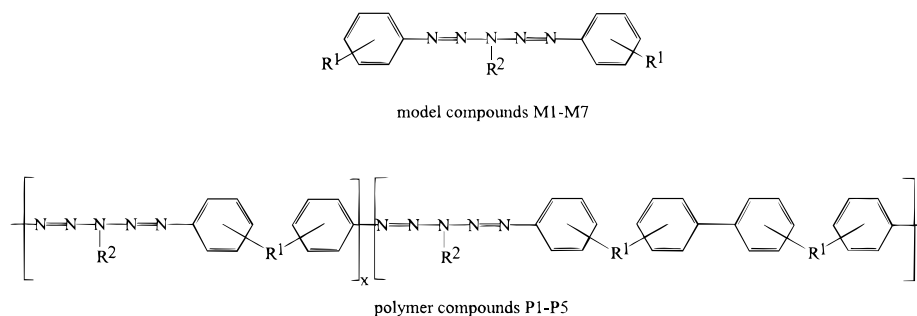
TABLE 1: Investigated Pentazadiene Monomers

compd	substituents at phenyl ring R^1	substituents at N^3, R^2
M1a	*p*-Ome	Me
M1b	*o*-Ome	Me
M2	*p*-Me	Me
M3	*p*−H	Me
M4	*p*-CN	Me
M5	*p*-Cl	Me
M6	*p*-COOEt	Me
M7	*p*-OC$_6$H$_5$	(CH$_2$)$_2$OH

TABLE 2: Investigated Pentazadiene Polymers

compd	substituents at phenyl ring R^1	substituents at N^3, R^2
P1	(CH$_2$)$_2$	hexyl
P2	O	hexyl
P3	O	cyclohexyl
P4	O	benzyl
P5	O	(CH$_2$)$_2$OH

into the spectrometer. The UV−vis spectra were recorded with a diode-array spectrometer from Polytec (XDAP) (a) immediately, (b) 25 s, and (c) 50 s after the laser pulse. The same setup was used to investigate the kinetics during the dark reaction. In the kinetic mode the spectrometer recorded several wavelengths with a sampling rate of 2 Hz for a period of 1000 s. Temperature-controlled cuvettes were used for these kinetic experiments. To prevent condensation on the cuvettes at low temperatures the windows were flushed with N$_2$ gas during the experiments.

Materials. The model compounds M have been synthesized by the reaction of aromatic diazonium salts and primary amines. Incorporation of pentazadiene chromophores into a polymeric chain was achieved by interfacial polycondensation of primary amines and bisdiazonium salts. The procedure has been described in detail elsewhere.[10] The structural formula is shown in Scheme 1. The substituents for the monomers are identified in Table 1 and for the polymers in Table 2.

Results and Discussion

UV−vis spectroscopy is suitable for the investigation of pentazadiene photochemistry. The UV−vis spectra of the

pentazadiene compounds are characterized by at least two differently intense absorption bands. A very strong absorption maximum (Tables 3 and 4) is found at about 380 nm which is assigned to an intense $\pi \rightarrow \pi^*$ transition. A weaker absorption band is found at wavelengths shorter than 300 nm, which is assigned to a $\pi \rightarrow \sigma^*$ transition. A comprehensive discussion of the electronic structure of the pentazadienes is given by Bugaeva and Kondratenko.[12] The proposed energy level diagram consists of a $\pi\pi^*$ state and a dissociative $\pi\sigma^*$ state which would intersect the ground state potential curve with lengthening of the N=N bond. Since these two states have identical symmetry, an energy gap is formed by interaction. This means that after excitation to the $\pi\pi^*$ state and transition to the lower $\pi\sigma^*$ state the molecule may relax to the ground state or dissociate. Further, the avoided crossing gives rise to an energy barrier for thermolysis or recombination of the dissociation products. With respect to electronic structure and therefore to the photochemical properties, the class of the pentazadienes is similar to aromatic triazenes and aromatic diazonium salts.
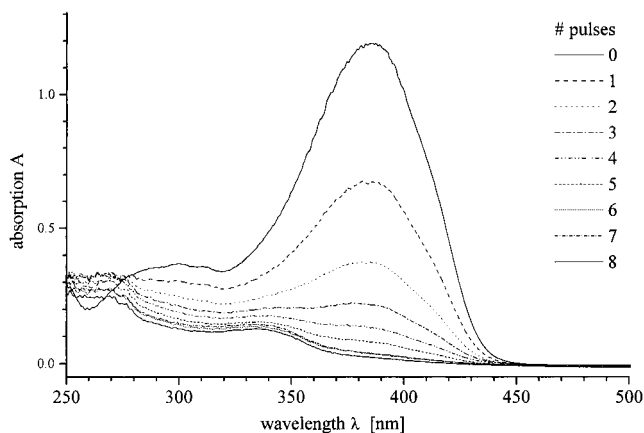
Photochemical Decomposition. Samples of the monomer compounds as well as of the polymer compounds in different solvents were irradiated with intense UV laser pulses (190 mJ), and the course of the decomposition was recorded with UV−vis spectroscopy. According to Lambert−Beer's law, the degree of decomposition was correlated with the absorption at the maximum of the $\pi \rightarrow \pi^*$ transition. The influence of the substituents R$_1$ and R$_2$ on the photochemistry of the chromophores was studied. A typical course of such a photolysis is shown in Figure 1. The almost complete decay of the strong $\pi−\pi^*$ transition at 387 nm within 8 pulses at a pulse energy of 190 mJ indicates the photochemical decomposition of the chromophore.

For CW photolysis (mercury lamp), the photocleavage mechanisms depicted in Scheme 2[10] were postulated. Depending on the solvent polarity, the compound is cleaved either into ionic or radical transient products after an initial isomerization. In acetonitrile and benzene as solvents, radicalic intermediates were verified by EPR spectroscopy.[6] Accordingly, we propose the radicalic decomposition for photolysis in tetrahydrofuran as well.

According to the method developed by Mauser et al.[11]

TABLE 3: Photophysical and Photochemical Parameters of Pentazadiene Monomers

compd	wavelength of absorption maximum in THF, λ_{max} (nm)	molar extinction coefficient ϵ in THF (l M^{-1} cm^{-1})	quantum yield of photolysis (%)	wavelength of absorption maximum in dioxan λ_{max} (nm)	molar extinction coefficient ϵ in dioxan (l M^{-1} cm^{-1})	quantum yield of photolysis (%)
M1a	387	38010	6.3	385	59155	7
M1b	384	29300	8.3	386	36885	5.7
M2	370	31530	9.4	372	33233	10
M3	363	29800	8.7	364	32258	6.2
M4	377	37960	7.5	375	52692	4
M5	373	36900	7.3	372	36232	6.8
M6	378	37500	7.2	378	46154	5.2
M7	385	39460	8.5	381	40816	7.7

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Figure 1. UV−vis absorption spectra of pentazadiene monomer M1a in THF. A sequence of eight excimer laser pulses (187 mJ at 308 nm) was delivered to the sample.

TABLE 4: UV−Vis Data of Pentazadiene Polymers

compd	wavelength of absorption maximum in THF λ_{max} nm	molar extinction coefficient ϵ in THF M^{-1} cm^{-1}
P1	372	19800
P2	383	20700
P3	375	18800
P4	384	24200
P5	382	19100

absorption-difference (AD) diagrams were used for the characterization of the kinetics. The decrease of the absorption at several wavelengths $\Delta A_i(n)$ was plotted against the decrease of the absorption maximum $\Delta A_{max}(n)$, where n is the number of photolysis pulses. The linear dependence with a zero intercept indicates a uniform reaction A→B, with only A absorbing in the observed spectral range. As a representative example, the AD diagram of compound M1a is shown in Figure 2. The linear dependence is obtained for all other compounds as well.
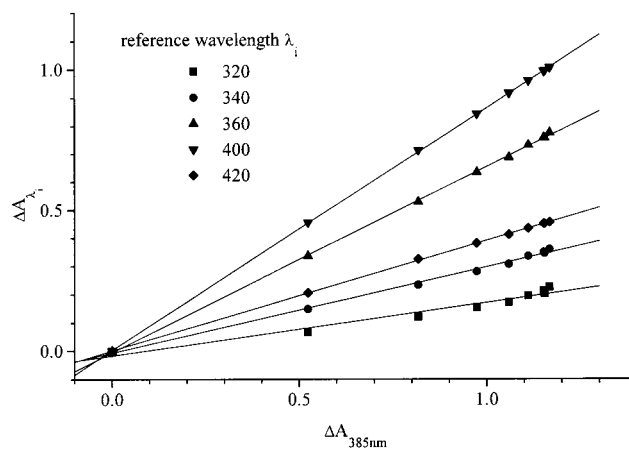

Figure 2. Absorption difference diagram of the photolysis course of M1a in THF.

To compare the rate constants of the different compounds, the logarithm of the reduced absorption $A_0/A(t)$ is plotted against the number of pulses ($\propto t$), supposing a first-order reaction (Figure 3). For the first (≈ 5) pulses, a straight line is obtained; with increasing pulse numbers the required linearity in the progress of the photolysis is lost. This indicates that side products with an absorption in a spectral region close to the one of the reactants are formed. The slope of the lines is assigned to an effective rate constant of the first-order reaction. The compounds with electron withdrawing substituents (M4, M5, M6) decompose more slowly than the unsubstituted M3, in good agreement with former photolysis studies performed with a high-pressure HgXe lamp.[6]

To compare the photolability of the differently substituted compounds we have evaluated the quantum yield of the photolysis. This quantity is defined as the ratio of the decomposed molecules to the number of absorbed photons used for this process. We find the quantum yield between 6% and 10% for the model compounds M in THF and dioxane (Table 3,

SCHEME 2. Postulated Photocleavage Mechanism for Model Compounds with Electron-Donating Substituents
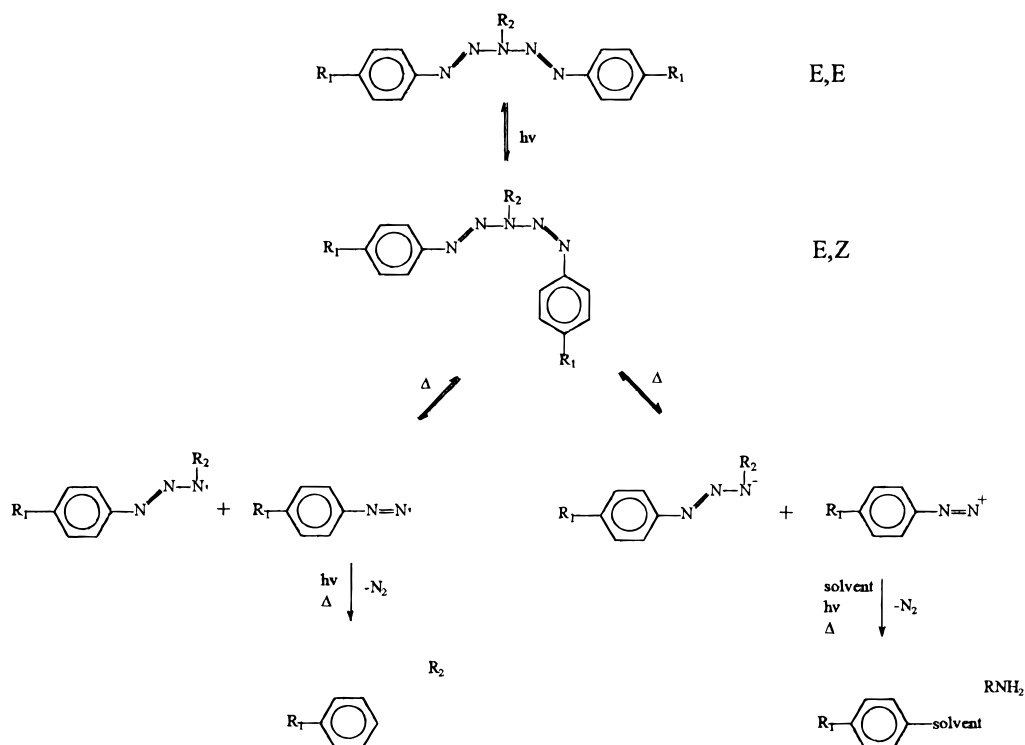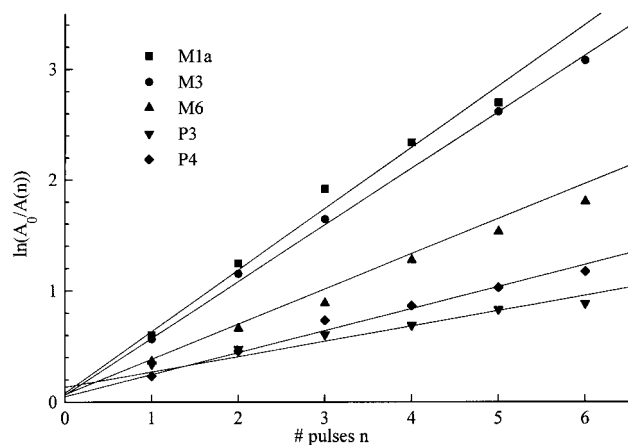
Figure 3. First-order kinetics plot for decomposition of monomer and polymer pentazadienes.
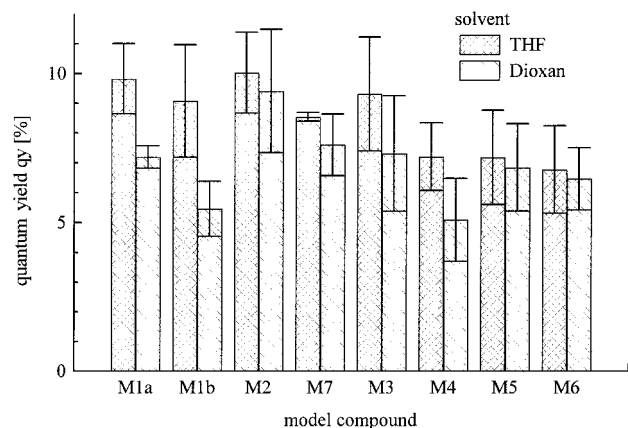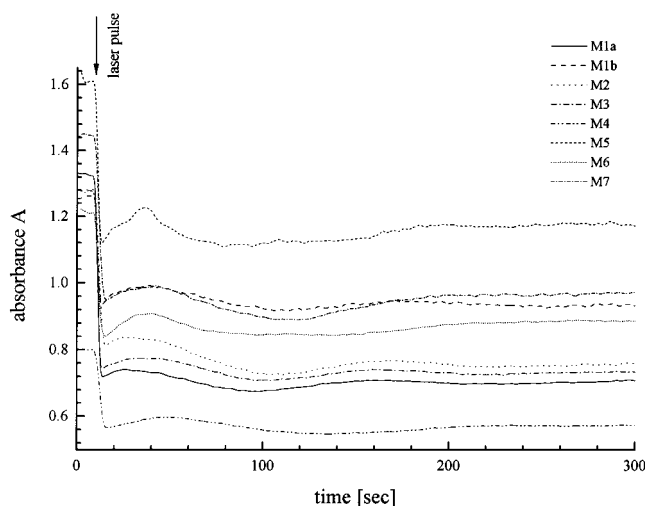

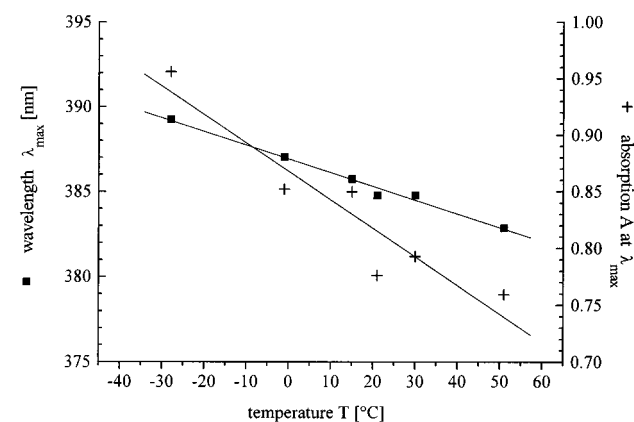**Figure 4.** Quantum yields for the pentazadiene model compounds in different solvents.

Figure 5. Dark reaction of the model compounds after irradiation with one pulse at room temperature.

Figure 6. Temperature dependence of the absorption maximum of M1b in THF.

Figure 4). These values are larger by an order of magnitude as compared to the triazenes,[2] where a quantum yield around 1% has been reported. According to Bugaeva and Kondratenko,[12] the main reason is the fact that the cis−trans isomerization reduces the quantum yield of the photolysis of the pentazadienes only to a small extent since the substituent R^2 sterically hinders the rotation around the −N=N bond.

Oscillatory Behavior and Temperature Dependence. We found that the chemical reactions associated with the decomposition continue over a time that is significantly larger than the pulse length. Therefore, the spectrometer was set to record several wavelengths over a time interval of 1000 s. Ten seconds after starting the measurement the first laser pulse was delivered to the solution, and the next two pulses were delivered with a delay of 400 s each. Directly after the pulse the absorption decreases within one data point ($t < 1$ s) and increases again to a level lower than the original value. The time for this regeneration is very short compared to the time of the subsequent dark reaction (≈ 300 s). After the initial transient, a strong but damped oscillation of the absorption band was observed for all investigated compounds. Finally, the absorption settles to a constant value. Up to three periods could be observed during a time of five minutes. In Figure 5 the time dependent behavior of the absorption at λ_{max} for several model compounds in THF as solvent is shown. These experiments were carried out at room temperature without temperature control.

To further investigate this dark reaction, temperature controlled experiments were performed. The cuvettes were thermostated with a flow cryostat. After establishment of thermal equilibrium, the experiments were performed in the same way as described above. Before and after recording the kinetics, a complete spectrum of the compound was taken. For the monomers and as well for the polymers, the absorption at λ_{max} decreases with the temperature and the position is shifted to shorter wavelength as shown in Figure 6.

The temperature dependence of the dark reaction for the monomer substituted with a methoxy group is illustrated in Figure 7. Obviously there is a narrow temperature region in which the oscillatory behavior is observed. For lower temperatures the absorption increases continuously after the irradiation up to the final value; at higher temperatures the absorption reaches a maximum and decreases slowly subsequently. In an intermediate temperature region, the damped oscillations are reproducibly observed.

Distinctive oscillations are found in the temperature range from 8 to 45 °C (Figure 8). After the decay of the oscillation a further pulse was delivered to the solution. The experimental data recorded at three different temperatures (8, 24, and 45 °C) could be well represented by the model of a damped harmonic oscillator, as described by the following equation:

$$A(t) = \Delta A \sin(\omega(t - t_0) + \varphi) \exp(-k(t - t_0)) + A_e$$

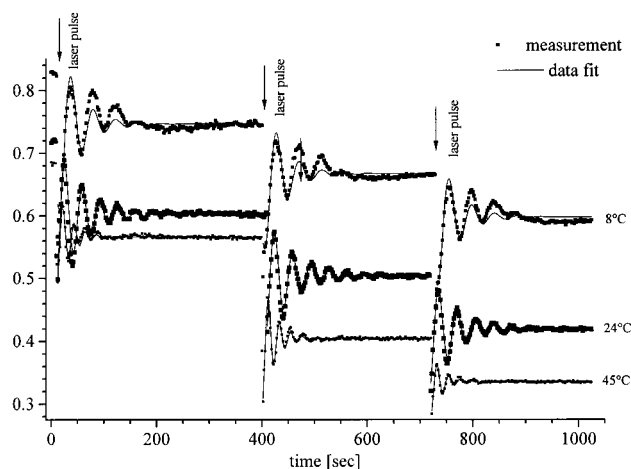with ΔA, amplitude of the harmonic oscillator; ω, oscillator frequency; φ, phase shift; and k damping constant of the system.

The experimental data were fit to this model. It was found that the amplitude ΔA of the oscillation decreases with the
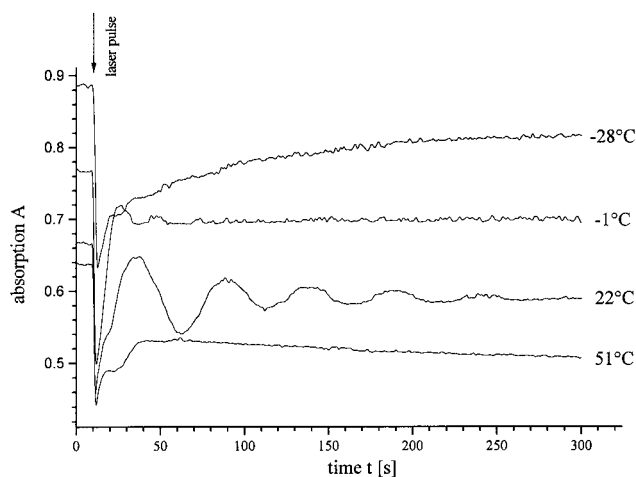
Figure 7. Dark reaction of M1b after 1 pulse in a temperature controlled cuvette.

Figure 8. Fit of the experimental data of M1b with the model of a damped harmonic oscillator. The arrows show the time of delivery for one laser pulse.

temperature, in parallel with the absorption *A* of the nonirradiated solution as shown in Figure 6. Since the concentration of the chromophores and hence the absorption decreases with the pulse number delivered to the sample, the amplitude recorded after the third pulse is smaller than after the first pulse. The frequency ω and the damping constant k might be associated with characteristic rate constants of the dark reaction. If we take the amplitude ΔA as an indicator for the extent of the dark reaction, we notice that the conversion from reactants to products is smaller at temperatures where the dark reaction is prevailing, and vice versa.

To decrease the possibility that the oscillations would be caused by convection,[13] attention was paid to the fact that the entire front face of the cuvette was irradiated consistently. Additionally, the experiments were repeated with a smaller thickness (4 mm) of the cuvette along the light propagation direction. In all of these variants, oscillations could be registered. However, upon stirring the oscillations disappeared. This observation shows that the reason for the oscillation phenomenon is a spatio-temporal nonuniformity. A simple calculation of the energy balance supports this interpretation: The maximum possible temperature increase is too small to cause convection. The latter can be easily calculated, if it is assumed that the entire pulse energy (190 mJ) is absorbed by the solution and converted directly into heat. The reaction enthalpy of typically −230 kJ/mol can be neglected in comparison to the pulse energy for the

used concentration ($\approx 1 \times 10^{-5}$ mol/L) and the used volume (2 mL). For tetrahydrofuran the heat capacity is 1.72×10^3 J/kg/K and the density is 0.89 kg/L. It follows that the solution would be heated by 1.6×10^{-3} K for each pulse of 190 mJ energy. Even if it is taken into account that there exists a temperature gradient in the direction of light propagation due to the attenuated laser beam, convections are not expected for the very small temperature gradients.

Discussion of the Oscillatory Behavior. A variety of models for chemical oscillations have been presented in the literature. In general, chemical instabilities occur in systems which are maintained far from equilibrium and which involve some kind of feedback mechanism. For example, Vorobiev[14] predicted an oscillatory behavior for monomer−dimer equilibrium in a closed isothermal system. Gray and Scott[15] discussed several models which are capable of exhibiting oscillations, such as an autocatalytic model or a thermal feedback system. All of these examples are complex light-free chemical systems. Nitzan and co-workers,[16,17] pointed out that there are intrinsic differences between chemical and photochemical systems that easily lead to thermokinetic instabilities in the latter ones. They predicted oscillations, multiple steady states, and instabilities in even the simplest reaction A ↔ B and additionally analyzed more complex consecutive and cyclic reactions. Another group discussed the occurrence of nonlinear dynamics in thermostated photochemical systems[18] and stated two main reasons for this phenomenon: First, the photon flux that keeps the system away from equilibrium and second, the peculiar photon−chemical interaction that is governed by the highly nonlinear Lambert−Beer law. Bistabilities were observed experimentally in a number of photochemical systems,[19,20] but no oscillatory behavior to our knowledge.

An assumption used in many of the above references, i.e., the homogeneity of concentration and temperature, is obviously not fulfilled in our case. In a study[19] dealing with A↔B systems, spatial inhomogeneities accompanying temporal bistabilities could be demonstrated experimentally. We believe that spatial concentration variations are also present in our system: For highly absorptive states, the laser intensity is decreased as the beam transverses the sample. The system is therefore subject to a parameter which varies spatially in the direction of light propagation (*z*-axis). In this context, a recent experimental and theoretical study dealing with the influence of natural convection on propagating polymerization fronts[21] cannot help to explain our observed oscillations, because the temperature gradients are very small as mentioned above.

Possibilities to better understand the mechanisms causing the observed oscillations are emerging on the basis of *reaction−diffusion* simulations, within the framework of a novel theory developed by Dogaru and Chua[22] for a general class of dynamic systems called cellular nonlinear networks (CNN). The theory states that two necessary conditions for a nonconservative reaction−diffusion system to exhibit complex behavior (i.e., chaos, spiral waves, Turing patterns, oscillations, etc.) are *local activity* and *stability* of at least one equilibrium point. One of the interesting results is the observation that in many situations, complex dynamics arises only from the combined action of diffusive coupling among the cells, and the chemical reactions proceeding within them. Uncoupled cells with the same parameters are shown to exhibit only trivial relaxation dynamics.

Another mechanism leading to the observed damped oscillations of absorption might be based on the homogeneous nucleation of N_2 bubbles produced by the investigated process. First observed in 1916, and thoroughly investigated in the 1980s

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by R. M. Noyes and others,[23] so-called gas evolution oscillators (GEO) show damped oscillations of pressure in a closed reaction vessel because of the formation and growing of bubbles in a highly supersaturated solution.

First attempts to simulate oscillations with a reaction−diffusion model for different plausible dark reaction mechanisms gave promising results and clearly demonstrate the possibility for damped oscillations in limited portions of parameter space without any thermal or convective instability involved. However, additional experiments are needed to decide whether the observed oscillations are of chemical or rather of physical nature (bubbles). A detailed discussion including these new experiments and propositions for the underlying mechanism on the basis of simulations will be published elsewhere.

Conclusions

The investigated 1,5-diaryl-3-alkyl-1,4-pentazadiene monomers follow an overall first-order kinetics during the pulsed laser photolysis. In comparison to the triazenes, quantum yields larger by 1 order of magnitude ($\approx$10%) were determined. Because of the concomitant thermostability, this class of compounds, monomers as well as polymers, is predestined for applications in laser ablation. After the irradiation a subsequent complex dark reaction was observed and was shown to be due to spatio-temporal inhomogeneities. The oscillation behavior of the absorbance was studied in dependence of the temperature; in a intermediate region, near room temperature, well defined and reproducible damped harmonic oscillations were observed and fitted to a mechanical model of an oscillator.

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