Gas Phase Thermolysis of Pyrazolines. 5. Electronic Structure and Gas Phase Thermolysis of Tetrazole Derivatives Studied by Photoelectron Spectroscopy

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The photoelectron spectra of substituted tetrazoles **1-3**, 1,4-dihydro-5*H*-tetrazol-5-ones **4-9**, and 1,4-dihydro-5*H*-tetrazole-5-thiones **10-15** have been recorded. Based on PM3 and some *ab initio* calculations, the ionization potentials have been assigned to molecular orbitals. Gas-phase thermolyses of **1-15** have been studied by real-time gas analysis controlled by photoelectron spectroscopy. Compounds **1** and **2** lose formaldehyde and thioformaldehyde, respectively, leaving unsubstituted tetrazole (**16**), which decomposes mainly through extrusion of a nitrogen molecule and formation of cyanamide. Thiirane is split off from **3**, and the remaining molecule decomposes into smaller products. Compounds **4-9** are cleaved by [3+2] cycloreversion to isocyanates and azides. Some of the unsymmetrically substituted compounds exhibit a marked selectivity in this reaction. For thiones **10-15** [3+2] cycloreversion is the main way of decomposition affording isothiocyanates and azides. In addition, the sulfur atom can split off and dimerize or abstract hydrogen atoms to form hydrogen sulfide. Some products like thiirene, formaldehyde, thioformaldehyde and acetaldehyde are generated solely from substituents. Photoelectron spectroscopy proved to be an excellent method for such thermolysis studies.

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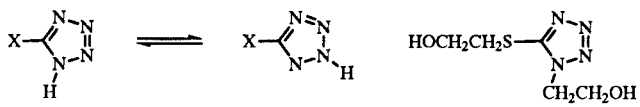
Introduction.

The photochemical or thermal extrusion of molecular nitrogen from five-membered cyclic azo compounds represents a convenient route to cyclopropanes and their hetero analogues [1,2]. The photolysis of tetrazolinones and tetrazolinethiones was investigated by Quast and coworkers [3]. Gas phase thermolysis of pyrazoles [4-6], triazoles [7] and tetrazolines [8] was studied by Rademacher, Quast and coworkers. The previous investigations were mainly centered on the parent systems with no or few additional substituents. Since substituents may induce alternative reaction pathways and lead to new interesting products, we have now studied the electronic structures and the gas phase thermolyses of the substituted tetrazoles **1-3**, the 1,4-disubstituted 1,4-dihydro-5*H*-tetrazol-5-ones **4-9**, and the 1,4-disubstituted 1,4-dihydro-5*H*-tetrazole-5-thiones **10-15** by variable-temperature photoelectron spectroscopy.

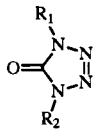
Formulas 1



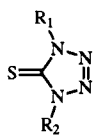
X = OCH_3 **1a**
X = SCH_3 **2a**

1b
2b

3



	4	**5**	**6**	**7**	**8**	**9**
R^1	H	H	H	H	CH_3	CH_3
R^2	H	CH_3	C_2H_5	C_6H_5	CH_3	C_6H_5



	10	**11**	**12**	**13**	**14**	**15**
R^1	H	H	H	CH_3	CH_3	CH_3
R^2	CH_3	C_2H_5	C_2H_4OH	CH_3	CH_2OH	C_6H_5

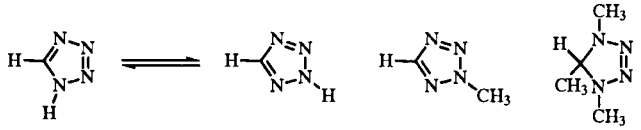
Electronic Structures.

We have measured the photoelectron spectra of compounds **1-15** at elevated temperatures (35-200°) in order to obtain sufficient vapour pressure (about 10-50 Pa). No decomposition of the compounds occurred under these conditions except for **14** which loses formaldehyde already at 35°. The spectra were analysed in the limits of the Koopmans approximation [9], $IP_i \approx -\varepsilon_i^{SCF}$, which correlates ionization potentials IP_i with molecular orbital energies ε_i. The SCF calculations were performed using the PM3 [10] method.

Tetrazoles **1-3**.

The photoelectron spectra of **1-3** are depicted in Figures 1-3. The spectrum of the unsubstituted tetrazole **16** was measured previously [11]. This compound was considered to be in the 2*H*-tautomeric form **16b** in the gas phase owing to the similarity of its photoelectron spectrum with that of 2-methyl-2*H*-tetrazole (**17**) [12,13], and it might as well be possible to distinguish the 1*H*- **a** and 2*H*-tautomers **b** of **1** and **2** from their photoelectron spectra. That **16b** is by far the prevailing tautomer in the gas phase has recently been proved by Maier and coworkers [14].

Formulas 2



16a **16b** **17** **18**

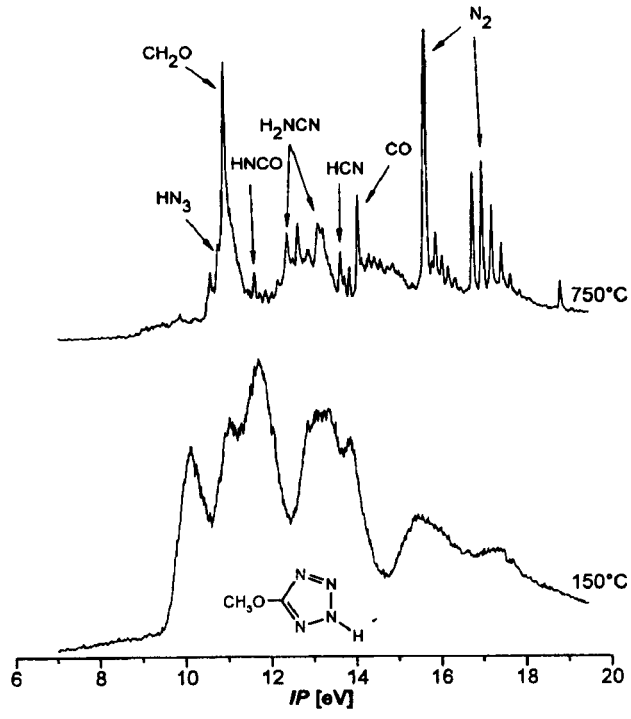


Figure 1. Photoelectron spectrum of tetrazole **1** measured at different temperatures.

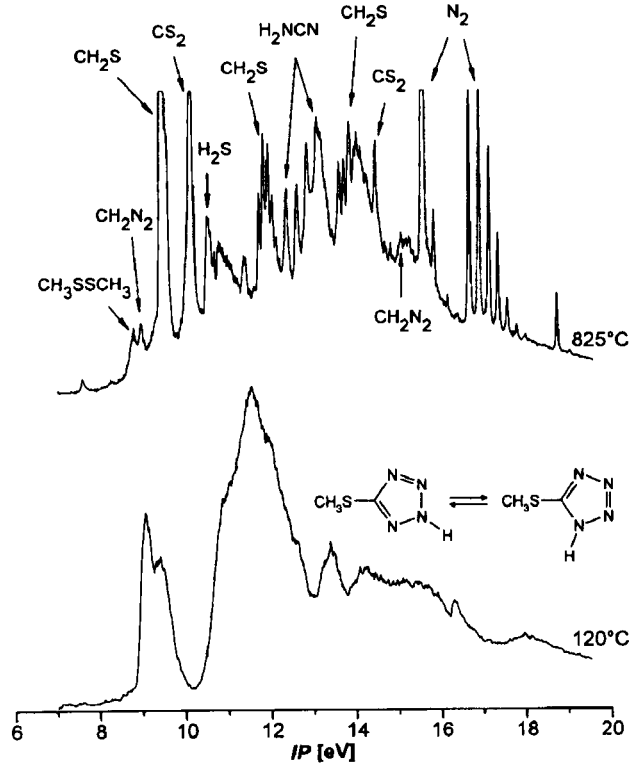


Figure 2. Photoelectron spectrum of tetrazole **2** measured at different temperatures.

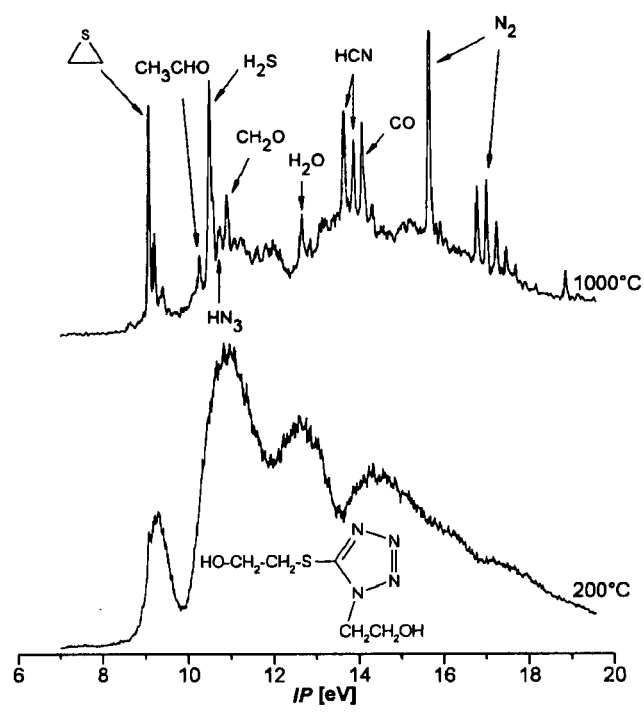


Figure 3. Photoelectron spectrum of tetrazole **3** measured at different temperatures.

The electronic structure of the tetrazole ring is characterized by three occupied π molecular orbitals (π_1-π_3) and three n_N orbitals (n_N^1-n_N^3) which result from combinations of the three n_N orbitals [11]. The lone electron pairs of the oxygen and sulfur atoms of the substituents of **1-3** should lead to additional high-lying occupied orbitals n_X (X = O or S).

The orbital energies of the two tautomers of **1** and **2** and those of **3** were calculated using the PM3 method [10]. The results are summarized together with the ionization potentials in Table 1. For the characteristic molecular orbitals of **1-3** the following sequence is found: n_X (HOMO) > n_N^3 > π_3 > n_N^2 > π_2 > n_N^1 > π_1; only for **1a** are n_N^1 and π_2 reversed.

Table 1

Orbital Energies ε^{PM3} [eV] and Ionization Potentials IP [eV] of Tetrazoles **1-3**

		n_X	n_N^3	π_3	n_N^2	π_2	n_N^1
1a	-ε	10.64	10.97	11.49	11.53	13.35	13.13
1b	-ε	10.19	11.21	11.70	12.06	12.80	13.31
1	IP	10.05 (775) [a]	10.95	11.65	11.95	12.90	13.25
2a	-ε	9.55	11.09	11.48	11.65	12.15	13.26
2b	-ε	9.12	11.35	11.67	11.98	11.99	13.55
2	IP	9.06 (**2b**) 9.43 (**2a**)	10.88	11.55	11.95	12.60	13.40
3	-ε	9.55	11.00	11.14	11.53	12.07	13.16
3	IP	9.30 (940) [a]	10.90			12.70	

[a] Vibrational splitting [cm^{-1}].

The first band in the photoelectron spectra of **1-3** results from ionization of electrons from the n_x orbital. For compound **1** there is a better correlation of ionization potential- and ε-values (Table 1) with the 2*H*-tautomer **1b** than with the 1*H*-tautomer **1a**. Therefore, it is concluded that in the gas phase **1b** is the prevailing tautomer.

In the spectrum of compound **2** there are two bands at 9.06 and 9.43 eV with an intensity ratio of roughly 4:3. They are assigned to ionizations from the n_S orbital of **2b** and **2a**, respectively. This assignment is based on two reasons:

1) The difference between these two ionizations (0.37 eV) is nearly the same as that between the calculated orbital energies of **2b** and **2a** (0.43 eV).

2) The second ionization (9.43 eV), assigned to the 1*H*-tautomer **2a**, is close to that found for IP(n_S) of the 1*H*-tetrazole **3** (9.30 eV).

The other ionizations of **2** can not be assigned in a fashion similar to **2a** and **2b** because they are located in the unresolved σ part of the spectrum (> 11 eV). The photoelectron spectrum of **3** exhibits only one band below 10 eV which is assigned to ionization from the n_S orbital. Because of strong overlap, the rest of the spectrum has too little structure to permit detailed analysis. The n_O ionizations of the hydroxy groups of the substituents which are expected below 11.0 eV [15] also contribute to the second band which expands from 10.0 to 12.0 eV; ε^{PM3} values of -11.78 and -12.00 eV are calculated for the corresponding n_{OH} orbitals. To make Table 1 simpler, these data are not included in the table.

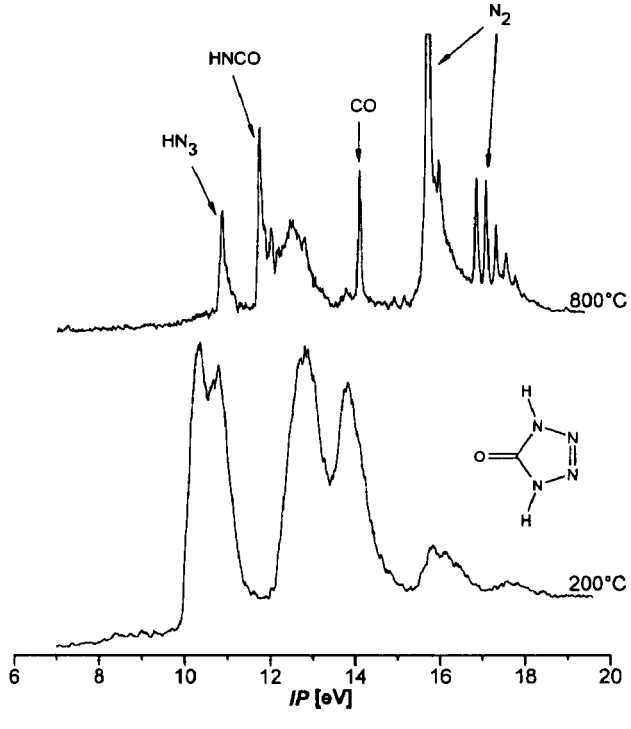


Figure 4. Photoelectron spectrum of tetrazolinone **4** measured at different temperatures.

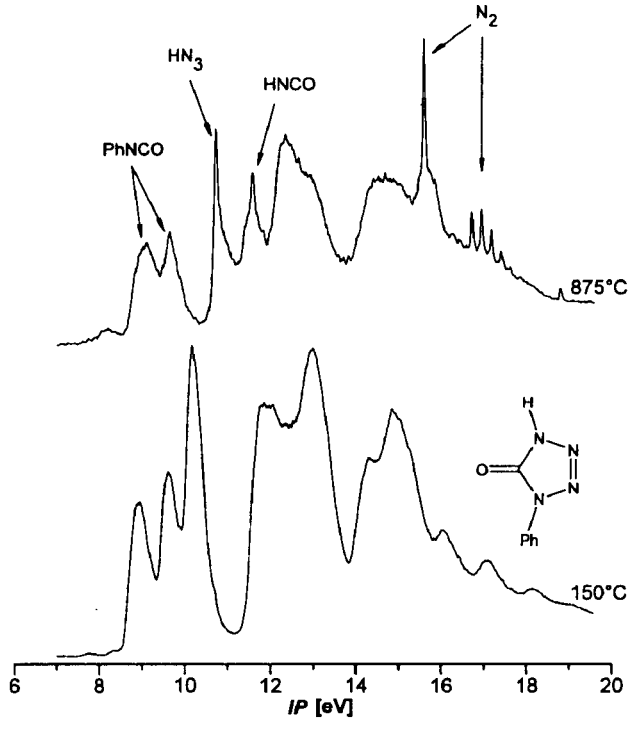


Figure 5. Photoelectron spectrum of tetrazolinone **7** measured at different temperatures.

Tetrazolinones **4-9**.

The photoelectron spectra of **4**, **7** and **8** are depicted in Figures 4-6 and the relevant data are summarized in Table 2. The photoelectron spectrum of compound **8** was studied previously [16].

The tetrazolinones **4-9** may be considered as a combination of an exocyclic C=O bond with a *cis*-2-tetrazene unit comprised in a five-membered ring, and their electronic structure can be expected to resemble closely that

Table 2

Orbital Energies ε^{PM3} [eV] and Ionization Potentials IP [eV] of Tetrazolinones **4-9**

		π_3^{Ar}/π_2^{Ar}	π_3	n_O	π_2	n^-_{NN}	n^+_{NN}
4	-ε		10.09	11.09	11.76	12.75	13.33
	IP		10.25	10.60	12.60	12.86	13.75
5	-ε		10.03	11.01	11.34	12.66	13.29
	IP		9.77	10.45	11.75	12.40	13.35
6	-ε		10.03	10.96	11.38	12.55	13.23
	IP		9.64	10.35	11.55	12.20	13.20
7	-ε	9.32/10.10	10.55	11.01	11.99	12.50	13.39
	IP	8.96/9.55 sh	9.67	10.23	11.90	12.15	13.10
8	-ε		10.09	10.93	11.00	12.66	13.27
	IP		9.37	10.17	11.00	11.95	12.90
9	-ε	9.43/10.10	10.34	10.97	11.66	12.42	13.37
	IP	8.72/9.72	9.88	10.05 sh	11.35	11.80	12.80

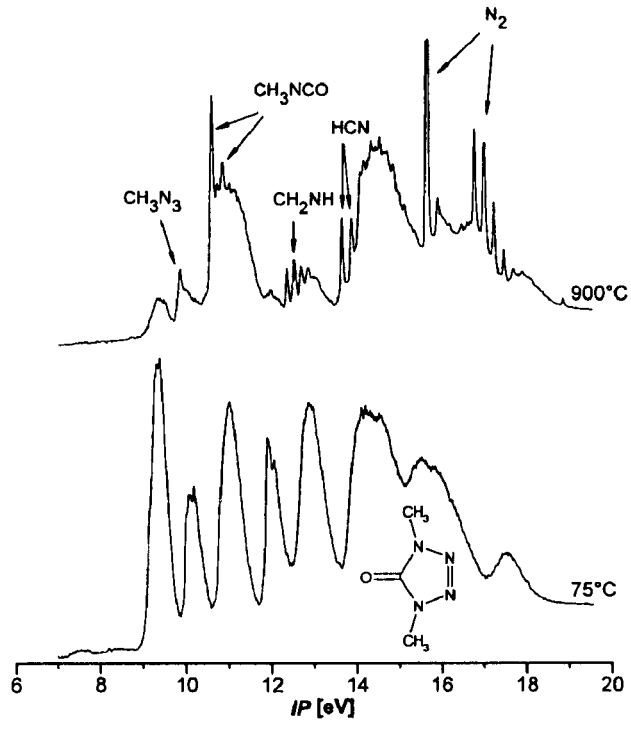


Figure 6. Photoelectron spectrum of tetrazolinone **8** measured at different temperatures.

of tetrazolines. The latter is characterized by three occupied π-type MOs (π_1-π_3) of the 2-tetrazene unit and two n-type orbitals (n^-_{NN} and n^+_{NN}) centered on the azo group [8]. The $\pi_{C=O}$ and n_O have to be added for tetrazolinones. The PM3 calculations revealed the energy sequence π_3 (HOMO) > n_O > π_2 > n^-_{NN} > n^+_{NN} > $\pi_{C=O}$ > π_1 for the characteristic orbitals of **4-9** (Table 2). In general, our analysis confirms the assignments given for the photoelectron spectrum of compound **8** [16]. The only major modification concerns the sequence of the ionizations related to the orbitals n^+_{NN} and $\pi_{C=O}$ which was reversed. Since there is little band overlap, analyses of the spectra of **4-9** and assignments of the ionizations are much easier than for **1-3**. For the phenyl substituted compounds **7** and **9**, the ionization potentials related to the molecular orbitals π_3^{Ar} and π_2^{Ar} are found below those of the tetrazolinone orbitals (< 10.5 eV).

In Figure 8 (see below), a correlation diagram is shown for the ionization potentials of compounds **4-6** and **8**. 1,4,5-Trimethyl-4,5-dihydro-1*H*-tetrazole (**18**) [8], which has no exocyclic C=O bond, was included for comparison. As expected, the ionization potentials of the tetrazolinones are higher than those of **18** because of the stabilizing effect of the carbonyl group. The variation of the ionization potentials of these compounds can be explained in terms of substituent perturbations. Additional alkyl groups destabilize both the π and n molecular orbitals.

Tetrazolinethiones **10-15**.

The electronic structures of the tetrazolinethiones **10-15** are similar to those of the analogous tetrazolinones, however, the characteristic 2-tetrazene orbitals are destabilized up to about 0.6 eV. The spectra are characterized by a strong band at about 8.5 eV which corresponds to the ionizations from the nearly degenerate orbitals π_3 and n_S. In some cases, this band exhibits vibrational fine structure. Analysis of the spectra is further complicated by strong band overlap between 11.5 and 12.5 eV. The observed ionization potentials and the calculated orbital energies are collected in Table 3. As an example, the photoelectron spectrum of **14** is depicted in Figure 7.

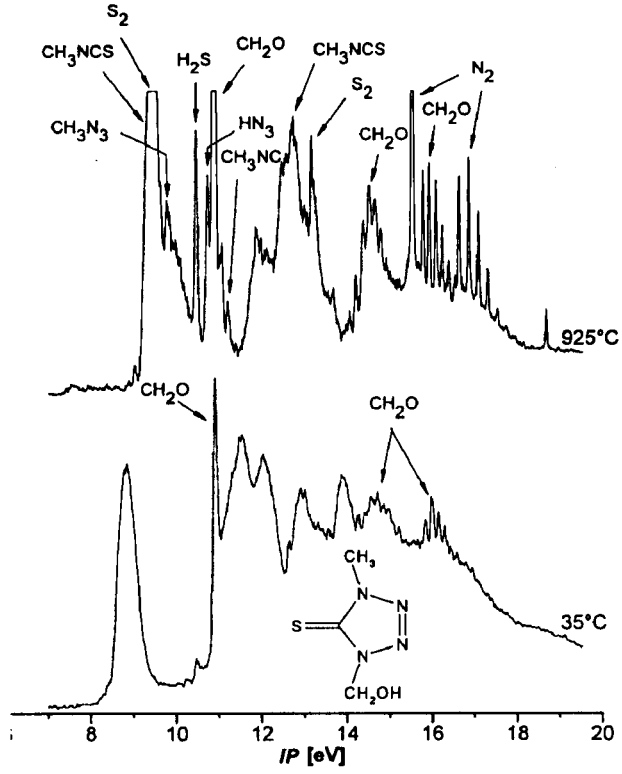


Figure 7. Photoelectron spectrum of tetrazolinethione **14** measured at different temperatures.

The photoelectron spectrum of compound **13** has been studied previously [16], and our analysis confirms the assignments for the first three ionization potentials given in the literature. However, the interpretation of the region between 11.5 and 13.0 eV is modified so that the sequence of ionizations related to n^-_{NN} and $\pi_{C=S}$ is reversed, *i.e.*, now IP($\pi_{C=S}$) is placed between the two n_{NN} ionizations. This assignment is based on the PM3 results (Table 3) as well as on highgrade *ab initio* calculations on compound **13** using the Becke3LYP (DFT) method [17] (basis set 6-31+G*) which proved optimal in the analysis of other systems with multiple vicinal lone

Table 3

Orbital Energies ε^{PM3} [eV] and Ionization Potentials IP [eV] of Tetrazolinethiones **10-15**

		π_3	n_S	$\pi_3^{Ar}/\pi_2^{Ar}/n_O$		π_2	n^-_{NN}	$\pi_{C=S}$	n^+_{NN}
10	-ε	9.25	9.29			11.78	12.33	13.09	13.62
	IP	8.64	8.76			11.65	11.9	12.25	12.95
			(1210) [a]						
11	-ε	9.21	9.24			11.62	12.24	12.86	13.57
	IP	8.53	8.69			11.45	11.7	12.15	12.85
			(941) [a]						
12	-ε	9.35	9.40		11.55	11.65	12.40	13.24	13.69
	IP	8.76	8.81			11.00	11.85	12.1	12.92
13	-ε	9.15	9.16			11.37	12.19	12.79	13.53
	-ε [b]	6.26	6.27			9.19	9.41	9.63	10.34
	IP	8.40	8.56			11.08	11.5 sh	11.8	12.65
			(1344) [a]						
14	-ε	9.34	9.39			11.56	12.19	12.95	13.67
	IP	8.77	8.84			11.57	12.05	12.25 sh	12.95
15	-ε	9.01	9.08	10.12/10.20		11.85	12.16	12.91	13.57
	IP	8.24	8.39	9.53/9.85 sh		11.50	11.80	12.3 sh	12.60

[a] Vibrational splitting [cm^{-1}]. [b] *Ab initio* Becke3LYP (DFT) results.

electron pairs [18]. The results of these computations are included in Table 3. Although there is a greater difference between ionization potential and -ε values than for the PM3 results, the linear correlation between experimental and theoretical results is substantially better (correlation coefficients R^2 are 0.998 and 0.992), and the slope of the correlation line is closer to 1.00 (0.991 and 0.947).

The most surprising feature in the photoelectron spectra of **10-15** is the fact that the ionizations of the two highest occupied molecular orbitals are found in one band. Even variation of the substituents R^1 and R^2 does not remove this degeneration.

Compounds **10**, **11** and **13** have been included in the correlation diagram given in Figure 8. Of special interest is a comparison of the IP values of equally substituted pyrazolinones and pyrazolinethiones, **5/10**, **6/11**, and **8/13**. While π_3, n^-_{NN} and n^+_{NN} are destabilized by substitution of oxygen for sulfur, π_2 remains essentially unchanged. This is not fully in accord with the PM3 results (Tables 2 and 3) which indicate that π_2 should be stabilized by about 0.2-0.4 eV. The large destabilization of π_3 by about 0.9 eV can be explained easily by interaction with the $\pi_{C=S}$ molecular orbital which has the same symmetry (B_1 in point group C_{2v}).

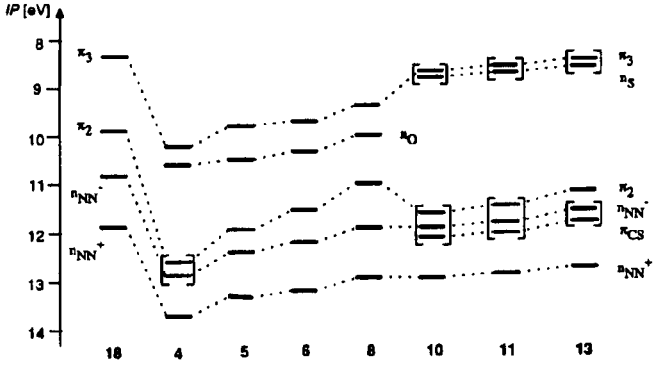


Figure 8. Correlation diagram for ionization potentials of compounds **4-6**, **8**, **10**, **11**, **13** and **18**.

Thermolyses.

We have studied gas phase thermolyses of **1-15** at low pressure (10-50 Pa) and elevated temperatures up to 1000°, using real-time gas analysis by photoelectron spectroscopy [19,20]. The products are identified by their characteristic ionization peaks. Since in most cases only small, unsaturated molecules containing heteroatoms like nitrogen, oxygen or sulfur are generated, the compounds studied here are excellent objects for photoelectron spectroscopy-monitored thermolysis reactions. Up to nine different products could be identified simultaneously which probably would have caused severe difficulties for most other analytical real-time methods. The thermolysis products are listed in Table 4; references to their photoelectron spectra are given in the following text.

Tetrazoles **1-3**.

Matrix photolysis [21] and flash vacuum pyrolysis [22] of 2,5-disubstituted tetrazoles cause elimination of molecular nitrogen and formation of nitrilimines. For the parent compound, unsubstituted tetrazole (**16**), photoelectron spectroscopy-monitored gas phase thermolysis affording cyanamide (preferentially) and diazomethane has been investigated by Guimon *et al.* [23]. Flash vacuum pyrolysis at 800° and photolysis in cryogenic matrices in combination with ir spectroscopy were recently studied by Maier and coworkers [14]. The latter authors found nitrilimine HCNNH as a product in both fragmentations.

Table 4

Products of Thermal Gas Phase Decomposition of Tetrazoles **1-3**, Tetrazolinones **4-9** and Tetrazolinethiones **10-15**

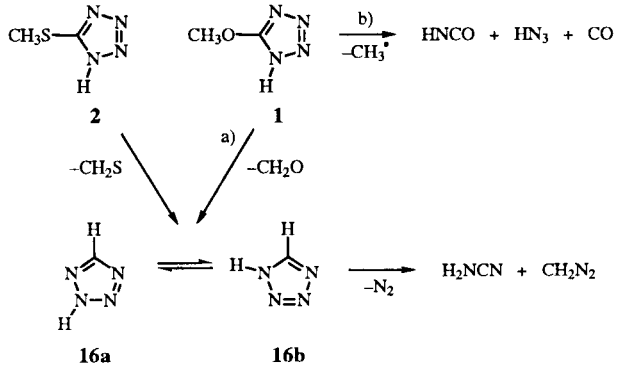
Compound	Products
1	CH_2O, H_2NCN, CO, HN_3 [a], HNCO [a], HCN [a], N_2
2	CH_2S, CS_2, H_2NCN, CH_2N_2 [a], CH_3SSCH_3 [a], H_2S [a], N_2
3	C_2H_4S, H_2S, HCN, CO, CH_3CHO [a], HN_3 [a], CH_2O [a], H_2O [a], N_2
4	HNCO, HN_3, CO, N_2
5	CH_3NCO, HN_3, N_2
6	C_2H_5NCO, HN_3, HNCO, CO, N_2
7	C_6H_5NCO, HN_3, HNCO, N_2
8	CH_3NCO, CH_3N_3, CH_2NH, HCN, N_2
9	C_6H_5NCO, CH_3N_3, CH_2NH, HCN [a], N_2
10	CH_3NCS, S_2, H_2S, CH_3N_3, HN_3, CH_3NC [a], N_2
11	C_2H_5NCS, S_2, H_2S, HN_3, $C_2H_5N_3$ [a], HCN, N_2
12	CH_3NC, S_2, H_2S, CH_3N_3, HN_3 [a], CH_2O [a], N_2
13	S_2, H_2S, CH_3NC, CH_3NCS, CH_3N_3, HCN, N_2
14	CH_2O, CH_3NCS, S_2, H_2S, CH_3N_3, HN_3, CH_3NC [a], N_2
15	C_6H_5NCS, CH_3N_3, N_2

[a] Minor amount.

5-Methoxytetrazole (**1**).

Compound **1** decomposes in two ways (Scheme 1, Figure 1): a) Elimination of formaldehyde [15] leads to unsubstituted tetrazole (**16**), which decomposes as was reported in the literature [23], mainly through extrusion of nitrogen and formation of cyanamide. This is the main pathway for the pyrolysis of **1**. b) Methyl radicals [24] are split off and the remaining portion of the molecule decomposes to isocyanic acid [25], hydrazoic acid [26] and carbon monoxide [15]. This is the minor pathway for the pyrolysis of **1**.

Scheme 1



Unsubstituted nitrilimine which is probably formed as the primary reaction product in the decomposition of **16** [14], cannot be identified from the photoelectron spectra. This means that HCNNH must be rather short-lived under the reaction conditions. Also for carbodiimide HN=C=NH, detected in minor amounts in the pyrolysis mixture by matrix isolation [14], no bands were found by photoelectron spectroscopy.

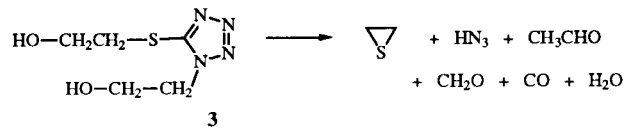
5-Methylthiotetrazole (**2**).

This compound decomposes mainly through the elimination of thioformaldehyde [27,28] and the formation of tetrazole (**16**) which is split into a nitrogen molecule and cyanamide [23] (Scheme 1, Figure 2). In addition, carbon disulfide [15] and small amounts of hydrogen sulfide [15], dimethyldisulfide [28] and diazomethane [29] were observed in the thermolysis mixture. Dimethyl disulfide, which is generated by dimerization of methylmercapto radicals, is known to decompose to carbon disulfide, hydrogen sulfide, thioformaldehyde and a small amount of methanethiol at high temperatures in the photoelectron spectrometer [28]. Cyanamide and diazomethane are probably formed through isodiazirine [23].

1-(2-Hydroxyethyl)-5-(2-hydroxyethylthio)-1*H*-tetrazole (**3**).

The tetrazole **3** begins to decompose at 350° through the formation of thiirane [30]. The rest of the molecule decomposes to hydrazoic acid [26], acetaldehyde [15], formaldehyde [15], water [15] and carbon monoxide [15] (Scheme 2, Figure 3). Thiirane, which is obviously formed from the 2-hydroxyethylthio group, is thermally very stable and was reported to decompose in the photoelectron spectrometer above 930° to ethylene, acetylene and carbon disulfide [31]. Isomerization to thioacetaldehyde is not observed. We have investigated the possibility that thiirane might be formed from 2-mercaptoethanol. However, no thiirane was detected in the photoelectron spectrum of this compound up to 950°. On the other hand, acetaldehyde is generated from the 2-hydroxyethyl group and is preferred over its cyclic isomer oxirane obviously because the latter compound is considerably less stable than the aldehyde. Formaldehyde is probably formed from the hydroxymethyl units of the substituents in a similar way as from methoxy groups.

Scheme 2

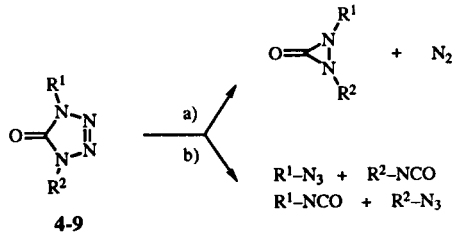


Tetrazolinones **4-9**.

For the thermolysis of tetrazolinones (Scheme 3, Figures 4-6) two decomposition paths can be expected: a) Ring contraction leading to diaziridinones. b) [3+2] Cycloreversion yielding isocyanates and azides. a) was observed by Quast *et al.* [3] in the photolysis of **8** and other alkyl substituted tetrazolinones. The photolysis of the phenyl substituted compounds **7** and **9** yields benzimidazolones [3]. Electron

impact induced decomposition was found to proceed *via* [3+2] cycloreversion to azides and isocyanates (path b) [3].

Scheme 3



4-9

In the gas phase thermolysis of **4-9** only the products of path b) (cycloreversion) are observed. The unsymmetrically substituted compounds **6** and **7** seem to decompose in the two alternative ways, because both isocyanic acid [25] and hydrazoic acid [26] are detected simultaneously. However, among the complementary products, only ethyl [32] and phenyl isocyanate [33], but not the corresponding azides, which are thermally much less stable [34], are found. Compounds **5** and **9** decompose only in one way, affording methyl isocyanate [25] and hydrazoic acid [26], and phenyl isocyanate [33] and methyl azide [34], respectively, as the primary reaction products.

Isocyanates are stable to about 1000° in the photoelectron spectrometer, while azides are split to smaller products. For example, methyl azide decomposes above 580° to a nitrogen molecule, hydrogen cyanide and methane imine [34].

The selectivity observed in the cleavage of some of the compounds could be due to either thermodynamic or kinetic reasons. We will investigate this question in some detail on compounds **5** and **9**. Neglecting entropy effects, since these parameters are not known, from the experimental enthalpies of formation (Table 5) it follows for **5** that the decomposition products HN_3 + CH_3NCO are favored by 47.3 kJ mol^{-1} over their counterparts CH_3N_3 + HNCO. This is in accord with the experimental findings. For the cleavage of **9**, however, PhN_3 + CH_3NCO, and not CH_3N_3 + PhNCO, should be expected, owing to an enthalpy difference $\Delta\Delta H_f$ of 157.8 kJ mol^{-1}, which contradicts the experiment.

Table 5

Enthalpies of Formation $\Delta H^\circ_{f,gas}$ [kJ mol^{-1}], Energies ε [eV] and Coefficients c of HOMO and LUMO of Possible Thermolysis Products of Tetrazolinones **5** and **9**

	$\Delta H^\circ_{f,gas}$ [a]	HOMO [b]			LUMO [b]		
		ε	c(N1)	c(N3)	ε	c(N1)	c(N3)
HN_3	1230.5	-10.36	0.848	0.604	0.45	0.443	0.591
CH_3N_3	1172.8	-9.96	0.796	0.554	0.50	0.453	0.602
$C_6H_5N_3$	1610.4	-9.11	0.540	0.364	0.77	0.432	0.417
		ε	c(N1)	c(C2)	ε	c(N1)	c(C2)
HNCO	-437.7±52.7	-10.59	0.807	0.250	1.27	0.524	0.781
CH_3NCO	-542.7	-10.13	0.760	0.259	1.27	0.495	0.774
C_6H_5NCO	52.7	-9.18	0.551	0.286	1.38	0.805	0.912

[a] From ref [35]. [b] PM3 results.

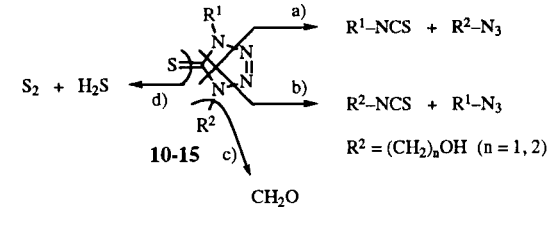
The kinetic aspects of these reactions can be inspected by the frontier molecular orbital (FMO) method [36,37] for the 1,3-dipolar or [2+3] cycloaddition reactions of RN_3 + R'NCO or R'N_3 + RNCO affording the corresponding tetrazolinone. Making use of the Klopman [38] and Salem [39] equation, the energies of the HOMOs and the LUMOs (Table 5) and the orbital coefficients on the respective atoms of the reactants can be used to estimate the energies S associated with the interactions of the frontier molecular orbitals. The following values for S are obtained: HN_3 + CH_3NCO → **5** (S = 0.135), CH_3N_3 + HNCO → **5** (S = 0.135); PhN_3 + CH_3NCO → **9** (S = 0.097), CH_3N_3 + PhNCO → **9** (S = 0.151). Only in the second case, a clear distinction is possible with the S values: the latter reaction is predicted to be faster than the former. Under the assumption that cycloaddition and cycloreversion have identical transition states, the same should hold for the decomposition of **9** into CH_3N_3 and PhNCO. This is actually observed. It can thus be concluded that the thermolytic cleavage of tetrazolinone **9** is a kinetically controlled reaction, whereas the cleavage of **5** and the other aliphatic tetrazolinones probably is thermodynamically controlled. At present, we cannot answer the question why these tetrazolinones should behave in a different manner, however, it should be mentioned here that the data used in the thermodynamic as well as in the kinetic study are questionable. The $\Delta H^\circ_{f,gas}$ value of HNCO is rather uncertain and orbital energies as well as the coefficients cannot be calculated with high precision for the molecules under consideration by semi-empirical methods. For a more reliable thermodynamic result, ΔG values should be used.

Tetrazolinethiones **10-15**.

As shown in Scheme 4, there are several possible ways (paths a-d) for the thermolysis of compounds **10-15**: a) and b) [3+2] cycloreversion affording isothiocyanates and azides; c) cleavage of functionalized substituents; d) cleavage of sulfur.

Pathway d), followed by molecular nitrogen extrusion affording carbodiimides, was determined as the main way of photolysis of tetrazolinethiones [3]. However, [3+2] cycloreversion to isothiocyanates and azides (pathways a

Scheme 4



and b) was observed as the main mechanism in the scission induced by electron impact ionization [3].

Most of the compounds studied here decompose thermally in more than one way: **10-13** are cleaved through cycloreversion (pathways a and b) and the elimination of sulfur (pathway d), which is followed by cycloreversion of the remaining ring.

In a uniform reaction, **15** undergoes cycloreversion to phenyl isothiocyanate [33] and methyl azide [34] (pathway b). The products corresponding to pathway a) are not observed, and **15** is the only case where no sulfur (S_2) and hydrogen sulfide [15] are formed. Methyl [25] and ethyl isothiocyanate [32] are generated together with hydrazoic acid [26] from **10** and **11**, respectively, in pathway b), and at the same time, methyl and ethyl azide [34] are formed, although in minor amounts, *via* pathway a).

Compound **14** is unstable already at about 35° and loses formaldehyde (pathway c) affording **10**, which decomposes at higher temperatures (> 600°) as discussed above.

Sulfur is observed as a dimer (S_2) which is the most stable modification under the thermolysis conditions [40]. It is always accompanied by hydrogen sulfide [15]. This is evidence that sulfur is cleaved as a free atom, which dimerizes or abstracts two hydrogen atoms forming hydrogen sulfide. There are two further indications for pathway d) as an independent route for the decomposition of tetrazolinethiones: Methyl isonitrile [41] which is identified in the pyrolysis mixtures of **13** and **14** can only be formed *after* sulfur has been split off. Most likely sulfur is not cleaved from the products *after* cycloreversion, since methyl, ethyl and phenyl isothiocyanate are stable under the pyrolysis conditions. This was proved by measuring their photoelectron spectra at temperatures up to 900°. However, it cannot be excluded that the mentioned isothiocyanates could be generated from the tetrazolinethiones in a thermally activated state and decompose readily. Such "chemical activation" has been observed repeatedly in fast vapor pyrolysis studies [42].

There is no indication for the formation of carbodiimides like dimethyl carbodiimide [43] or methyl phenylcarbodiimide [44] as in the photolysis of **13** and **15** [3], respectively, in the photoelectron spectra of the pyrolysis mixtures.

Conclusions.

With respect to the photoelectron spectra of the compounds studied here, the most important results for tetrazoles is that 1*H*- and 2*H*-tautomers can be distinguished. The electronic structures of tetrazolinones and tetrazolinethiones are closely related to those of tetrazolines [8]. The photoelectron spectra of **4-9** can be explained with stabilizing effects of the carbonyl group on the characteristic tetrazoline orbitals. On the other hand, in the corresponding sulfur compounds **10-15** these orbitals are again destabilized (Figure 8).

In the thermolysis reactions always several (up to nine) products are formed, which generally are small unsaturated molecules containing heteroatoms like nitrogen, oxygen or sulfur. Because of this, they are readily identified by their characteristic sharp peaks in the photoelectron spectra of the pyrolysis mixture even when they appear only in small amounts. Therefore, photoelectron spectroscopy may be considered as the analytical method of choice for this investigation. It is also appropriate to point out that some products like thioformaldehyde, isocyanic and hydrazoic acid are unstable under normal conditions which precludes analysis by conventional methods like gas chromatography. Although, at least in principle, quantitative measurements would be possible, no efforts were made in this direction, mainly because such data would be of limited relevance with respect to products that are short-lived under the reaction conditions.

The large variety of products generated from the tetrazoles **1-3** can primarily be attributed to the substituents from which some are formed irrespectively of the rest of the molecule. The tetrazole ring can thus be used as a carrier for substituents whose thermolysis one wants to study. The carbonyl group present in the tetrazolinones **4-9** induces a uniform cleavage of the five-membered ring by [3+2] cycloreversion. For asymmetrically substituted compounds two different decompositions are possible for this reaction type of which one may be favored. The marked selectivity found for the decomposition of compound **9** could be explained by application of the frontier molecular orbital method on the 1,3-dipolar cycloaddition of an azide to an isocyanate. In such a manner, studying thermolysis reactions might contribute to the understanding of cycloaddition reactions. To our knowledge, this has not been attempted previously.

The main difference in the thermolyses of tetrazolinones and tetrazolinethiones is the generation of sulfur (S_2) and hydrogen sulfide from the latter compounds. The sulfur atom is split off from the starting molecules and not from a thermolysis product like an isothiocyanate in a secondary reaction. The sulfur-free tetrazole is then cleaved by cycloreversion affording the corresponding isonitrile as a product that cannot be explained otherwise.

There is little in common between photolysis and thermolysis of tetrazolinones and tetrazolinethiones, only elemental sulfur is generated by both methods from the latter compounds. On the other hand, mainly the same products are formed by thermal and by electron impact induced decomposition.

EXPERIMENTAL

Photoelectron Spectra. For details see reference [5].

The PM3 calculations were carried out with the program package MOPAC 6.1 [45]. For *ab initio* computations the program Gaussian94 [46] was used. Molecular structures were preoptimized by molecular mechanics calculations [47] with the program

PCMODEL4, Serena Software, Bloomington, Indiana/USA, on a personal computer.

Syntheses of compounds **1** [48], **2** [49], **3** [50], **4** [48], **5** [51], **6** [52], **7** [53], **8** [54], **9** [53] **10** [55], **11** [55], **12** [56], **13** [3] and **15** [3] have been described in the literature.

1-Hydroxymethyl-4-methyl-1,4-dihydro-5*H*-tetrazole-5-thione (**14**).

Compound **14** was prepared by alkylation of 3.0 g (26 mmoles) of 1,4-dihydro-1-methyl-5*H*-tetrazole-5-thione (**10**) with 10 ml of 37% formaldehyde solution at 60° for 2 hours. After cooling, the reaction mixture was extracted with methylene chloride (3 x 25 ml). The collected organic layers were evaporated *in vacuo* and the residue was crystallized from chloroform/petroleum ether 40-60°, yield 2.4 g (63%), mp 47-49°; ir (potassium bromide): ν 3406 (OH), 1474, 1360, 1299, 1277, 1193, 1065, 1002, 974, 786 cm^{-1}; ^1H nmr (200 MHz, deuteriochloroform): δ 3.89 (s, 3H, NCH_3), 5.72 (d, J = 8 Hz, 2H, CH_2), 4.45 (t, J = 8 Hz, 1H, OH); ^{13}C nmr (75 MHz, deuteriochloroform): δ 34.4 (NCH_3), 71.2 (NCH_2OH), 164.5 (C=S); ms: (70 eV), m/z (%) 146 (32) [M^+], 116 (100) [M^+-CH_2O], 85 (15), 73 (35) [CH_3NCS^+], 59 (20) [$HNCS^+$].

Anal. Calcd. for $C_3H_6N_4OS$ (146.2): C, 24.56; H, 4.12; N, 38.00. Found: C, 24.62; H, 4.13; N, 38.01.

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