Electronic Structure and Gas-Phase Thermolysis of 2-Tetrazenes with Acyclic or Cyclic Amino Groups Studied by Photoelectron Spectroscopy[☆]

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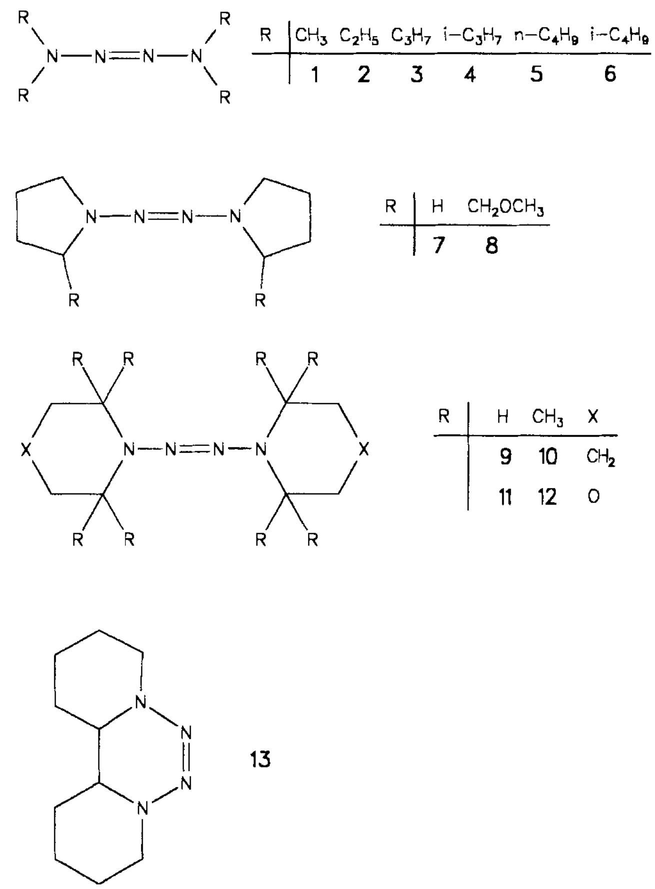
The electronic structures and the gas-phase thermolyses of the 2-tetrazenes **2**–**13** have been studied by He(I) photoelectron spectroscopy. The compounds are characterized by at least three ionization potentials with energies less than 10 eV which are assigned to the molecular orbitals π_3 (HOMO), n^+, π_2, and n^-. In the thermolyses either the formal disproportionation products (amine and imine) of the respective aminyl radical are found, or the latter is stabilized by loss of an alkyl radical affording also an imine. Further products which can be explained by radical reactions are detected in flash vacuum pyrolyses. The tricyclic *cis*-2-tetrazene **13** is cleaved by [2 + 2 + 2] cycloreversion. The methoxymethyl-substituted compound **8** exhibits a more complex cleavage pattern.

2-Tetrazenes are valuable precursors of aminyl radicals and their reaction products like hydrazine derivatives[1]. Continuing our studies of the thermolysis of acyclic[2] and cyclic[2–4] 2-tetrazenes by variable-temperature photoelectron spectroscopy[5], we have investigated some acyclic alkyl-substituted 2-tetrazenes (**2**–**6**) and some derivatives in which the two terminal nitrogen atoms are part of a secondary amine ring (**7**–**13**). The latter are 1,2-dipyrrolidinodiazene (**7**), 1,2-dipiperidinodiazene (**9**), 1,2-dimorpholinodiazene (**11**), the octamethyl derivatives **10** and **12** of **9** and **11**, respectively, the bis(methoxymethyl) derivative **8** of **7**, and 1,2,3,4-tetraazatricyclo[8.4.0.0^{4,9}]tetradeca-2-ene (**13**) in which the 2-tetrazene unit is fixed in a *cis* configuration.

From acyclic aliphatic 2-tetrazenes like 1,1,4,4-tetramethyl-2-tetrazene (**1**) it is known[2] that in the gas phase at 10–50 Pa the corresponding amine and imine are formed in a disproportionation reaction which is characteristic of aliphatic aminyl radicals[6]. The electronic structure[7] and the thermolysis[8] of the unsubstituted parent compound, 2-tetrazene N_4H_4, affording hydrazine, molecular nitrogen, and the isomerization product ammonium azide, have been investigated by Wiberg et al. For cyclic 2-tetrazenes a correlation between ring size, electronic structure, and thermal stability has been discovered[2,3]. For the gas-phase thermolysis of most of the compounds studied now a similar behavior as for **1**[2] might be expected, i.e. disproportionation to the respective amine and imine by transfer of a β-hydrogen atom. However, this is not possible for compounds **10** and **12** which therefore must lead to other products. For the 2-tetrazenes with further heteroatoms such as **8**, **11**, and **12** a similar or divergent behavior might be expected depending on the reactivity of the intermediate aminyl radicals.

Scheme 1



R	CH_3	C_2H_5	C_3H_7	$i\text{-}C_3H_7$	$n\text{-}C_4H_9$	$i\text{-}C_4H_9$
	1	2	3	4	5	6

R	H	CH_2OCH_3
	7	8

R	H	CH_3	X
	9	10	CH_2
	11	12	O

Electronic Structures of 2-Tetrazenes 2–13

PE spectra of aliphatic acyclic[2,9,10] and cyclic[2–4] 2-tetrazenes including **1**–**7**, and **9** have been studied pre-

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viously, but in most cases only the first ionization potential is reported. The characteristic MOs of the 2-tetrazene unit can be described as follows: the two lone pairs of the azo group occupy the orbitals n^+ and n^-. The two lone pairs of the amino groups and the electron pair of the NN π bond fill the MOs $\pi_1-\pi_3$. For 2-tetrazenes with a *trans* configuration of the azo group the following sequence of the MOs may be expected: π_3 (HOMO) $> n^+ > \pi_2 > n^- > \pi_1$. However, depending on substitution, the sequence of the second and the third highest occupied MO might be reversed. For *cis*-2-tetrazenes the MO sequence π_3 (HOMO) $> \pi_2 > n^- > n^+ > \pi_1$ has been found[2,3]. For compounds **8**, **11**, and **12** ionizations of the oxygen lone pairs are to be expected in addition to these MOs in the low-energy region of the spectra (<12.0 eV).

The PE spectra of **2**–**6**, recorded at ambient temperature, closely resemble that of **1**[2], and therefore we refrain from depicting all spectra here. As a characteristic example, spectra of **4** recorded at different temperatures are shown in Figure 1. Selected spectra of **7**–**13** are depicted in Figures 2–5. In Table 1 the observed ionization potentials of **1**–**13** are collected; these data are obtained from the spectra recorded at the lowest temperatures. The assignments are also based on AM1[11] calculations making use of Koopmans' theorem[12], $IP_v(i) \approx -\varepsilon_i \mathrm{SCF}_{(i)}$, by which ionization potentials and orbital energies are related.

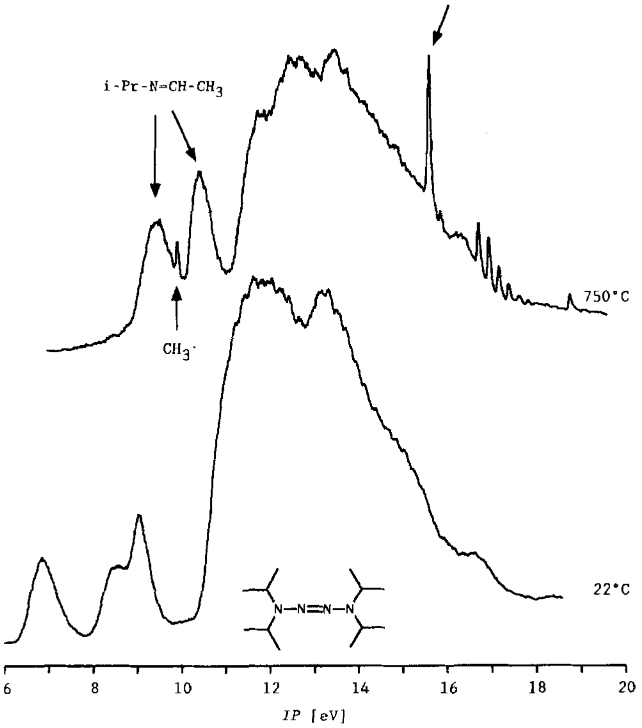


Figure 1. PE spectra of 1,1,4,4-tetraisopropyl-2-tetrazene (**4**) recorded at different temperatures

The observed ionization potentials show the variations which might be expected because of the electronic effects of the substituents. The effects of the oxygen atoms in **11** and **12** are clearly perceptible from the shifts of the ionization bands relative to **9** and **10**, respectively, by up to 0.4 eV.

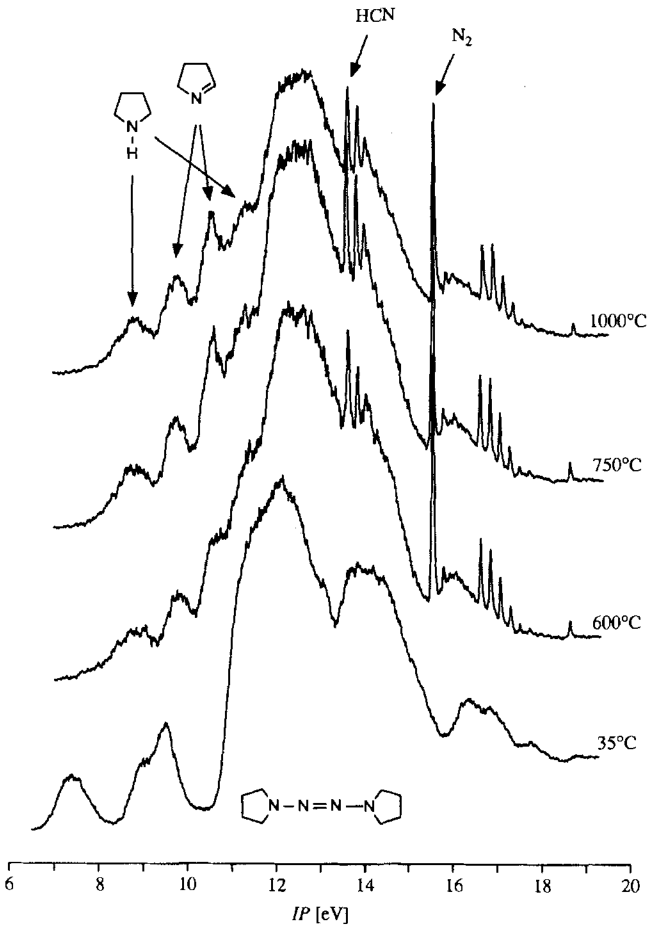


Figure 2. PE spectra of 1,2-dipyrrolidinodiazene (**7**) recorded at different temperatures

Thermolysis of 2-Tetrazenes 2–13

Photoelectron spectroscopy is well suited to analyze gas-phase thermolysis reactions[5]. The reaction takes place in the inlet system of the spectrometer at low pressure (10–50 Pa) and can be monitored readily at different temperatures. The beginning of the thermolysis (usually at a temperature >350°C) is recognized by the appearance of the needle-like ionization peaks of molecular nitrogen. The temperature is increased until starting material is no longer detected in the spectrum. In most cases also further thermolysis of the reaction products is observed, leading to secondary products.

Acyclic 2-Tetrazene 2–6

As a typical example, the thermolysis of **4** is depicted in Figure 1. At temperatures above ca. 600°C besides the peaks of molecular nitrogen two new strong bands are observed at 9.5 and 10.4 eV, which are assigned to ethylideneisopropylamine (**15**). In addition, a sharp band of lower intensity is found at 9.88 eV which is attributed to the methyl radical[13]. The products are obviously formed by β cleavage of the diisopropylaminyl radical **14**. This is confirmed by a flash vacuum pyrolysis of **4** at 400°C which affords the imine **15** (90%) and diisopropylmethylamine (**16**, 5%), the latter being formed by radical radical reaction.

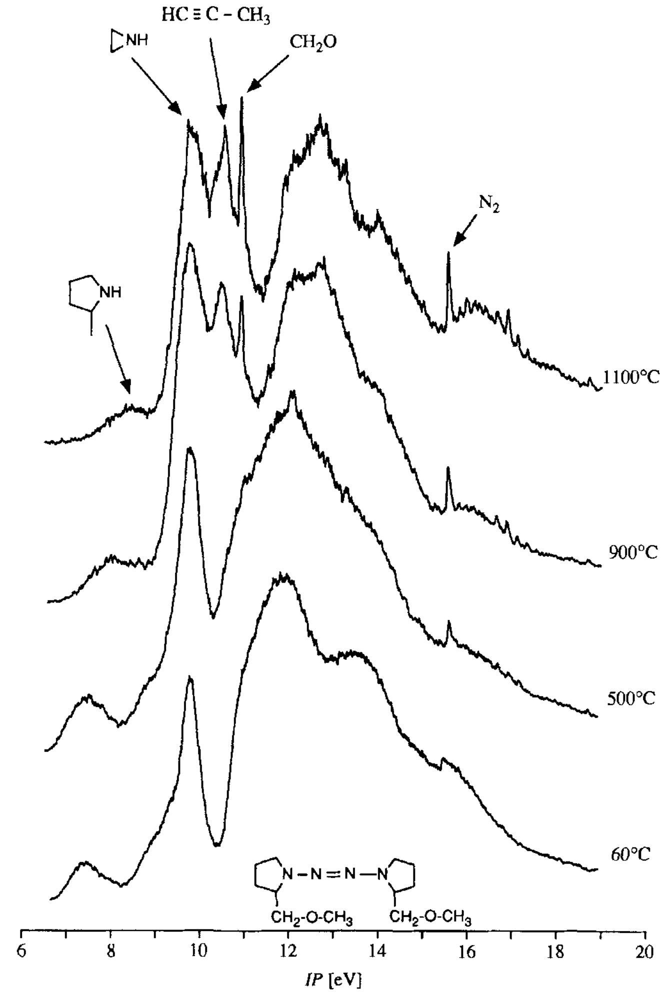


Figure 3. PE spectra of (*S*,*S*)-1,2-bis[2-(methoxymethyl)pyrrolidino]diazene (**8**) recorded at different temperatures

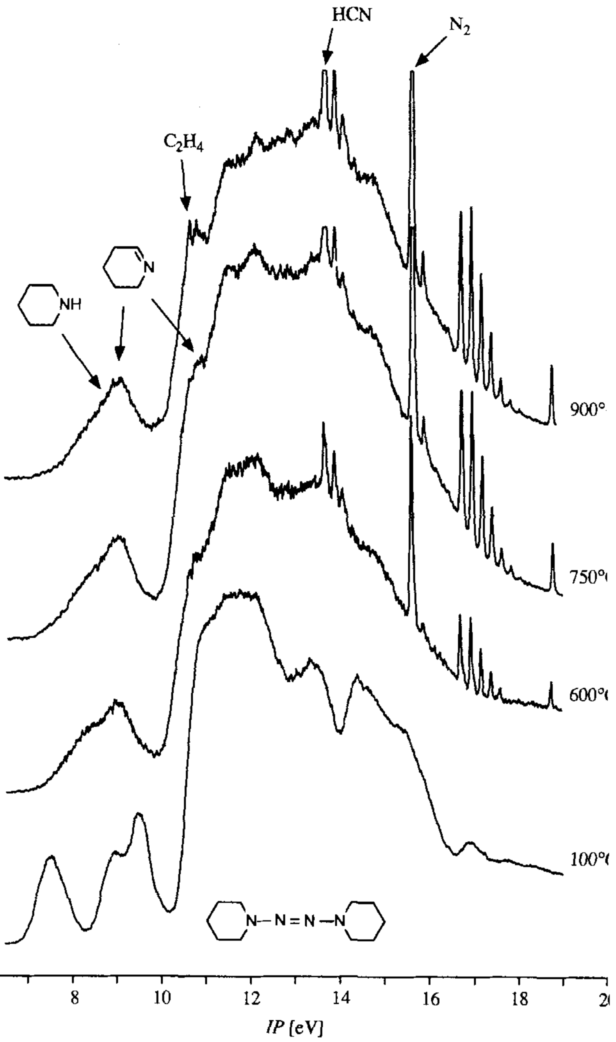


Figure 4. PE spectra of 1,2-dipiperidinodiazene (**9**) recorded at different temperatures

Further products which might be expected like, e.g., methane and ethane, have not been found. To our knowledge, aliphatic aminyl radicals have not yet been investigated by PE spectroscopy. In order to detect such transient species by our technique, lifetimes of >100 ms would be required.

In a similar way as described for **4**, in the thermolysis PE spectra of **2**, **3**, **5**, and **6** the imines ethylmethyleneamine (**17**), methylenepropylamine (**18**), *n*-butylmethyleneamine (**19**), and isobutylmethyleneamine (**20**), respectively, are observed. The ionization potentials of the imines are collected in Table 2. PE spectra of some aliphatic imines have been studied by Bock and Dammel[14]. The assignments to the n and π MOs consistent with the vibrational structure ($\tilde{v} \approx 1000$ cm^{-1}) of the second band. In the thermolysis spectra of **2** the methyl radical is detected in the same way as for **4**. For the other compounds, ethyl or higher alkyl radicals are expected, which have broader ionization bands of lower intensity between 6.7 nd 9.0 eV[13,15] and are difficult to detect besides other molecules with signals in this region. For **2** diethylmethylamine is detected in the PE spectra by its ionization at 8.30 eV as a reaction product, but for **3**–**6** no amines can be found. All products observed in the PE spectra are also formed by flash vacuum pyrolysis. In addition, the following products have been found and identified in the condensate by mass spectrometry: propylpropylideneamine (from **3**, 2%), diethylamine (from **2**, 49%), ethyldipropylamine (from **3**, 1%), 1,2-diethyl-1,2-diazetidine (from **2** by dimerization of ethylmethyleneamine (**17**)[16], 10%). The formation of these products can be explained by reaction of the aminyl or the alkyl radicals formed from the 2-tetrazenes.

Cyclic 2-Tetrazenes 7–13

The high-temperature measurements of **7** (Figure 2) indicate that simultaneously with molecular nitrogen, hydrogen cyanide, pyrrolidine (**22**), and 3,4-dihydro-2*H*-pyrrol (**23**) are formed. The latter two compounds obviously are the direct disproportionation products of the initially formed pyrrolidinyl radical (**21**). The PE spectra of these compounds are known and it is no problem to identify them by their ionization bands at 8.4 and 11.0 eV (**22**) and at 9.71 and 10.56 eV (**23**)[14,17]. However, the second band of **23** is superimposed by another IP. As a secondary thermolysis

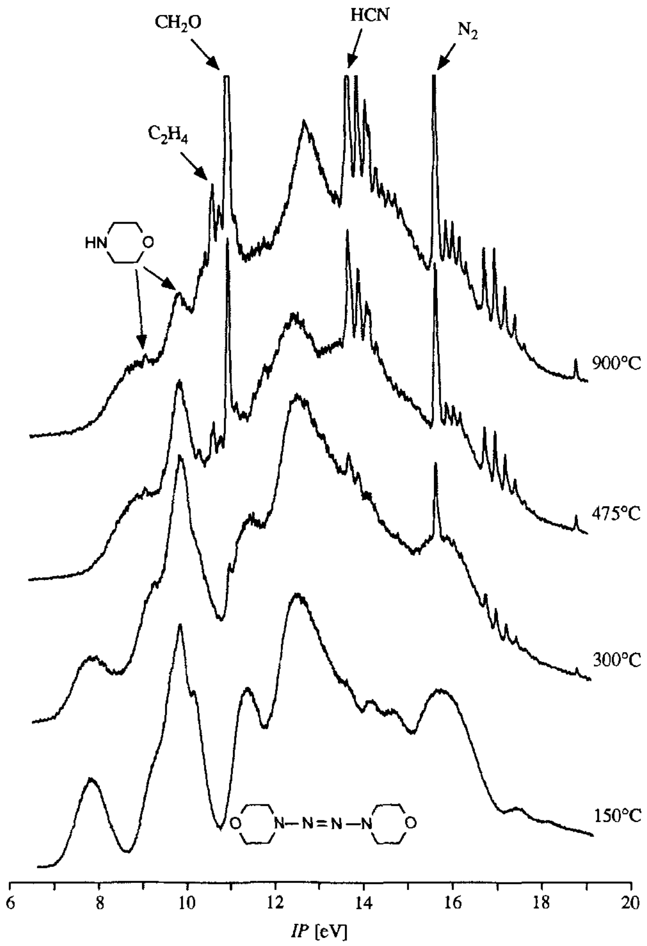


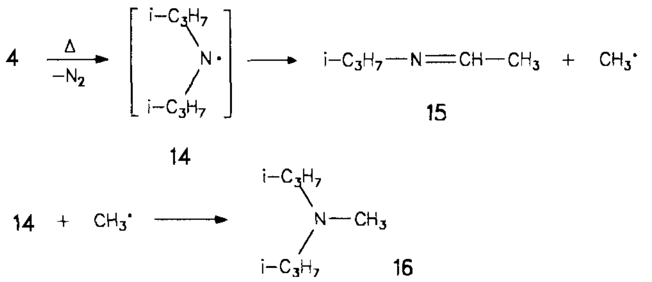
Figure 5. PE spectra of 1,2-dimorpholinodiazene (**11**) recorded at different temperatures

Table 1. Ionization potentials [eV] of 2-tetrazenes **1**–**13**

	π_3	n^+	π_2	n_O
1[2]	7.66	9.38	9.78	
2	7.26	8.92	9.40	
3	7.09	8.75	9.21	
4	6.85	8.49	8.99	
5	7.08	8.70	9.18	
6	7.07	8.76	9.16	
7	7.32	9.00	9.45	
8	7.24	8.88	9.24	9.68
9	7.45	8.92	9.43	
10	7.21	8.12	8.79	
11	7.84	9.24	9.33	9.84
12	7.37	8.46	9.17	9.60
13	7.63	9.63[a]	8.94	

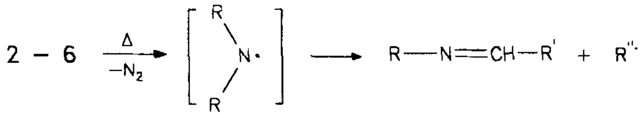
[a] Ionization from n^-.

Scheme 2[a]



[a] The thermolysis of **4** has been studied by PE spectroscopy by Bock et al. (*Chem. Ber.* **1994**, in press).

Scheme 3



$R'' = CH_3, C_2H_5, C_3H_7$

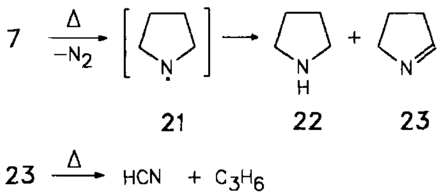
	17	18	15	19	20
R	C_2H_5	C_3H_7	$i\text{-}C_3H_7$	$n\text{-}C_4H_9$	$i\text{-}C_4H_9$
R'	H	H	CH_3	H	H

Table 2. Ionization potentials [eV] of imines $R^1{-}N{=}CR^2R^3$

	R^1	R^2	R^3	n	π
17	C_2H_5	H	H	9.78	11.27
18	C_3H_7	H	H	9.76	11.18
15	$i.C_3H_7$	CH_3	H	9.46	10.42
19	C_4H_9	H	H	9.78	10.9
20	$i.C_4H_9$	H	H	9.76	10.98
23[a]	$\text{-}(CH_2)_3\text{-}$		H	9.74	10.55
26[a]	$\text{-}(CH_2)_4\text{-}$		H	9.04	10.52
28	$\text{-}C(CH_3)_2\text{-}(CH_2)_2\text{-}$		CH_3	8.64	9.74
33	$\text{-}C(CH_3)_2\text{-}O\text{-}CH_2\text{-}$		CH_3	8.80	10.3

[a] Cf. ref.[14].

Scheme 4



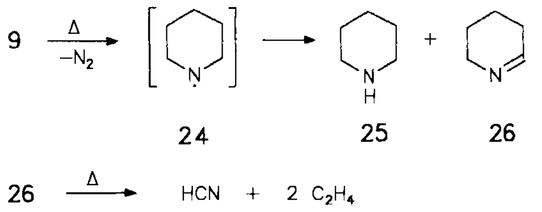
product hydrogen cyanide (IP_V = 13.60 eV[18]) is formed from **23**, which is instable under the reaction conditions.

The cleavage of HCN from **23** leaves C_3H_6, which might either be cyclopropane or propene. The latter alkene should be easily recognized by its characteristic band at 10.03 eV[18] which is absent in the pyrolysis spectra of **7**. Cyclopropane, on the other hand, has two broad ionization bands at 10.60 and 11.30 eV[18], which fall in the same region as the second IPs of **22** and **23**, respectively. The decomposition of **23** resembles that of Δ^1-pyrazoline which, under similar conditions in the PE spectrometer, forms molecular nitrogen and cyclopropane[19].

In the high-temperature PE spectra of 1,2-dipiperidinodiazene (**9**) (Figure 4) the following products are identified:

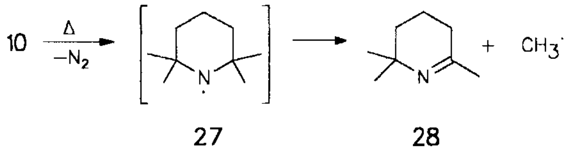
molecular nitrogen, piperidine (**25**), 2,3,4,5-tetrahydropyridine (**26**), hydrogen cyanide, and ethylene. Compounds **25** and **26** are the disproportionation products of the piperidinyl radical (**24**), while HCN and C_2H_4 are formed by the fragmentation of **26**. These compounds are identified by their known ionization potentials: 8.64 eV (**25**), 8.95 and 10.40 eV (**26**)[17], 13.60 eV (HCN)[18], 10.51 eV (ethylene)[18].

Scheme 5



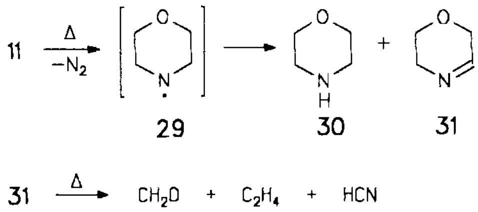
The octamethyl derivative **10** of **9** has a rather simple spectrum at elevated temperature. In addition to molecular nitrogen, only one compound seems to be formed which by its strong ionization bands at 8.64 (n_N) and 9.74 eV ($\pi_{C=N}$) is identified easily as 2,3,4,5-tetrahydro-2,2,6-trimethylpyridine (**28**). Compound **28** is formed from the aminyl radical **27** by loss of a methyl radical (β cleavage). The characteristic IP of the latter 9.84 eV[13] is discernible in the spectra on top of the second band. Compound **28** is probably fragmented by [2 + 2 + 2] cycloreversion.

Scheme 6



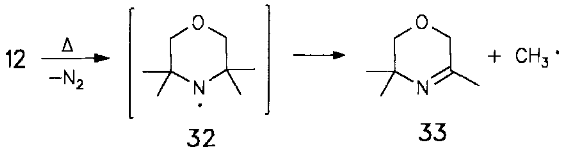
The pyrolysis of the morpholinodiazene **11** led to rather complex PE spectra (Figure 5) indicating primary and secondary decomposition products. Easily identified by their characteristic peaks are molecular nitrogen, hydrogen cyanide, formaldehyde, and ethylene. Two broader bands at 8.9 and 9.8 eV are attributed to morpholine (**30**). These products can be explained by the following decomposition path: Primary cleavage products which are formed from the aminyl radical **29** are morpholine (**30**) and dihydro-1,4-oxazine (**31**). The latter, for which ionization bands at about 9.0 and 10.0 eV are expected, is split into C_2H_4, CH_2O, and HCN by [2 + 2 + 2] cycloreversion. Whether **31** has a substantial stationary concentration under the reaction conditions cannot be ascertained from the PE spectra because its ionization bands are covered by those of **30**.

Scheme 7



Similar to **10**, compound **12**, the octamethyl derivative of **11**, has rather simple spectra at elevated temperatures. Besides molecular nitrogen, only a single product is formed which has two ionization bands (8.80 and 10.3 eV). The latter exhibits more than twice the intensity of the former, indicating that it actually results from the superposition of at least two bands. In analogy to the decomposition of **11**, 5,6-dihydro-3,5,5-trimethyl-2*H*-1,4-oxazine (**33**) is expected to be generated as a cleavage product of **12**. AM1 calculations give the following energy values for the three highest occupied MOs of **33**: −9.77 eV (n_N), −10.62 eV (π_{CN}), −11.30 eV (n_O). These values compare well with the observed ionization potentials. In contrast to **10**, the peak of the methyl radical (9.84 eV) is not present in the pyrolysis spectra of **12**. A fragmentation of **33** cannot be concluded from the spectra, not even at 1050°C.

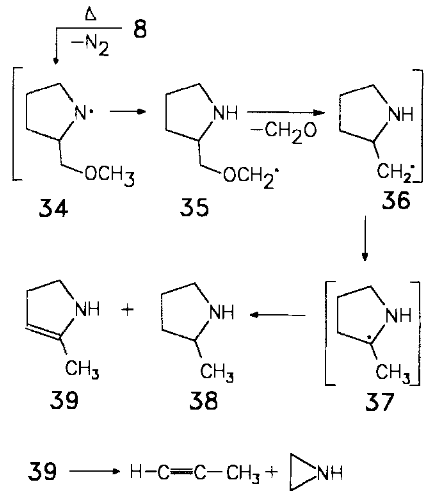
Scheme 8



In the thermolysis mixture of compound **8** (Figure 3) the products molecular nitrogen and formaldehyde are easily identified. In contrast to the cyclic 2-tetrazenes **7**, **9**, and **11**, hydrogen cyanide is not formed. The broad peak at ca. 8.45 eV is probably related to a primary reaction product, while the strong and sharper bands at 9.8 and 10.5 eV are caused by final products. If we assume that the decomposition of **8** is initiated by loss of nitrogen, the aminyl radical **34** is formed which – by hydrogen shift – affords the corresponding alkoxymethyl radical **35**. Loss of CH_2O leads to the methylenepyrrolidine radical **36**, which isomerizes to the more stable tertiary radical **37**. This, by loss or capture of a hydrogen atom, affords 2-methylpyrrolidine (**38**) and 2,3-dihydro-5-methylpyrrol (**39**). The latter is cleaved to propyne and aziridine.

The spectrum recorded at 900°C corresponds well to the expected ionization potentials of the enamine **39**. Compound **38** should have its first IP near that of pyrrolidine (**22**) at 8.4 eV[17]. The first band in the spectrum recorded at 1100°C is probably also caused by this compound. As the spectra at 900 and 1100°C indicate, **39** disappears at higher temperature, and the formation of propyne and aziridine becomes apparent. Especially the latter compound is

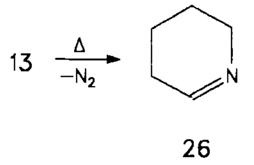
Scheme 9



indicated by its ionization bands at 9.84 and 11.94 eV[20] the former even showing its characteristic vibrational fine structure. Propyne has a first IP of 10.37 eV[18]; the appearance of the PE spectra obtained at high temperatures is consistent with the presence of this molecule.

Thermolysis of the tricyclic *cis*-tetrazene **13** affords only a single product besides molecular nitrogen which is easily identified as 2,3,4,5-tetrahydropyridine (**26**). This reaction can be explained as a [2 + 2 + 2] cycloreversion.

Scheme 10



Conclusion

Except for compound **13**, the thermolyses of the 2-tetrazenes studied here can be explained by the formation of short-lived aminyl radicals, which cannot be detected in the PE spectra. In most cases the aminyl radical is stabilized by loss of an alkyl radical and formation of an imine. The imines and the methyl radical are identified by their characteristic ionization bands. Higher alkyl radicals are difficult to detect PE-spectroscopically in a reaction mixture. As has been found for tetramethyl-2-tetrazene (**1**)[2], in some cases, namely for **7**, **9**, and **11**, the disproportionation products (amine and imine) of the respective cyclic aminyl radicals are the reaction products. Whether these are formed by a bimolecular reaction of two aminyl radicals, which seems to be unlikely because of the low pressure (10–50 Pa), or directly from the parent tetrazene cannot be decided here.

The loss of a methyl radical from **27** and **32** instead of ring opening permits some conclusions regarding the stereochemistry of this β cleavage. It can be assumed that the singly occupied molecular orbital (SOMO) of the radical and the opening CC σ bond are antiperiplanar in order to facilitate the formation of the π bond of the imine. In **27** and **32** the SOMO should be in an axial position[6] so that a neighboring axial methyl group is split off. Aminyl radicals like **27** and **32** are assumed to play an important role in the function of sterically hindered amines as light stabilizers of polymers[21]. However, neither in the thermolysis nor in the photolysis[22] of 2-tetrazene **10** or analogous compounds in solution the formation of an imine by loss of a methyl group has been observed.

As is exemplified by **8**, the thermolysis of 2-tetrazenes bearing cyclic amino groups is greatly modified by substituents on the α carbon atoms. While the unsubstituted and the methyl-substituted compounds show a relatively simple cleavage pattern, the methoxymethyl groups in the α position give rise to a more complex behavior. More or less all important steps in the decomposition of the 2-tetrazenes can be easily determined by the employed technique proving once more the advances of variable-temperature photoelectron spectroscopy in vapour-phase thermolysis studies. The data obtained so far stimulate further studies of the thermolysis of functionalized 2-tetrazenes.

This work was supported by the *Fonds der Chemischen Industrie*.

Experimental

PE Spectra: UPG200 spectrometer of Leybold-Heraeus equipped with a He(I) radiation source (21.21 eV). The spectra were calibrated with the lines of xenon at 12.130 and 13.436 and of argon at 15.759 and 15.937 eV. The accuracy of the measurements was approximately ±0.03 eV for ionization potentials, for broad or overlapping signals it was only ±0.1 eV. The thermolyses were carried out at 10–50 Pa in a molybdenum tube of 80 mm length and 4.5 mm inner diameter, which was placed between the sample inlet system and the ionization chamber. The distance between thermolysis tube and ionization chamber was about 35 mm. Temperatures are accurate to ca. ±5°C.

Flash Vacuum Pyrolyses were carried out in an apparatus according to Seybold and Jersak[23]. The quartz tube had a length of 350 mm and an inner diameter of 22 mm. The products were condensed on a cold finger (−196°C) covered with a diethyl ether matrix. About 0.2–0.5 g of the 2-tetrazene was pyrolyzed at temperatures between 350 and 500°C and the pressure of 0.1 Pa or lower. The products were analyzed by GC/MS and ^{1}H NMR. – NMR: Varian XL-200 or Bruker AMX300, tetramethylsilane as internal standard. – IR: Pye Unican SP 3–100. – The 2-tetrazenes were prepared from the corresponding cyclic secondary amine by nitrosation with sodium nitrite, reduction of the nitrosoamine with $LiAlH_4$, and oxidation of the hydrazine with iodine or mercuric oxide.

Syntheses of compounds **2**[24], **3**[25], **4**[26], **5**[10], **6**[10], **7**[27], **9**[1b], **10**[22], **11**[1b], and **13**[28] have been described in the literature.

(S,S)-1,2-Bis[2-(methoxymethyl)pyrrolidino]diazene (**8**): Oxidation of (*S*)-1-amino-2-(methoxymethyl)pyrrolidine (SAMP)[29] with yellow mercuric oxide afforded **8**. The crude product was distilled under reduced pressure, and a colorless oil was obtained; yield: 6.6 g (67%), b.p. 115°C/0.07 hPa. – IR (neat): $\tilde{\nu}$ = 3000 cm^{-1} (s, CH), 2960 (s, CH), 2860 (s, CH), 1475 (m, CH), 1345 (m, CH), 1130 (s, C–O–C). – ^{1}H NMR ($CDCl_3$): δ = 1.7–2.1 (m, 8H, CH_2), 3.10 (m, 2H, CH), 3.3–3.5 (m, 4H, CH_2N), 3.40 (s, 6H, CH_3), 3.65 (m, 4H, CH_2O). – ^{13}C NMR ($CDCl_3$): δ = 22.03 (CH_2), 27.11 (CH_2), 50.00 (CH_2N), 60.90 (CH), 61.05 (CH_3), 74.87 (CH_2O). – $C_{12}H_{24}N_4O_2$ (256.4): calcd. C 56.23, H 9.44, N 21.86;

found C 56.91, H 9.77, N 21.68. – α_D^{20} (0.6660 g, 0.4540 g, 0.8500 g, $CHCl_3$): $-328.2°$.

1,2-Bis(3,3,5,5-tetramethylmorpholino)diazene (**12**) was synthesized in the usual way from the secondary amine 3,3,5,5-tetramethylmorpholine[30], m.p. 168°C (decomp.). – ^1H NMR ($CDCl_3$): $\delta = 1.21$ (s, CH_3), 3.40 (s, CH_2). – ^{13}C NMR ($CDCl_3$): $\delta = 24.56$ (CH_3), 56.08 (quart. C), 78.98 (CH_2). – $C_{16}H_{32}N_4O_2$ (312.5): calcd. C 61.51, H 10.32, N 17.93; found C 61.57, H 10.62, N 17.67.

☆ Dedicated to Professor *Wolfgang Luettke* on the occasion of his 75th birthday.

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