Journal of Photochemistry and Photobiology A: Chemistry 112 (1998) 63–72

Journal of Photochemistry and Photobiology A:Chemistry

Photolysis and thermolysis of diaryl(pentazadiene) compounds in solid matrix investigated by infrared spectroscopy

D. Franzke [a], J. Kritzenberger [a,1], E.E. Ortelli [a], A. Baindl [b], O. Nuyken [b], A. Wokaun [a,c,*]

[a] *Paul Scherrer Institute, Villigen CH-5232, Switzerland*
[b] *Technical University of Munich, Garching D-85747, Germany*
[c] *Swiss Federal Institute of Technology (ETHZ), Zürich CH-8092, Switzerland*

Abstract

The photochemically and thermally induced decay of four 1,5-diaryl-3-methyl-pentazadiene compounds in KBr matrix is investigated by infrared spectroscopy. The decomposition proceeds under the release of nitrogen and leads to substituted aromatic compounds. No intermediates are detected in photolytic experiments in solid, which is in contrast to former experiments in solution. We show that thermolysis proceeds via a reversible step. Particularly in the case of compound **II**, there is significant recovery of some peaks if a sample heated to a temperature slightly below the decomposition point is subsequently cooled down to room temperature again. In the case of compound **III**, neither intermediates nor condensed end products are observed, which indicates the generation of small volatile fragments. © 1998 Elsevier Science S.A.

Keywords: 1,5-Diaryl-3-methyl–pentazadiene; Thermolysis; Photolysis; Infrared spectroscopy

1. Introduction

In recent years significant efforts have been made to develop materials which may be used for microstructuring by photoablation [1–4]. In this technique, a short UV laser pulse is absorbed by a (polymeric) material [5]. Bonds near the surface are subsequently destroyed and the polymer is decomposed into small fragments. These fragments are partially gaseous and give rise to a rapid volume expansion resulting in a micro explosion near the surface. One method to make this process efficient for macromolecules (which have none or low absorption at the irradiation wavelength) is through physical doping with chromophores. These specifically developed dye molecules cause not only enhanced absorption of the material; they are also designed to decompose photochemically into small fragments, producing in this way a driving gas which makes the ablation process more efficient. One class of such molecules are 1,5-diaryl-3-alkyl-pentazadienes [4,6,7]. Their characteristic structural feature is a chain of five conjugated nitrogen atoms, which gives rise to a high absorption coefficient in the wavelength range from 300 to 400 nm. Pentazadienes undergo photochemical cleavage when irradiated with UV laser light, releasing nitrogen. First promising ablation experiments with pentazadiene dopants have already been performed [8]. Polymers have been synthesised with the pentazadiene unit in the main chain, which also proved to be useful materials for microstructuring [4].

Recently the synthesis of a series of compounds of the type R-Ph-N=N-NR′-N=N-Ph-R (1,5-diaryl-3-methyl-pentazadienes, $R' = CH_3$) was reported [4], which differed in the nature of the substituents R attached to the phenyl rings. First investigations of the influence of the substituent (R=H, 4-CN, 4-OCH_3, 2-OCH_3, 4-Cl, 4-CH_3) on the stability against thermal and photochemical decay were made in solution. The results of DSC measurements are summarised in Table 1. We can see that the temperature of maximum enthalpy release varies by 50°C, and was highest in the case of 4-cyano substitution.

From earlier investigations [9–11] it is known that the decay of pentazadienes may involve several reaction steps. To elucidate the mechanism, photolysis experiments in solution have recently been performed with monitoring by UV/Vis spectroscopy [8]. However, as the envisaged application of pentazadienes is the photochemistry (laser ablation) in a *solid* matrix, the present investigation focuses on the photolysis and thermolysis of pentazadienes in solid KBr matrix.

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* Corresponding author.

[1] Present address. Patentanwaltskanzlei Diehl, D-80639 München, Germany.

PII S1010-6030(97)00265-7

Table 1
Decomposition temperatures (from DSC) of substituted pentazadienes

R	H (III)	4-Cl	4-CN (II)	2-OCH$_3$ (I)	4-OCH$_3$	4-CH$_3$ (IV)
T_{max}/DSC	144	179	196	158	136	145

This matrix was chosen because it allowed us to monitor the decay by infrared spectroscopy.

A mechanism commonly discussed [12] for the decay of azo containing compounds consists of two steps. The first step is an isomerisation of a stable ground state to a less stable intermediate state (e.g., from a *Z* to an *E* isomer). This process may be induced either photochemically or thermally. The intermediate state may react thermally to the stable end products, or else it may undergo the reverse reaction to the initial isomer of the azo compound.

2. Experimental

2.1. Synthesis

The synthesis of the pentazadienes was carried out via aromatic diazonium ions, according to a method described by Howard and Wild [13], as shown in Scheme 1.

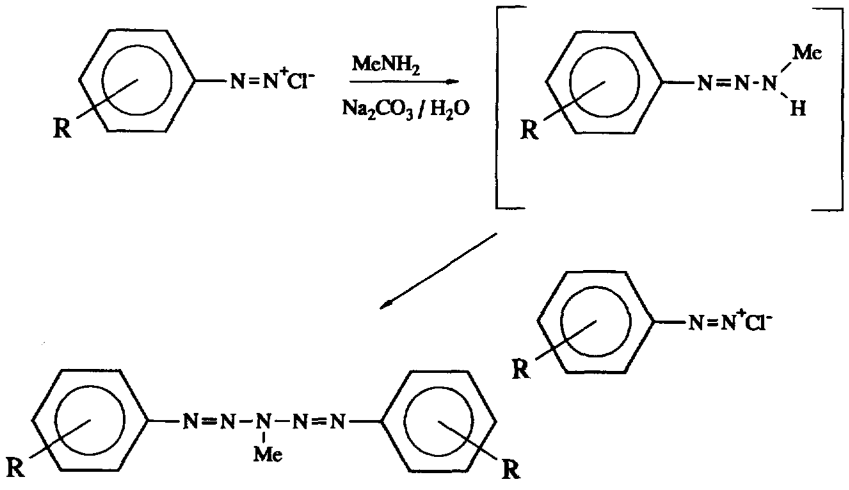
Starting from the aromatic amines with different substituents R, diazonium salts are formed in hydrochloric acid solution. Said solution is added at 0°C to another one containing sodium carbonate and the primary amine. One molecule of the latter one reacts with two molecules of the diazonium salt to yield the desired 3-alkyl-pentazadienes. In the present study we used compounds with the substituents listed in the scheme. The colours of the compounds varied from yellow to red, depending on the substitution pattern. All materials were characterised by ^{1}H NMR, ^{13}C NMR, IR and UV/Vis spectroscopy, respectively [4].

2.2. Sample preparation and infrared measurements

2.2.1. Photolysis experiments

For the photolysis experiments, pentazadiene-doped KBr pellets of 1.2 cm diameter and a thickness of about 1 mm have been pressed. The concentration of the pentazadienes was chosen in such a way that there was sufficient IR-transmission to obtain infrared spectra with good signal to noise ratio. Spectra were recorded on a BOMEM DA8 FT spectrometer equipped with a nitrogen cooled MCT detector, which allowed us to record spectra in the range from 400 to 4000 cm^{-1}. To obtain an adequate signal-to-noise ratio, 10 to 20 scans were averaged. The resolution was set to 1 cm^{-1}.

For irradiation XeCl excimer lasers from Lambda Physik (LPX 300 and Compex 205) have been used, with a wavelength of 308 nm and a pulse length of about 20 ns. For our experiments the energy of the laser pulses was adjusted such that fluences between 10 and 250 mJ/cm^2 were incident on the sample surface. Care was taken that the pulse energy did not exceed a certain value which depended on the nature and the concentration of the pentazadiene. If this value was exceeded the decomposition proceeds in the fashion of a micro explosion, and the surface of the KBr pellet is roughened. This gives rise to a strong increase of the background in the transmission spectra by scattering effects, and may even lead to complete destruction of the pellet. We have carried out two types of experiments. In the first series, the sample was irradiated subsequently from both sides outside of the spectrometer, i.e., directly within the laser beam path.



R	compound
2-OCH$_3$	*I*
4- CN	*II*
H	*III*
4-CH$_3$	*IV*

Scheme 1. Preparation and identification of substituted pentazadienes investigated in this work.

From time to time the irradiation was interrupted for a transmission measurement. In the second series we irradiated the KBr pellets directly in the sample holder in the spectrometer through a quartz window.

2.2.2. Thermolysis experiments

To monitor the thermal decomposition of the pentazadienes in transmission, the KBr pellets prepared as described above were heated in an oven. In regular time intervals spectra were recorded. Infrared transmission measurements were carried out using the BOMEM DA8 FT spectrometer. Measurements of changes in the diffuse IR reflectivity were performed using a Bruker EQUINOX 55/S FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. The thermolysis experiments were performed in a diffuse reflectance (DRIFT) unit (Spectra-Tech) with the sample positioned within a controlled environmental chamber equipped with NaCl windows. A LabView programme (National Instruments) was developed for PC control of the set-up. Spectra were obtained from the accumulation of at least 64 scans at a resolution of 4 cm^{-1}, and were referenced versus a background spectrum of KBr powder recorded at the thermolysis temperature (1024 scans, 4 cm^{-1} resolution). The thermolysis was performed under a stream of helium (1 bar, 10 l/h).

Raman measurements were performed in a Raman microscope (DILOR, model LabRam) with 632.8 nm excitation wavelength and in an FT–Raman instrument (Bruker, model FRA 106/S) equipped with a Nd:YAG laser (1064 nm excitation wavelength), respectively.

3. Results and discussion

3.1. 2-Methoxypentazadiene (I)

Spectra recorded during photolysis of **I** in a KBr pellet are shown in Fig. 1. Starting from trace (a), the sample is irradiated with 400 pulses (trace b) of UV light; trace (c) shows the spectrum after delivering 2400 pulses to the sample. The band at 1597 cm^{-1} is assigned to stretching motions of the aromatic ring [14–16]. During the reaction it is shifted towards higher energies by a few wavenumbers. This observation suggests that the substitution pattern of the ring is changed. Around 1515 cm^{-1}, a band is seen to grow while the strong peak at 1492 cm^{-1} vanishes almost completely. In the same region a small doublet appears with frequencies of 1491 cm^{-1} and 1497 cm^{-1}, respectively. Above ≈ 1450 cm^{-1}, a broad band with unresolved fine structure is growing. This might be a hint to the formation of anisole ($CH_3O–C_6H_5$) which exhibits three bands in this region. The three absorption peaks below 1300 cm^{-1} (1292, 1274 and 1244 cm^{-1}) show an interesting behaviour. The intensity ratio of the 1274 and the 1244 cm^{-1} peak is inverted, while both bands are becoming broader. The 1244 cm^{-1} peak is assigned to the C–O–C vibration [14–16]. The fact that this band remains present in the spectra shows that the methoxy group is still attached to the benzene ring after the reaction. The broadening of this band may be due to the presence of different compounds containing the methoxy group generated during the reaction. The peak at 1292 cm^{-1} vanishes almost completely, while at 1223 cm^{-1} a shoulder is growing. The peak at 1022 cm^{-1} becomes less intense and a growing shoulder at 1045 cm^{-1} can be seen.

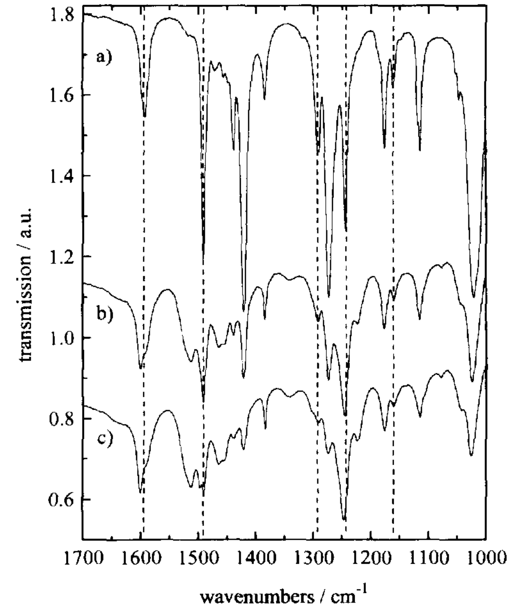


Fig. 1. Transmission spectra of the photolysis of **I** in KBr matrix irradiated with UV laser pulses at 308 nm (2 Hz). Trace (a) shows the sample before irradiation, trace (b) after 400 pulses of 100 mJ/cm^2, trace (c) 2400 pulses with 100 mJ/cm^2.

In the region between 750 and 650 cm^{-1} (since thermolysis experiments yield similar results, see also Fig. 2), the

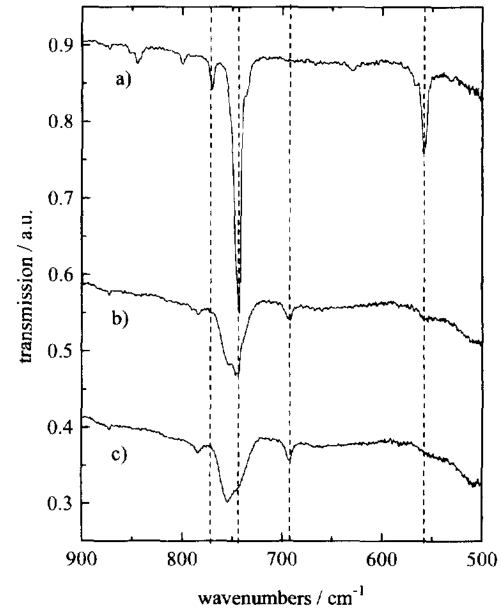


Fig. 2. Transmission spectra of the thermolysis of **I** in KBr at 120°C after (a) 0 min, (b) 30 min, (c) 60 min. This experiment was performed in an oven under atmospheric conditions.

changes observed can be interpreted in terms of an aromatic reactant with two substituents (1,2 substitution pattern) that is converted into an aromatic product with only one substituent [14]. The peak at 743 cm^{-1}, which is a typical feature for the 1,2-substituted phenyl ring, decreases while two new peaks grow at 694 and 755 cm^{-1}, respectively, which can be interpreted as being due to an aromatic compound with only one substituent. This is also in agreement with the generation of anisole.

For the thermolysis experiments a few milligrams of **I** were dispersed in KBr. The sample was heated rapidly to 95°C under a continuous flow of helium, and kept at this temperature for 2 h. Spectra were recorded every 2 min. Then the sample was heated to 120°C. The resulting changes in the spectra were very similar to those described for the photolysis and for the thermolysis under atmospheric conditions in an oven (Figs. 1 and 2, respectively). A slight difference could only be seen in the range between 1525 and 1450 cm^{-1}. The peak growing at about 1520 cm^{-1} is weaker as compared to the photolysis experiment, and the structures around 1490 cm^{-1} are less sharp. This could indicate that side products are generated.

The peaks centred at 1421 cm^{-1} and 1292 cm^{-1} exhibit a dramatic decrease during thermolysis (see Fig. 1). The well-known fact that azo compounds decompose by releasing nitrogen suggests to assign the above-mentioned bands to vibrations involving nitrogen atoms. The frequency of 1421 cm^{-1} correlates well with the range observed for an azo group in *p*-methoxybenzene and *p*-hydroxyazobenzene (around 1415 cm^{-1}) [15]. Therefore, we assign the band at 1421 cm^{-1} to a stretching vibration of the –N=N– bond. As the range around 1300 cm^{-1} is known to be characteristic for absorptions of the aryl-N bond [15,16], we attribute the band centred at 1292 cm^{-1} to the anisole-N vibration.

An additional thermolysis experiment was set up to investigate whether a reversible thermal isomerisation step is involved in the decay process. For this purpose the sample was held at 95°C for 20 min, and cooled down to room temperature thereafter.

We have monitored several peaks (e.g., 1439 cm^{-1}) which decreased during the heating period and subsequently increased again. This gives a hint that the decomposition process proceeds via an intermediate compound which is in quasi-equilibrium with the starting material, but can also decay as well. To monitor this behaviour, we took a closer look at the peaks in the range 1355–1200 cm^{-1}. The area of the peaks centred at 1244 cm^{-1} (1254 to 1200 cm^{-1}) and 1292 cm^{-1} (1310 to 1284 cm^{-1}) were calculated and normalised by division through the integral over the whole range (1355 to 1200 cm^{-1}). In Fig. 3 curve (a), the normalised peak area of the peak centred at 1244 cm^{-1} (integrated from 1200 to 1254 cm^{-1}) is plotted versus time. It can be seen that the peak area increases fast when the heating period starts and continues growing, however with a weaker slope, while the temperature is held constant at 95°C. Cooling of the sample to room temperature causes decrease of the peak area back to the starting value.

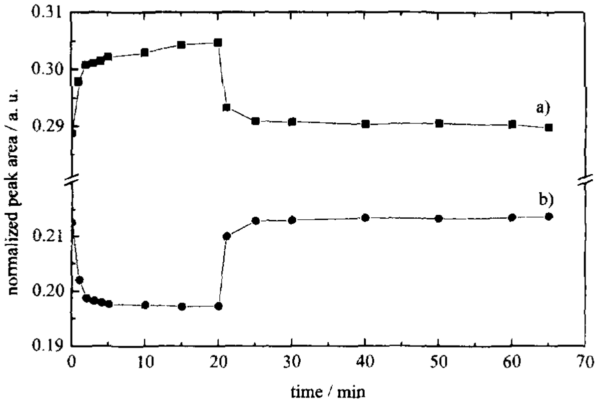


Fig. 3. Normalized integrated peak areas from the diffuse reflectance spectra recorded during thermolysis of I in KBr; trace (a) peak at 1244 cm^{-1}; trace (b) peak at 1292 cm^{-1}. Starting from room temperature the sample was rapidly heated to 120°C. After 20 min, it was cooled down to room temperature again. For further details, see text.

The integrated peak at 1292 cm^{-1} (curve b) shows an opposite behaviour. During the heating period the area decreases and recovers almost completely when the heating is turned off. This could be explained by the thermally induced formation of an intermediate which contributes to the peak area plotted in curve (a). The main peaks which change during the reaction are summarised in Table 2.

The described time dependence will be interpreted below in terms of the formation of an intermediate structure containing one or both of the –N=N– groups in *cis* conformation. The latter intermediate will either isomerise to return to the initial state, or decompose into stable end products.

The characteristic temperature dependence of intensity of the bands assigned to the C–O–C vibration as well as to the aryl-N vibration (see Fig. 3), might be explained by the reversible formation of species exhibiting different specific absorptions in the wavenumber regions around 1244 cm^{-1} and 1292 cm^{-1}. The observed behaviour may be explained if we assume that the C–O–C vibration in a molecule with N=N-*cis* conformation has a higher infrared absorption cross section, as compared to the same vibration in molecules with N=N-*trans* conformation; for the aryl-N vibration the difference between the specific absorptions has the opposite sign.

Temperatures higher than 120°C were also investigated. In this range, compound **I** already evaporates by sublimation and is deposited onto the cell windows, which causes an increasing scattering background and finally inhibits monitoring of the decay reaction.

*3.2. 4-Cyanopentazadiene (**II**)*

*3.2.1. Photolysis of **II***

The photolytic decay of **II** is reflected by drastic changes in the absorption spectra (Table 3; Fig. 4, trace a: untreated sample, traces b and c: increasing energy deposition on the sample). We note that the peak centred around 2220 cm^{-1},

Table 2
Vibrational frequencies in cm^{-1} of **I** affected by thermolysis

Band remains	Decreases	Increases	Shifts/broadens	Assignment
			1593/1601	aromatic ring
		1520		
	1492			–N=N–
		1466		
	1439			
	1421			–N=N–
1384				
	1292			anisole-N
	1274			
			1244	C–O–C
		1223		
	1177/1162			
	1115			
	1022			
	928			
	845			
	771			
		755		monosubstituted aromatic ring
	743			disubsubstituted aromatic ring
		694		monosubstituted aromatic ring
	558			

Table 3
Vibrational frequencies in cm^{-1} of **II** affected by thermolysis

Band remains	Decreases	Increases	Assignment
2222 (br)			CN
1600 (br/sh)			aromatic ring
		1520 (1513)	
	1490 (d)		–N=N–
		1448	
	1435		
	1400		
		1321	
	1286		Ar–N
		1250	
	1190		
		1174	
		1163	
	1154		
	1111		
		1100	
	1007		
	850		
		822	
	759		
		723	
	688		
	647		

which is assigned to the cyano group attached to the aromatic ring [14–16], continues to be observed during the photolysis as well as during thermolysis. However, this band shows a broadening towards lower energies. This behaviour can be interpreted in such a way that the CN group is not split off the aromatic ring during the decomposition reactions. The broadening is explained by a change of the substitution pattern at the phenyl ring, caused by destruction of the phenyl-N bond.

The band at 1600 cm^{-1}, which is assigned to the aromatic ring, is also broadened and shows a fine structure, which supports the assumption that more than one photo product is generated.

Between 1600 cm^{-1} and 1500 cm^{-1} a strong new band is growing. Its maximum shifts from 1513 cm^{-1} to 1520 cm^{-1} during the reaction. The doublet at 1492/1481 cm^{-1} disappears, and only a shoulder at about 1500 cm^{-1} remains in this region of the spectrum. The doublet at 1298/1286 cm^{-1} decreases almost to zero while new peaks are created at 1319 cm^{-1} as well as at 1250 cm^{-1}. The 1190/1154 cm^{-1} doublet which may be assigned to the C–N stretching of the N–CH_3

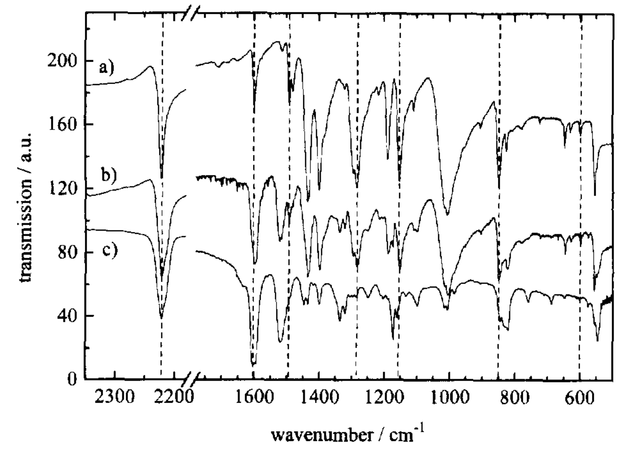


Fig. 4. Transmission spectra of the photolysis of **II** in KBr with 308 nm. Trace (a) untreated sample; traces (b) and (c) increasing energy deposition on the sample.

group [15,16] also disappears while a new doublet at 1174/1161 cm^{-1} is increasing. A drastic change can be seen around 1000 cm^{-1} where the very strong band at 1004 cm^{-1} is replaced by two small peaks at 1018 and 984 cm^{-1}, respectively. In the region below 1000 cm^{-1}, the intensity of five peaks in the range between 590 and 800 cm^{-1} decreases to zero.

*3.2.2. Thermolysis of **II***

DSC and thermogravimetry measurements [4] have shown that compound **II** exhibits the highest thermal stability of the substances investigated in this study. This was confirmed by our experiments. At 120°C, even after 12 h no change in the spectra can be observed, which is in contrast to the results obtained with compounds **I**, **III** and **IV** under the same conditions. In order to find a convenient temperature to follow the decay path of **II**, we performed a dynamic experiment in which the sample was heated with a rate of 2 K/min. Every 5 min, a spectrum was recorded. Up to 200°C, no change could be observed in the spectra under these conditions. Subsequently, in a temperature interval of 10° almost the entire decay was completed. Subsequent heating to 230°C did not cause further changes in the spectra. This behaviour is in agreement with DSC experiments where spontaneous decomposition is reported [4].

Based on this experiment, we selected a temperature of 185°C to monitor the decomposition in the infrared spectrometer, and recorded a spectrum every 2 min. Selected results are shown in Fig. 5 (trace a: sample at room temperature; trace b: 40 min at 185°C; traces c, d, e: 80, 120, 160 min at 185°C, respectively). The changes in this experiment are similar to the photolysis results mentioned above. However, due to the measurement method (diffuse reflection within the Bruker instrument instead of transmission with the BOMEM spectrometer), positions of the peaks are slightly shifted with spectral resolution reduced to 4 cm^{-1}. In the thermolysis as well, we found that the cyano band centred at 2222 cm^{-1} remains present but becomes slightly broadened. The band at 1600 cm^{-1}, which we assign to a vibration of the aromatic ring, broadens too and is shifted towards higher energy by a few wavenumbers. At 1514 cm^{-1}, a new band appears which becomes very intense with progressing thermolysis while shifting to 1520 cm^{-1}. The bands in the region between 1500 cm^{-1} and 1000 cm^{-1} exhibit a behaviour similar to the photolytic experiments. Furthermore, a strong peak at 555 cm^{-1} (not shown) is split into a weaker doublet, from which two peaks at 510 and 425 cm^{-1} arise towards the end of the reaction. This is a hint that the products of the initial cleavage reaction undergo further decomposition.

In view of the high thermal stability of **II**, isomerisation effects are expected to be observable more clearly, as compared to **I**, before the compound decays thermally. Therefore, the sample was heated to a temperature some degrees below its decomposition point, and after a few minutes it was cooled down to room temperature again in order to observe reversible changes in the spectra. The results presented in Fig. 6 (trace a: room temperature, trace b: immediately after heating to 175°C, trace c: after 1 h at 175°C, trace d: after cooling to room temperature, trace e: 1 h at room temperature) show that upon heating to 175°C the peak at 1490 cm^{-1}, which we assign to the *trans*-N=N bond [17], is decreasing while the peak at 1480 cm^{-1}, assigned to the *cis*-N=N bond, is growing.

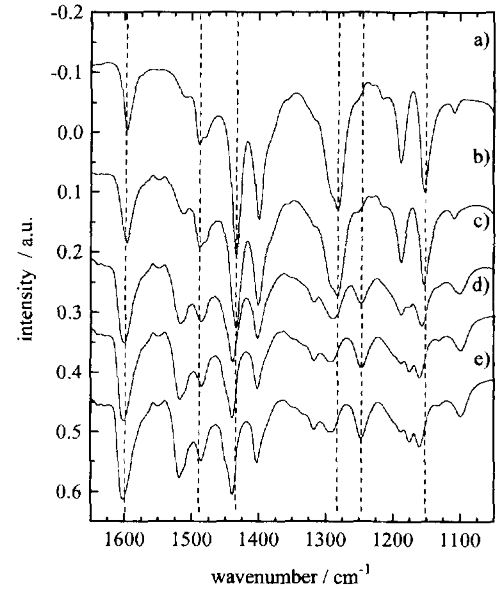


Fig. 5. Diffuse reflectance spectra of the thermolysis of **II**. Trace (a) sample at room temperature; trace (b): 40 min at 185°C; traces (c), (d) and (e) 80, 120, 160 min at 185°C, respectively.

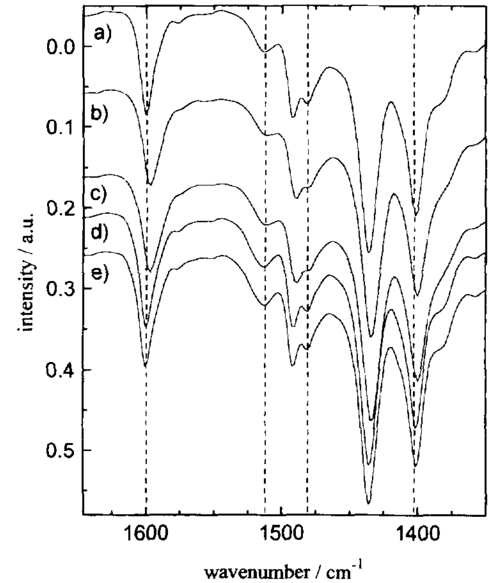


Fig. 6. Diffuse reflectance spectra of **II** in KBr at 175°C. The heating period was interrupted to monitor the reversible back reaction of an intermediate. The different traces correspond to: (a) room temperature, (b) immediately after heating to 175°C, (c) after 1 h at 175°C, (d) after cooling to room temperature, (e) 1 h at room temperature.

We emphasise that the change in peak shape observed is due to the decrease of 1490 cm^{-1} band and the growing of the 1480 cm^{-1} *cis*-N=N band. Nevertheless, the overall change of the intensities is low. This might be due to a coupling or overlap of the bands assigned to the –N=N– stretching vibrations with bands of the aromatic ring, which absorbs in the range of 1500 cm^{-1}. Despite the fact that the bands centred at 1490 and 1480 cm^{-1} might not be exclusively due to absorption of the N=N group, we will henceforth refer to the peak at 1490 cm^{-1} as to the stretching motion of the *trans*-N=N bond, and associate the peak at 1480 cm^{-1} with the *cis*-N=N stretching.

In parallel with the described behaviour, the shoulder at 1380 cm^{-1} disappears, and a new band (assigned to a product) is seen to grow at 1514 cm^{-1}. When the sample is cooled to room temperature again, we observe that the *trans*-N=N peak as well as the shoulder at 1380 cm^{-1} reappear within less than a couple of minutes while the 1513 cm^{-1} still slightly grows (Fig. 6, trace d). This leads to the conclusion that heating causes isomerisation from the *trans*- to the *cis*-state for one or both N=N bonds of the molecule. The *cis* configuration is less stable than the ground state, and may decompose into fragments. When the ensemble is cooled down again, a part of the unstable isomer converts back to the ground state, as demonstrated by the recovery of the peak at 1490 cm^{-1}.

Subsequent to the first experiment, we started a second cycle of heating to 175°C, waiting for 1 h, and then cooling down again to room temperature. Again we observed changes in the spectra of the same type as described above. This implies that even after 1 h at 175°C, we still observe reisomerisation to the starting material.

After this second cycle, the sample was heated to 175°C again and held at that temperature for 2 h. Subsequently, the temperature was raised to 230°C in several steps in order to achieve complete decomposition of the sample. Nevertheless, even after holding for 1 h at 230°C and subsequent cooling to room temperature a peak at 1336 cm^{-1} exhibits a growing intensity (not shown). All other peaks, however, remain unchanged.

To make sure that the interruptions of the heating process and the selected temperature did not affect the course of the reaction, we repeated the experiment and held the sample for 2.5 h at 220°C. We found no differences in the spectra of the reaction products.

3.2.3. Analysis of peak area changes

Changes in selected peak areas, as derived from the experiment described above, are plotted in Fig. 7. The area of the C≡N peak centred at 2222 cm^{-1} was used to normalise the areas of all other peaks, because we assume that the C≡N group remains bound to the phenyl ring during the photolysis, and that the associated absorption coefficient does not change significantly. From this plot the effect of the temperature changes can be clearly seen (Fig. 7).

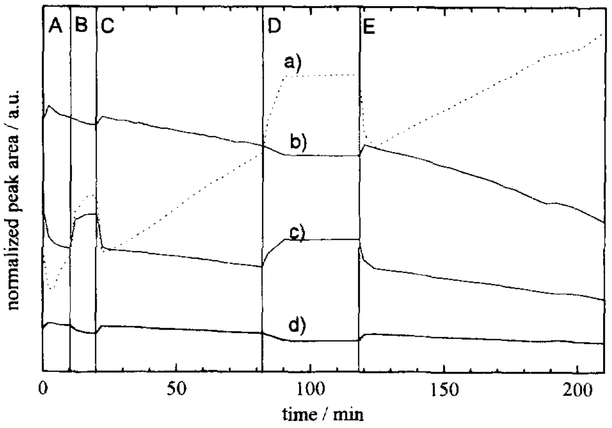


Fig. 7. Temperature cycles of **II** in KBr. The sample was heated to 175°C three times (time intervals A, C and E) and cooled down to room temperature again (intervals B and D). The time needed for the temperature changes was about 2 min. The curves show different peak areas, which were normalized to the peak of the CN group around 2222 cm^{-1}. It can be seen that relaxation occurs when the hot samples are cooled again. The integrated regions correspond to (a) 1539–1502 cm^{-1}, (b) 663–634 cm^{-1}, (c) 1502–1483 cm^{-1}, and (d) 1483–1466 cm^{-1}.

We first consider the area of the peak centred at 1490 cm^{-1} (trace c), which is assigned to the *trans*-N=N bond. As the temperature is raised for the first time from room temperature to 175°C (interval A) the peak area shows an (approximately exponential) decay. A few minutes after the temperature is changed back to room temperature (interval B) the peak intensity recovers almost to the initial value. This indicates that the largest fraction of the observed decrease in peak area is due to a reversible reaction to an intermediate product. In a second cycle (intervals C and D) with a longer heating period, we observe a similar behaviour. The peak area recovers to a certain extent and remains on this level until the heating procedure is continued. When we continue to expose the sample to a constant temperature of 175°C, (interval E) we first observe peak areas to decrease with a nearly constant slope; after about 160 min the slope becomes gradually steeper. The described behaviour indicates that the peak at 1490 cm^{-1} monitored in trace (c) belongs to the reactant, which is in agreement with the above assignment of the band to the *trans*-N=N– bond.

Integration of the peak at 1480 cm^{-1}, which is assigned to the *cis*-N=N bond, shows an interesting behaviour (trace d): The peak grows rapidly at the beginning of the heating periods, after which it decreases with time. During the cooling periods we note a decrease of the peak intensity. We recall that all peak areas have been normalised, such that a thermal effect on signal strength can be excluded. Hence, we conclude that peak (d) at 1480 cm^{-1} belongs to the isomerised form of the reactant, i.e., a reaction intermediate, which is in agreement with the above assignment of the band to the *cis*-N = N– bond.

More difficult is the interpretation of trace (a), which corresponds to the peak intensity integrated from 1502 cm^{-1} to 1539 cm^{-1} (that can be assigned to the C=C region). The overall trend is a strong increase of the peak area, which clearly shows that it is mainly due to a product of the reaction. However, for a product it is not obvious that the area should show an increase when the temperature is set back to room temperature. This effect is seen during both cooling periods. At the beginning of the subsequent heating periods, however, the intensity of the peak first decreases again before it continues to increase. An explanation for this effect can be suggested by noting that the maximum position of this growing peak first is located at 1514 cm^{-1}, and at the end of the reaction at 1520 cm^{-1}. This means that two or more different compounds may contribute to the integrated area, the concentrations of which change in opposite directions during heating and cooling. A peak centred at 1090 cm^{-1} exhibits a behaviour similar to the peak assigned to the C=C vibration.

We have included in trace (b) the integrated intensity of the peak at 650 cm^{-1}; an unambiguous assignment of this frequency to a molecular moiety can not be indicated at present. The evolution of the peak area with time, which is similar to the one described for trace (d), shows that the signal corresponds to an intermediate. A possibility that we suggest is that the bond can be attributed to an extended bending vibration of the N–N=N bond structure.

As it has been demonstrated [17] that N=N stretching vibration can be observed in Raman spectra more sensitively than in infrared investigations, a sample of **II** in KBr was analysed in a Raman spectrometer. As expected, we observe a strong band at 1484 cm^{-1}, which we assign to the N=N stretch. Unfortunately, some products of the reaction give rise to strong fluorescence, such that we have not been able to obtain Raman spectra from the products even with an FT–Raman instrument using 1064 nm excitation.

In summary, we can state that the end products of photolysis and thermolysis experiments of compound **II** appear to be quite similar. The thermolysis reaction proceeds via an isomerised intermediate (from *trans*-N=N to *cis*-N=N). In contrast, in the photolysis experiments no hints of reversible reaction steps to intermediate products are obtained.

3.3. Phenylpentazadiene (III)

As with compounds **I** and **II**, the results of the thermolysis and photolysis experiments for compound **III** look very similar. However, in contrast to the investigations reported above, for sample **III** the peaks diminish in the whole spectral range without any significant change in shape and position (Table 4). This suggests that volatile decomposition products are generated by photolysis and thermolysis, which evaporate before they can be detected by infrared measurements. Upon closer inspection of the spectra recorded during the reactions we can observe some peaks which diminish faster than the others. For example during thermolysis the sharp peak centred at 910 cm^{-1} (not shown) disappears nearly completely within the first minutes while a broader one arises at somewhat higher energies which disappears some minutes later. During photolysis this behaviour could not be observed, and the mentioned peak diminishes with about the same rate as the others; the intermediate peak at higher energy is not observed. Another interesting detail is the fact that during thermolysis the doublet at 1150/1160 cm^{-1} first merges into a single peak before the intensity decays completely, whereas these two peaks remain separated during the whole photolytic experiment.

Table 4
Vibrational frequencies in cm^{-1} of **III** affected by thermolysis and photolysis

Band remains	Band decreases	Increases	Shifts/ broadens	Assignment
		1605		aromatic ring
	1586			aromatic ring
	1480			–N=N–
	1462			
	1428			
	1386			
	1299			Ar–N
	1285			
	1186			
	1160			
	1150			
	1072			
	1017			
	907			
	828			
			760 (d)	
			628	
	626			
	599			
			513	

With respect to the photolytic experiments, compound **III** was the most sensitive. Even at low irradiation intensities an explosion-like decomposition of **III** embedded in KBr was acoustically perceptible. The colour of the pellets turned from weakly yellow to dark brown already after the first few pulses. If the sample was irradiated with the same energies as used for compounds **I**, **II** and **IV**, the pellets have been completely destroyed.

3.4. 4-Methylpentazadiene (IV)

Photolysis and thermolysis experiments in KBr matrix have been performed for compound **IV**. As observed for compounds **I**, **II** and **III** there was no significant difference in the spectra of photolytic and thermolytic reaction products. The main spectral changes are summarised in Table 5.

As in the case of the decompositions of **I** and **II**, we can see the broadening and shift of the band near 1600 cm^{-1}. In addition the increase of a band at 1520 cm^{-1} can be clearly observed. We tried to monitor intermediate compounds during the photolysis by frequently interrupting the irradiation and monitoring changes in the spectra. However, in the entire spectral range investigated we could not find a band which was first growing and then disappearing, which leads to the conclusion that we do not observe long living intermediates for compound **IV**.

In the range around 700 cm^{-1}, we observed the same effect as seen in the decomposition spectra of **I** and **II**: The band at

Table 5
Changes in vibrational frequencies in cm^{-1} observed during decomposition of **IV**

Band remains	Band decreases	Increases	Shifts/broadens	Assignment
			1600	aromatic ring
	1580			
		1520		
	1503			
			1492	toluene
	1477			
	1437		1437	
	1402			
	1377			
	1288			Ar–N
	1185			
		734	toluene	monosubstituted aromatic ring (toluene)
	710			disubstituted aromatic ring
		692	toluene	monosubstituted aromatic ring (toluene)

710 cm^{-1} which is an indicator for a disubstituted aromatic ring decreases, and new bands are growing at 692 cm^{-1} and 734 cm^{-1}, as is typical for mono-substituted benzenes. From the structure of compound **IV** we can assume that toluene is a possible fission product. Indeed the peaks at 1494 cm^{-1}, 734 cm^{-1} and 692 cm^{-1} can be assigned to the toluene spectrum. However, the growing peak at 1520 cm^{-1} shows that there is a major contribution of at least one additional compound to the product spectrum.

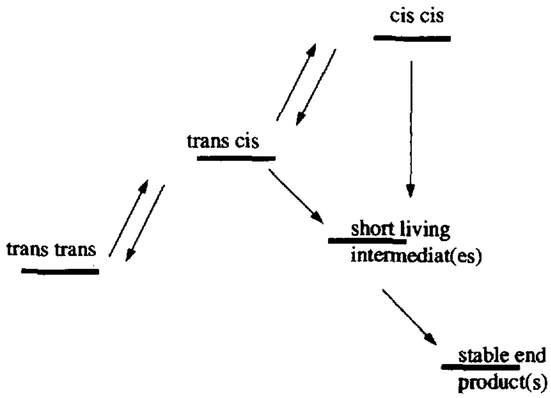
4. Conclusions

The thermolytical and photolytical decay of 1,5-aryl-3-alkyl-pentazadienes in solid matrix can be conveniently monitored by infrared spectroscopy. During photolysis in solution, no intermediate products have been detected by UV spectroscopy [18]. For a KBr matrix the thermolysis experiments generally lead to the same end products as the photolytic decompositions. However, especially in the case of compound **II**, which is the thermally most stable molecule among the investigated compounds, evidence for at least one intermediate has been obtained. The latter is produced thermally and coexists in quasi equilibrium with the most stable isomer, but can also decay irreversibly to stable end products. To a smaller extent such a behaviour could also be detected for compound **I**.

The common feature of the decomposition reactions of all compounds is the broadening and shift of the band near 1600 cm^{-1}. This is an indication that the aromatic ring remains undestroyed; however, as expected, its substitution pattern is changed. Compounds **I**, **II** and **IV** have in common that in all three cases a new band is generated at about 1514 cm^{-1}, which shifts to 1520 cm^{-1} during the reaction. Another common feature is that these compounds decay partially to monosubstituted molecules such as anisole, benzonitrile and toluene, respectively.

Compound **III**, which has no further substituents at the aromatic ring, is obviously decomposed into small volatile fragments, as most peaks disappear during photolysis as well as during thermolysis without significant alteration in position or intensity ratio. Broadening of the band at 1600 cm^{-1} indicates the presence of a mixture of substituted aromatic compounds. In detail, some differences between the photolytically and thermolytically induced decomposition can be seen.

A common reaction sequence for the entire decomposition chain is suggested in Scheme 2. From a stable ground state, e.g., the *trans*/*trans* form with respect to the two N=N groups which is dominant in the ensemble at room temperature, the molecule can be excited to an isomer which contains one or both of the N=N groups in *cis* conformation. Since the infrared frequencies of the N=N stretching vibration of *trans* and *cis* isomer are different [4], and since the two N=N groups hardly influence each other, infrared spectroscopy can discriminate only two concentrations of the three possible isomers (*trans*/*trans*, *cis*/*cis* and *cis*/*trans*) in a mixture. The isomers containing at least one N=N group with *cis* conformation are expected to be less stable compared to the *trans*



Scheme 2.

form, and tend to either return to the initial state or to decompose via instable intermediates to stable end products.

Acknowledgements

This work was financially supported by the Swiss National Science Foundation. We like to thank B. Voit (TU Dresden), Th. Kunz and Ch. Hahn for constructive discussions. Further we are indebted to A. Scholz for measurements with the Raman microscope.

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