Gas-Phase Thermolysis of Pyrazolines, 2[1]

Electronic Structure and Gas-Phase Thermolysis of 4,5-Dihydro-3*H*-pyrazoles Studied by Photoelectron Spectroscopy, Semiempirical Quantum-Chemical Calculations, and Flash Vacuum Pyrolysis

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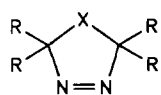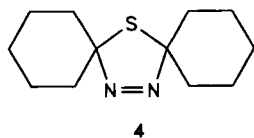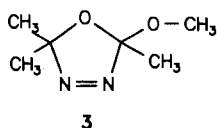Universitätsstraße 5–7, D-45117 Essen

The PE spectra of the 4,5-dihydro-3*H*-pyrazoles **1**, **2**, of 2,5-dihydro-1,3,4-oxadiazole **3**, and 2,5-dihydro-1,3,4-thiadiazole **4** have been recorded. Based on HAM/3, MNDO, AM1, and PM3 calculations, the ionization potentials have been assigned to molecular orbitals. The gas-phase thermolyses of **1**−**4** have been studied by PE-controlled gas analysis. Extrusion of molecular nitrogen leads to reactive species which cyclize to three-membered rings of different stability. At higher temperatures and in flash vacuum pyrolysis, consecutive reactions may lead to smaller acyclic molecules. The cyclopropanol **7**, obtained by denitrogenation of **2**, is thermally rather stable. Its PE spectrum has been recorded and analyzed.

Elimination of molecular nitrogen in a thermolytic or photochemical way is the most important reaction of azo compounds. In cyclic azo compounds this leads to ring-contracted or highly strained compounds[2]. From 4,5-dihydro-3*H*-pyrazoles (Δ^1-pyrazolines) cyclopropane derivatives and acyclic products are formed under different conditions. As has been shown in our work on 4-substituted 3,5-dihydro-3,3,5,5-tetramethyl-4*H*-pyrazoles[1], the substituents of the five-membered ring are of essential importance for the way the compounds decompose. We have now studied the electronic structure and the thermolysis of Δ^1-pyrazolines **1**−**4**, substituted with heteroatoms, using variable-temperature photoelectron spectroscopy[3,4].

Electronic Structure of Compounds 1−4

4,5-Dihydro-3*H*-pyrazoles contain a *cis*-azo group in a five-membered ring, and their electronic properties are essentially determined by this group. The PE spectra and the electronic structures of cyclic and bicyclic azo compounds have been investigated by several authors[5−10]. The characteristic MOs are the symmetric (n_{NN}^+) and the antisymmetric (n_{NN}^-) combination of the n_N orbitals and the π MO of the N=N bond ($\pi_{N=N}$). The energies of these orbitals have been calculated for the unsubstituted parent compound **1** with various methods[5,6], the sequence of the orbital energies being $n_{NN}^- > \pi_{N=N} > n_{NN}^+$.

The PE spectrum of **1**, which has been measured previously[11], is depicted in Figure 1. The observed ionization potentials are summarized in Table 1 together with the results of MNDO[12], AM1[13], PM3[14], and HAM/3[15] calculations. Although from a microwave study[16] it is known that **1** has an envelope conformation, most calculations lead to planar structures, only the HAM/3 calculation relates to a puckered conformation. However, these discrepancies do not affect the interpretation of the PE spectrum.

The Koopmans approximation[17], $IP_{(i)} \approx -\varepsilon_{(i)}$, allows the correlation of ionization potentials with molecular orbital energies, and the observed *IP*s are assigned accordingly.

The first ionization band exhibits a remarkable shape which is not found for other 4,5-dihydro-3*H*-pyrazoles but resembles that of some other five-membered rings like thiazole[18]. The band is rather broad and exhibits a fine structure with alternating intensities of neighboring lines. From

	X	R
1	CH₂	H
2	CH–OH	CH₃
5	CH₂	CH₃

Table 1. Observed vertical ionization potentials IP_v [eV], calculated ionization potentials IP_c [eV], and calculated orbital energies ε [eV] of compounds 1−4, 7, and 18

	IP_v	Assignment	IP_c HAM/3	−ε MNDO	AM1	PM3
1	9.20[a]	n^-_{NN}	8.91	11.04	10.90	10.12
	11.63	$\pi_{N=N}$	11.38	12.16	11.34	11.29
	11.94	n^+_{NN}	11.93	12.94	12.47	12.32
	12.9	π_{NN}, π_{CH2}	12.38	14.14	13.73	13.43
	13.8	σ_{CC}	13.25	13.37	13.02	13.63
2	8.64	n^-_{NN}	8.10	10.51	10.26	9.84
	10.37	n_O	10.25	11.59	11.19	11.39
	10.85(sh)	π_{CH3}	10.90	12.99	11.58	12.01
	11.05	$\pi_{N=N}$	11.28	12.01	11.88	12.15
	11.28	n^+_{NN}	11.92	12.51	12.78	12.60
3	9.33	n^-_{NN}	8.53	10.77	10.44	10.15
	10.30	n_O(ring)	10.20	11.46	11.21	11.43
	10.79	n_O(OCH$_3$)	10.50	12.77	11.83	11.71
	12.05(sh)	n^+_{NN}	12.25	13.47	13.03	12.85
	12.5	$\pi_{N=N}$	12.10	13.80	13.95	13.00
4	8.34	n_S		9.91	9.45	9.46
	8.55(sh)	n^-_{NN}		10.98	10.47	10.08
	10.4	n^+_{NN}, n_S		11.72	11.03	11.24
	10.7	n^+_{NN}, n_S		12.63	12.12	12.42
	11.4	$\pi_{N=N}$		13.40	13.05	13.06
7	9.00	ω_a, n_O	8.53	10.40	9.92	10.16
	9.60	ω_s	9.99	10.20	10.25	10.56
	11.3	π_{CH3}	11.33	10.50	11.78	11.85
	11.5	n_O, π_{CH3}	12.38	12.25	12.58	13.00
18	8.17	n_S		9.53	9.13	9.08
	9.45	ω_s		10.79	10.34	10.86
	9.93	ω_a		11.42	10.60	10.93
	10.9	π_{CH2}		11.74	10.92	11.35

[a] Vibrational splittings: 1850 and 620 cm^{-1}.

Figure 1. PE spectrum of 4,5-dihydro-3H-pyrazole (1) recorded at different temperatures

the calculated orbital energies (Table 1) it is unlikely that ionizations from other orbitals than the HOMO (n^-_{NN}) contribute to the first band, and the distance to the next ionization band should be 0.4 (AM1) to 2.5 eV (HAM/3). In fact, differences of about 2 eV are found between n^-_{NN} and $\pi_{N=N}$ in cis-azo compounds with a Δ^1-pyrazoline structure[5,7]. Also, the presence of a tautomer like Δ^2-pyrazoline can be excluded[19].

There are at least two vibrational transitions of the radical cation that contribute to the band structure. These are the N=N stretching vibration $\nu_{N=N} = 1850$ cm^{-1} (1552 cm^{-1} in the parent molecule[20]) and the N=N torsion $\tau_{NN} = 620$ cm^{-1} (428 cm^{-1} in the molecule[20]). The other infrared or Raman-active vibrations are localized in other parts of the molecule[20]. Since n^-_{NN} is an antibonding MO,
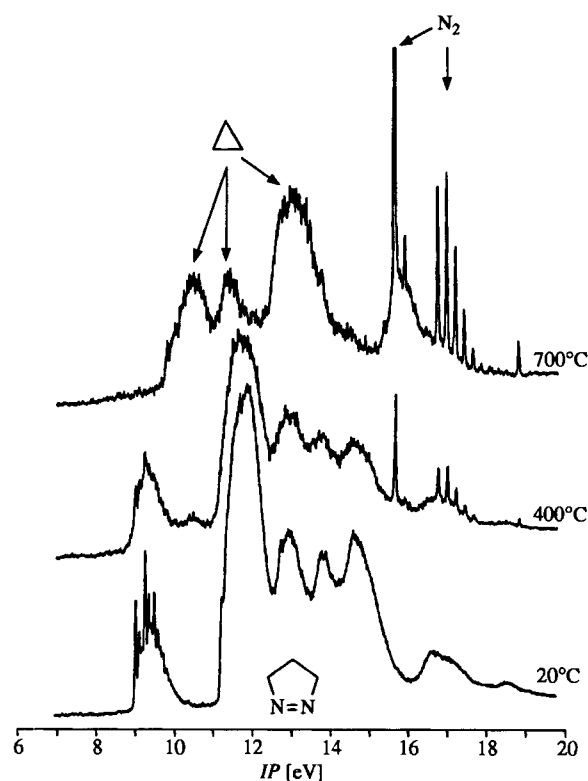
both frequencies of the radical cation are higher than in the molecule.

The data in Table 1 reveal that the HAM/3 results show the best agreement with the experimental results. The large separation of the first two IP_v values has also been found by ab initio calculations[6].

The PE spectra of 4,5-dihydro-4-hydroxy-3,3,5,5-tetramethyl-3H-pyrazole (2), 2,5-dihydro-2-methoxy-2,5,5-trimethyl-1,3,4-oxadiazole (3), and dispiro[cyclohexane-1,2'-[1,3,4]thiadiazole-5',1''-cyclohexane] (4) are depicted in Figures 2−4. A correlation diagram including also 4,5-dihydro-3,3,5,5-tetramethyl-3H-pyrazole (5)[7,10,21] is shown in Figure 5. The relevant data are summarized in Table 1. For these compounds additional ionizations from the heteroatoms (n_O and n_S) and σ orbitals of the alkyl groups are found, leading to further bands in the PE spectra. The PE spectrum of 4 has been reported previously by Houk et al.[7], but only the first two ionization potentials have been assigned.

As in the case of 1, the spectra of 2−4 have been analyzed with the aid of semiempirical calculations. The energies of the characteristic molecular orbitals depend on the electronegativity of the heteroatoms and their position relative to the azo group. A comparison of the PE spectrum of 2 with that of tetramethyl-Δ^1-pyrazoline (5) clearly shows the second band to arise from the ionization of the oxygen lonepair (Figure 5). This is in accord with the calculations (Table 1). Relative to 5, n^-_{NN} and n^+_{NN} are not affected in their energy. Only $\pi_{N=N}$ is slightly stabilized. The ionization
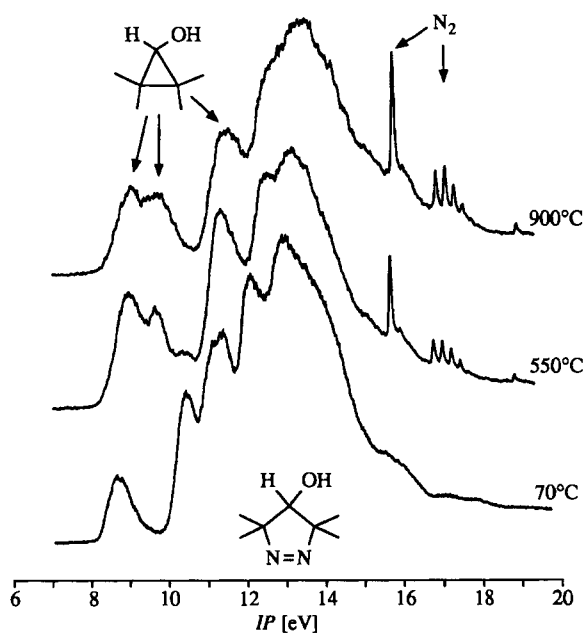
Figure 2. PE spectrum of 4,5-dihydro-4-hydroxy-3,3,5,5-tetrame-thyl-3*H*-pyrazole (2) recorded at different temperatures
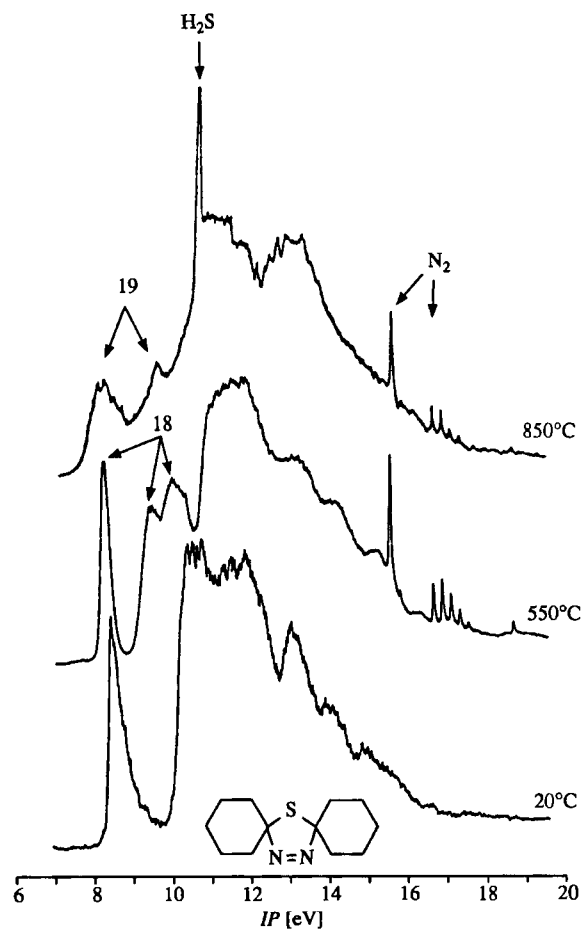

Figure 4. PE spectrum of dispiro[cyclohexane-1,2'-[1,3,4]thiadi-azole-5',1"-cyclohexane] (4) recorded at different temperatures
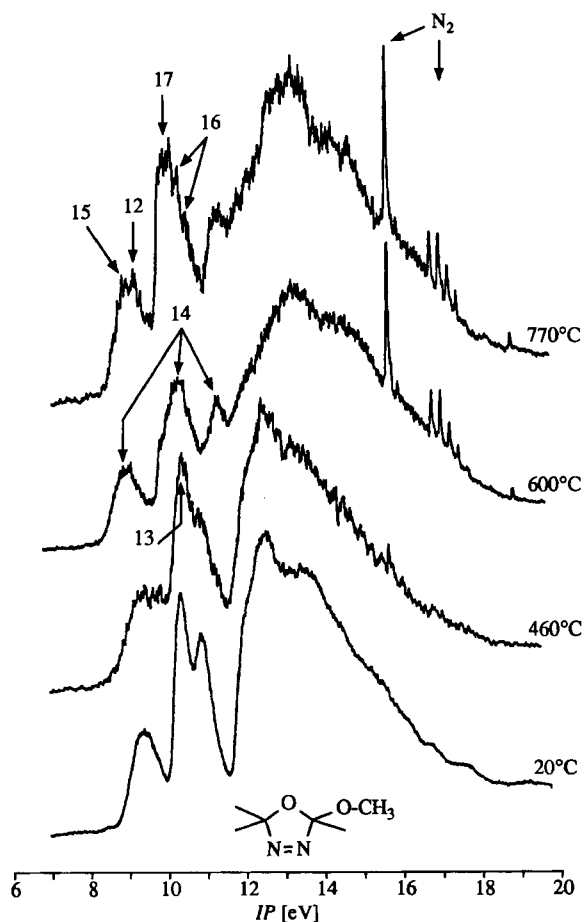

Figure 3. PE spectrum of 2,5-dihydro-2-methoxy-2,5,5-trimethyl-1,3,4-oxadiazole (3) recorded at different temperatures
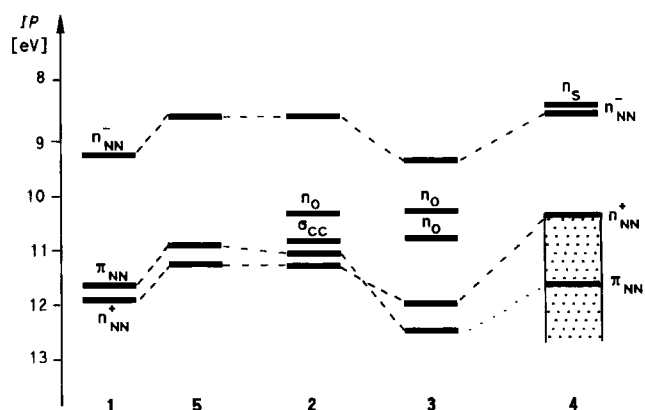

Figure 5. Correlation diagram for compounds 1—5

from a σ_{CC} MO is found as a shoulder in front of those of $\pi_{N=N}$ and n_{NN}^{+}, in accord with the calculated MO sequence.

In 3 there is an endo- and an exocyclic oxygen atom. The ionizations from the corresponding lonepairs (n_O) are found as the second and third band in the PE spectrum (Table 1). n_{NN}^{-} is stabilized by 0.7 eV relative to compound 5. This is caused by the electronegativity of the oxygen atoms. One can assume this to be also the case for $\pi_{N=N}$

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and n_{NN}^+. The additional interaction with the $2p_z$ lonepair of the oxygen atom $[n_O(\pi)]$ in the ring further stabilizes $\pi_{N=N}$. The calculations show that there is still another effect: the second lonepair of the heteroatom $[n_O(\sigma)]$ combines with n_{NN}^+ causing its destabilization. By both effects the sequence of n_{NN}^+ and $\pi_{N=N}$ is inverted which is untypical of Δ^1-pyrazolines.

The interpretation of the PE spectrum of the thiadiazoline 4 is difficult because of the large alkyl groups which cause a lot of σ ionizations, and IPs greater than ≈ 10.4 eV can only be estimated. Houk et al.[7] have assigned the first band to the ionizations from both n_S and n_{NN}^-. We assign an ionization of 11.4 eV to $\pi_{N=N}$. Ionization bands from n_{NN}^+ of Δ^1-pyrazolines are usually broad. The calculations show that n_{NN}^+ interacts with the second lonepair $[n_S(\sigma)]$ of the thioether group [for CH_3-S-CH_3: $n_S(\pi) = 8.72$ eV, $n_S(\sigma) = 11.30$ eV[22]]. These orbitals have about the same energy, and therefore the interaction should be strong leading to an inversion of the natural sequence of $\pi_{N=N}$ and n_{NN}^+.

Thermolyses of Compounds 1−4

The *cis*-azo group of 1−4 may be regarded as a preformed nitrogen molecule which can be split off at higher temperatures or on irradiation[23]. This leads to reactive species, often described as 1,3-diradicals, which can afford a wide range of products, depending on substitution and reaction conditions[24]. We have studied the gas-phase thermolyses at low pressure (10−50 Pa) and various temperatures, using real-time gas analysis by PE spectroscopy[4]. As the temperature is raised, the reaction is monitored by the characteristic bands of molecular nitrogen (15.60, 16.98, 18.78 eV[22]). Some pyrolyses have also been carried out in a flash vacuum pyrolysis apparatus described by Seybold and Jersak[25].

4,5-Dihydro-3H-pyrazole (1) *(Δ¹-Pyrazoline)*: After elimination of molecular nitrogen from Δ^1-pyrazoline only trimethylene remains. This can form cyclopropane (6) or propene. PE spectra of 1 recorded under pyrolysis conditions are shown in Figure 1. Cyclopropane (6, $IP_v = 10.53$, 11.30, 13.2 eV[22]) is unequivocally identified, and there is no indication of another product, although a trace of propene which has been observed by Crawford and Mishra[26] in a pyrolysis at 223°C cannot be excluded.
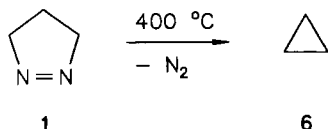

The gas-phase pyrolysis of 1 can be described as a direct cyclization of the reactive intermediate C_3H_6 after the loss of molecular nitrogen.

4,5-Dihydro-4-hydroxy-3,3,5,5-tetramethyl-3H-pyrazole (2): According to the PE spectra, which have been recorded up to 900°C, the thermolysis of the hydroxypyrazoline 2 follows a rather simple pattern: The reaction starts at

≈ 450°C, and the starting compound has disappeared at about 600°C (Figure 2). The spectrum does not change significantly as the temperature is raised further, which indicates that − besides molecular nitrogen − only a single product with IP values of ≈ 9.0, ≈ 9.6, and ≈ 11.3 eV is formed. These findings exclude the fragmentation of 2 to small molecules like water, formaldehyde, carbon monoxide, acetone (12), isobutene (11), or 2,3-dimethyl-2-butene (8). The product might be a cyclopropane derivative like 7, an oxirane like 9, or a vinyl ether like 10 which could be formed from the primary 1,3-diradical by ring closure and/or hydrogen shift.
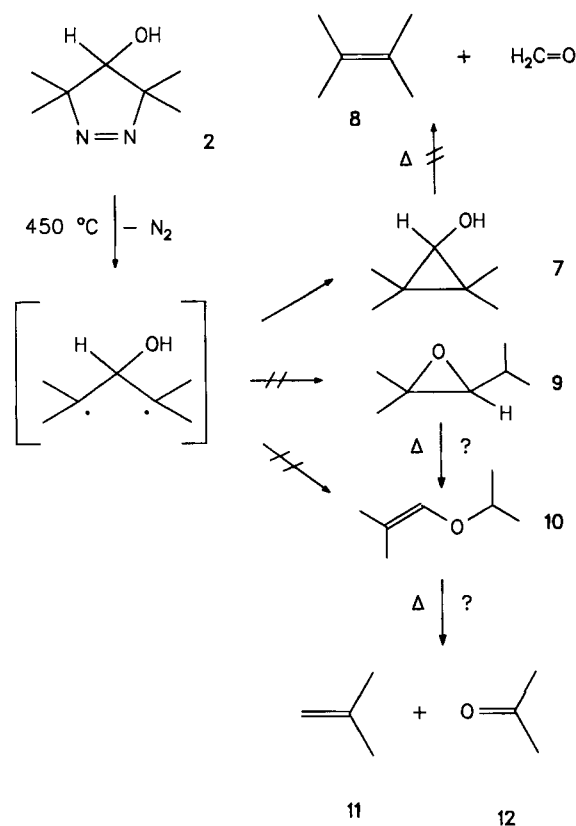
Inspection of the PE spectra of similar oxiranes[22,23] and vinyl ethers[27] excludes 9 and 10 as possible products. For 2,2,3,3-tetramethylcyclopropanol (7) the calculated ionization potentials and orbital energies are in good accordance with the observed values (Table 1). Although cyclopropane and its derivatives have been studied extensively by PE spectroscopy[28], to our knowledge cyclopropanols have not been investigated by this technique. It is surprising that 7 is not cleaved at high temperature, since one would expect formaldehyde and 2,3-dimethyl-2-butene (8) as stable products. Also the well-known isomerization of cyclopropanols to aldehydes or ketones[29] can be excluded. Fragmentation would also be expected for 9 and 10 which should split into acetone (12) and isobutene (11) in a similar way as observed for the oxadiazoline 3 (see below).

To confirm these findings, we have thermolyzed 2 by preparative flash vacuum pyrolysis at 500°C. The isolated

product (100%) has been identified as the cyclopropanol **7**. Compound **7** is a colorless solid which isomerizes to the corresponding aldehyde on contact with air. The PE spectrum of **7**, recorded at 25°C, is in accordance with the high-temperature spectra of **2**. The first four ionization potentials of **7** can be explained with the aid of the quantum-chemical calculations (Table 1). In analogy to cyclopropane[28,22] and simple alkanols[22] three high-energy MOs are to be expected for **7**: Two Walsh-type orbitals (ω_a and ω_s) and an oxygen lonepair orbital (n_O). Similar to cyclopropylamine[22], interaction between n_O and ω_a is to be expected. In addition to these orbitals, there are high-lying σ MOs mainly localized in the dimethylmethylene groups.

The gas-phase pyrolysis of the hydroxypyrazoline **2** is characterized by ring contraction and resembles that of the unsubstituted parent compound **1**.

2,5-Dihydro-2-methoxy-2,5,5-trimethyl-1,3,4-oxadiazole (**3**) *(Oxadiazoline)*: Warkentin et al.[30] have studied the thermolysis of **3** at 380°C in a quartz tube, at 80°C in a sealed flask, and in CCl$_4$ solution. The results vary considerably because of the different reaction conditions. They have determined the products from gas-phase pyrolysis by ^{1}H-NMR spectroscopy. In addition, the authors have monitored the thermolysis by PE spectroscopy, but have identified only molecular nitrogen as a product. Adam and Finzel[31] have observed diazo compounds besides methyl acetate (**16**) in the benzophenone-sensitized photolysis of Δ^3-1,3,4-oxadiazolines, but not in thermolysis.

We have repeated the gas-phase pyrolysis of **3** at 350 and 510°C in a flash vacuum pyrolysis apparatus[25]. Three products, namely 1-(isopropenyloxy)-1-methoxyethane (**14**), methyl acetate (**16**), and acetone (**12**), are identified by ^{1}H-NMR spectroscopy. Their amounts have been determined to be 63.5, 26.2, and 10.3%, resp., at 350°C and 46.7, 27.7, and 25.6%, resp., at 510°C. Compounds **12** and **16** are probably secondary products which are formed from **14** (see below).

The PE spectra recorded at higher temperatures (Figure 3) indicate that thermolysis starts at about 460°C when the characteristic bands of molecular nitrogen[22] appear. At 600°C the reaction seems to be complete, since the bands of **3** have vanished. Raising the temperature causes further changes. There are bands at about 9.1, 9.7, 10.0, and 10.6 eV, which become more intense up to 770°C. These bands correlate with the first ionization potentials of **15**[22], **12**[22], methyl vinyl ether (**17**[32]) and methyl acetate (**16**[33]), respectively.

The PE spectrum at 600°C shows some ionization bands in the lower region. According to the studies of Warkentin et al.[30], the methoxy vinyl ether **14** or methoxytrimethyloxirane (**13**) could be formed. We have tried — without success — to isolate **14** from the product mixture of the flash vacuum pyrolysis by distillation and preparative GC. Correlation of the ionization potentials (8.9, 10.2, 11.2 eV) with those of **14** calculated by semiempirical methods shows a good agreement (HOMO: $\varepsilon^{PM3} = -9.45$ eV, $\pi_{C=C}$). In particular, the first ionization band at 8.9 eV cannot be assigned to the other products **12**, **15**−**17**. The first ionization
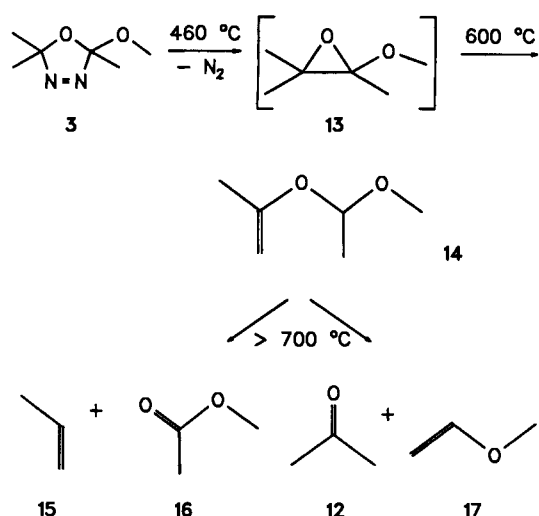
of oxiranes (n_O) is found at higher energies (oxirane: 10.57 eV[34]). Therefore, most probably **14** is an intermediate pyrolysis product of **3**, and **12**, **15**−**17**, which are found at higher temperatures or after longer reaction times, are cleavage products of this ether. This is confirmed by the observation of Warkentin et al.[30] that more **14** is formed in the flash vacuum pyrolysis at 380°C than by heating of **3** at 80°C for a whole week.

It is difficult to decide whether **14** really is the primary product of **3** after the loss of molecular nitrogen, or also a secondary product. In the PE spectrum recorded at 460°C there is a band at 10.3 eV, whereas the $n_O(O-Me)$ band of **3** at 10.79 eV has disappeared. This is in a region where we expect an ionization from the methoxyoxirane **13** [$\varepsilon^{PM3} = -10.95$ (ω_s), -11.08 ($n_O(O-Me)$), -11.54 ($n_O(ring)$) eV]. Compound **13**, formed by ring contraction of **3**, is probably the primary thermolysis product. This has been suggested by Warkentin et al.[30], who describe the formation of **14** from a 1,3-diradical by a sigmatropic hydrogen shift. Adam and Finzel[31], however, favor the formation of **14** via a diazenyl radical as an intermediate, because in the photolysis they also have found diazopropane as a product.

Under the conditions of the present study, the ether **14** is the first observable product after extrusion of molecular nitrogen from the oxadiazoline **3**. At higher temperatures, **14** decomposes either to **15** and **16** or to **12** and **17**. The second combination dominates at higher temperatures. It is possible that the products **12**, **15**−**17** are formed from **3** directly, but there is no doubt that they are also formed from the methoxy vinyl ether **14**. The formation of the secondary products from **14** is only possible by a repeated retro 1,4-H shift. This result leads to the assumption that a reactive intermediate, for example a 1,3-diradical, is involved.

Thermolysis of the oxadiazoline **3** affords fragmentation products **12**, **15**−**17**, most probably via a methoxyoxirane **13** and/or a methoxy vinyl ether **14**.

Dispiro[cyclohexane-1,2'-[1,3,4]thiadiazole-5',1''-cyclohexane] (**4**): The thermolysis of thiadiazoline **4** at 110°C in solution has been studied by Barton and Willis[35]. In the

PE spectrometer **4** is stable up to 250°C. At higher temperatures the characteristic bands of molecular nitrogen indicate the thermolysis reaction (Figure 4). The first ionization potential is shifted by 0.16 eV to lower energy. Above 650°C we observe a sharp band at 10.50 eV, which indicates the presence of hydrogen sulfide[22].
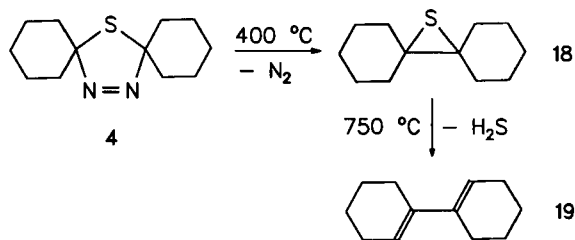
The analysis of the pyrolysis spectra above 350°C becomes easy, when we compare them with the PE spectra of a pure sample of the thiirane **18** recorded at different temperatures (Table 1). There is good correspondence with the pyrolysis spectra of **4**.

Above 650°C **18** decomposes with elimination of hydrogen sulfide. At 700°C the sharp band of the first ionization becomes broad and **18** has disappeared. The first ionization band is shifted below 8 eV. After elimination of hydrogen sulfide from **18**, there remains a butadiene derivative like bi-1-cyclohexen-1-yl (**19**). Only highly substituted[36] or conjugated C=C bonds in hydrocarbons give rise to such a low first ionization potential. Bicyclohexylidene can definitely be excluded as a product because of its first ionization potential of 8.21 eV which we have measured on an *authentic sample*.

In summary, the thermolysis of **4** leads to the thiirane **18** as the primary product. Above 750°C, a secondary product is formed by loss of hydrogen sulfide, which has a 1,3-diene structure like bi-1-cyclohexen-1-yl (**19**).

Conclusion

The PE spectra of some 4,5-dihydro-3H-pyrazoles including the unsubstituted parent compound **1**, the 1,3,4-oxadiazoline **3** and the 1,3,4-thiadiazoline **4** have been analyzed. The "natural" sequence of the characteristic MOs of Δ^1-pyrazolines is $n_{NN}^- > \pi_{N=N} > n_{NN}^+$. Substitution on the ring does not change this sequence. However, hetero atoms like oxygen or sulfur as in **2** and **3** invert the sequence of the second and the third of these MOs.

In contrast to our first studies of the thermolysis of Δ^1-pyrazolines[1], in compounds **1**−**4** there is no possibility of forming reactive trimethylenemethane intermediates, and this excludes the question for a least or non-least motion path. After the extrusion of molecular nitrogen, which in all cases is the first step of pyrolysis, there remain reactive intermediates like trimethylene diradicals, which react to form the corresponding three-membered rings. These are of different stability. Whereas cyclopropane (**6**) is found to be stable up to 1000°C, and the cyclopropanol **7** seems to be stable up to 900°C (under the conditions in the PE spectrometer), the thiirane **18** decomposes above 550°C forming

hydrogen sulfide, and the oxirane **13** is a short-lived intermediate which is difficult to identify by means of the PE spectra.

Experimental

For experimental details see ref.[1].

MNDO, AM1, and PM3 calculations were carried out with the program package MOPAC 5.1[37]. Ionization potentials were calculated with the program HAM/3 (version 1979 − Royal Institute of Technology, Stockholm, Sweden)[15]. Molecular structures were preoptimized by molecular mechanics calculations[38] with the program PCMODEL-PI (version 3.3), Serena Software, Bloomington, Indiana/USA, on a personal computer.

Compounds **1**[39], **2**[40], **3**[41,42], **4**[35,43], **17**[35], and bicyclohexylidene[35] were synthesized according to known procedures.

2,2,3,3-Tetramethylcyclopropanol (**7**): 0.50 g (3.5 mmol) of 4,5-dihydro-4-hydroxy-3,3,5,5-tetramethyl-3H-pyrazole (**2**) was thermolyzed at 500°C by flash vacuum pyrolysis. Yield of **7**: 0.40 g (100%) as colorless needles. M.p. 49°C. − IR (KBr): $\tilde{v}$ = 3295 (OH), 3010, 2942, 2863 (CH), 1145, 1096, 934 cm^{-1}. − ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.83 (s, 1H, CH), 1.74 (s, 1H, OH), 1.00 (s, 6H, CH$_3$), 0.99 (s, 6H, CH$_3$). − ^{13}C NMR (75 MHz, CDCl$_3$): δ = 63.5 (C−OH), 21.7 (C$_q$), 21.1 (CH$_3$), 15.0 (CH$_3$). − MS (70 eV), m/z (%): 114 (10) [M$^+$], 99 (100) [M$^+$−CH$_3$], 81 (28) [M$^+$ − CH$_3$ − H$_2$O], 71 (10), 57 (12) [C$_3$H$_5$O$^+$], 55 (18), 43 (64) [C$_3$H$_7^+$]. − C$_7$H$_{14}$O (114.2): calcd. C 73.63, H 12.36; found C 72.86, H 12.93.

[1] Part 1: M. K. Kindermann, R. Poppek, P. Rademacher, A. Fuß, H. Quast *Chem. Ber.* **1990**, *123*, 1161−1168. The 4-ketones and 4-thioketones in ref.[1] are named as 3,5-dihydro-4H-pyrazol-4-ones and 4H-pyrazole-4-thiones, resp., whereas in the present paper 4,5-dihydro-3H-pyrazole is correct (IUPAC rules).
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