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# Photoelectron spectroscopic and computational study of the thermolysis of 1,2,3,6-tetrahydro-1,2,4,5-tetrazines

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#### Abstract

Gas phase thermolyses of 3,6-dimethyl, -diethyl and -di-*n*-propyl substituted 1,2,3,6-tetrahydro-1,2,4,5-tetrazines **1a**-**1c** yielded the corresponding N-unsubstituted imines **2a**-**2c**. The He(I) photoelectron spectra of propanimine (**2b**) and butanimine (**2c**) are presented for the first time. First ionization potentials and orbital energies of the imines as determined with B3LYP/6-31 + G\*//HF/6-31 + G\* reproduce the experimental data. Ionization bands arising from N,N'-unsubstituted diazetidines **3a**-**3c** could not be detected in the pyrolysis spectra of **1a**-**1c**. Calculations for the extrusion of nitrogen from tetrahydrotetrazine **1a** resulted in a transition state for a [2 + 2 + 2]-cycloreversion that leads to the imine **2a** as product. © 1998 Elsevier Science B.V. All rights reserved

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### 1. Introduction

Photoelectron (PE) spectroscopy, when employed as real-time analytical method in gas phase thermolyses, allows for the detection of short-lived, unstable intermediates. C-Monosubstituted imines (RHC=NH) have been known to readily trimerize or polymerize in substance [1], yet they can be characterized by PE spectroscopy when generated and studied under close to unimolecular conditions in the gas phase [2–8]. Reactive alkanimines have been prepared through thermolysis of amines [4–6] and azetidine [4,5] as well as by retrotrimerization of hexahydro-

s-tetrazines [3,4]. In contrast to the product mixtures, which are often formed in these reactions, thermolysis of alkylazides in the gas phase yields imines selectively [2,7,8]. The azides, which may be explosive, can be safely evaporated to study their gas phase decomposition reactions [8]. Likewise, gas phase dehydrochlorination of explosive N-chloro substituted amines has been shown to yield imines [8.9]. These amines are prepared in the gas phase without prior isolation. This procedure requires a combination of a double-oven apparatus with a PE spectrometer. On the other hand, substituted 1,2,3,6tetrahydro-1,2,4,5-tetrazines-readily available, thermally labile but otherwise stable compounds-are promising precursors for C-monosubstituted imines. The tetrahydrotetrazines can extrude dinitrogen in a [2 + 2 + 2]-cycloreversion or via a 1,4-diradical,

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which subsequently might fragment along the central N–N bond or cyclize. While cyclization would afford N,N'-unsubstituted 1,2-diazetidines, the first two reaction paths would yield imines. Electronic structures of 1,2-diazetidines and alkylimines differ greatly which makes PE spectroscopy an ideal tool for the study of the thermolysis of tetrahydrotetrazines.

## 2. Experimental

PE spectra were recorded on a Leybold-Heraeus UPG 200 spectrometer with He(I) excitation (21.21 eV). Spectra were calibrated with lines of xenon (12.13 and 13.44 eV) and of argon (15.76 and 15.94 eV). The accuracy of the ionization potentials is  $\pm$  0.03 eV for sharp peaks and  $\pm$  0.05 eV for broad and overlapping signals.

Thermolyses were carried out in a heated molybdenum tube (80 mm length, 4.5 mm inner diameter) placed between sample inlet and ionization chamber in the PE spectrometer. The distance between the molybdenum tube and ionization chamber was about 35 mm. Temperatures are accurate to  $\pm 5^{\circ}$ C. To obtain thermolysis spectra, the temperature of the molybdenum tube was raised until characteristic ionization bands belonging to N<sub>2</sub> (15.60 eV) were observed (onset of thermolysis). Pyrolyses were considered complete when bands belonging to starting compounds were no longer present in the PE spectrum upon further temperature increase. PE spectra of tetrahydrotetrazines **1a**-**1c** recorded at different temperatures are given in Fig. 1.

Ab initio HF [10] and B3LYP (Becke3LYP) [11] calculations were performed with the program GAUSSIAN 94 [12] on an IBM RS/6000 model 350 computer. Geometries were fully optimized at the HF/6-31+G\* level of theory. A frequency calculation on the transition structure produced exactly one imaginary frequency and negative eigenvalue of the Hessian.



Fig. 1. He(I) photoelectron spectra of the pyrolysate of (a) 1a obtained at 975°C, (b) 1b obtained at 850°C and (c) 1c obtained at 750°C.

#### 3. Results and discussion

### 3.1. Thermolysis of 1,2,3,6-tetrahydro-3,6-dimethyl-1,2,4,5-tetrazine (**1a**)

The PE spectrum of **1a** as reported before [13] is unchanged up to a temperature of about 400°C. At 450°C, thermolysis is complete and bands belonging to ethanimine [4,9] (**2a**) and nitrogen compose the spectrum. The observed ionization potentials are given in Table 1. There are no ionization bands unaccounted for which could be associated with another possible product, 3,4-dimethyl-1,2-diazetidine (**3a**), whose PE spectrum is not known. HCN, with an ionization band at 13.63 eV (the literature value is 13.60 eV [14]), is not produced until a temperature of 725°C is reached. HCN ionization bands and fine structure of the second band of **2a** (Table 1) become more prominent up to 975°C, the final temperature recorded (Fig. 1(a)).



As **2a** was the only alkanimine in our series whose PE spectrum was known and to confirm the presence of imines **2b** and **2c** in the pyrolyses of **1b** and **1c**,

respectively (discussed below), we performed calculations for the first vertical ionization potential  $IP_{y}^{1}$  of 2a as well as for its orbital energies. We chose the ab initio HF method for geometry optimizations and the B3LYP method for single point energy calculations to account for electron correlation, both with the 6-31 + G\* basis set. B3LYP/6-31 + G\* has been shown to give excellent first adiabatic and vertical ionization potentials [15]. The first ionization potential  $IP^1$  can be calculated as the energy difference between a molecule and its radical cation [16]. By performing single point energy calculations for the radical cation (n-1 electrons) on the molecule's (*n* electrons) geometry, i.e. without allowing for relaxation during ionization, the first vertical IP,  $IP_{v}^{1}$ , is accessible. Total energies from these calculations and derived  $IP_{v}^{1}$ values are given in Table 2.

It is obvious from the calculated  $IP_v$ s of **2a** that the HF method ( $IP_v^1 = 8.90 \text{ eV}$ ) is not suited for this purpose, yet B3LYP ( $IP_v^1 = 10.10 \text{ eV}$ ) gives a very good agreement with the reported experimental value of 10.17 eV [9] (10.18 eV [4]). Computed orbital energies (given in Table 1) of **2a** show a similar result. While with HF/6-31 + G\* even relative energy differences are wrong, B3LYP/6-31 + G\*//HF/6-31 + G\* energy differences fit perfectly. If orbital energies are shifted uniformly by 2.8 eV (the difference between HOMO and  $IP_v^1$ , this large absolute difference is not unusual for B3LYP calculations) so that the calculated HOMO equals the calculated  $IP_v^1$  in energy, the projected values for **2a** are 10.1, 11.5 and 13.6 eV which underlines the high value of the calculations. A

Table 1

Experimental vertical ionization potentials  $IP_{v}$  (eV) and calculated orbital energies  $\epsilon$  (eV) for imines 2a-2c

| 2a                 |            |                    | 2b                 |                            |                    | 2c              |          |                    |
|--------------------|------------|--------------------|--------------------|----------------------------|--------------------|-----------------|----------|--------------------|
| IP <sub>v</sub>    | - <i>e</i> |                    | IP <sub>v</sub>    | - <i>e</i>                 |                    | IP <sub>v</sub> | - ε      |                    |
|                    | $HF^{a}$   | B3LYP <sup>b</sup> |                    | $\mathrm{HF}^{\mathrm{a}}$ | B3LYP <sup>b</sup> |                 | $HF^{a}$ | B3LYP <sup>b</sup> |
| 10.25 <sup>c</sup> | 11.37      | 7.29               | 10.01 <sup>d</sup> | 11.31                      | 7.26               | 9.94            | 11.27    | 7.23               |
| 11.60 <sup>e</sup> | 11.74      | 8.66               | 11.30 <sup>f</sup> | 11.73                      | 8.65               | 11.14           | 11.66    | 8.56               |
| 13.63              | 14.97      | 10.84              | 12.48              | 13.65                      | 9.76               | 11.9            | 13.12    | 9.31               |

<sup>a</sup>At the HF/6-31 + G\* level of theory.

<sup>b</sup>At the B3LYP/6-31 +  $G^*//HF/6-31 + G^*$  level of theory.

<sup>c</sup>Vibrational splitting 810 cm<sup>-1</sup>.

<sup>d</sup>Vibrational splitting 890 cm<sup>-1</sup>.

<sup>e</sup>Vibrational splitting 970 and 1210 cm<sup>-1</sup>.

<sup>f</sup>Vibrational splitting 970 cm<sup>-1</sup>.

| Table 2 |  |
|---------|--|
|---------|--|

Total energies  $E_{\rm T}$  (au) of imines **2a**-**2c**, diazetidines<sup>a</sup> **3a**-**3c** and **4** (M: *n* electrons) and their radical cations<sup>b</sup> (M<sup>+</sup>: *n* - 1 electrons) as well as derived first vertical ionization potentials  $IP_{\rm v}^{\rm I}$  (eV)

|                 | State             | HF/6-31 + G*   |              | B3LYP/6-31 + G*//HF/6-31 + G* |                |  |
|-----------------|-------------------|----------------|--------------|-------------------------------|----------------|--|
|                 |                   | E <sub>T</sub> | $IP_{v}^{1}$ | E <sub>T</sub>                | $IP_{\rm v}^1$ |  |
| 2a              | М                 | -133.076101    | 8.90         | -133.957049                   | 10.10          |  |
|                 | $M^{+.}$          | -132.748877    |              | -133.585762                   |                |  |
| 2b              | М                 | -172.113532    | 8.82         | -173.273736                   | 9.94           |  |
|                 | M <sup>+.</sup>   | -171.789352    |              | -172.908487                   |                |  |
| 2c              | М                 | -211.148759    | 8.77         | -212.588367                   | 9.83           |  |
|                 | M <sup>+.</sup>   | -210.826490    |              | -212.227186                   |                |  |
| 3a              | М                 | -266.123035    |              | -267.891395                   | 7.96           |  |
|                 | M <sup>+.</sup>   |                |              | -267.598772                   |                |  |
| 3a <sup>c</sup> | М                 | -266.120762    |              | -267.889317                   | 7.89           |  |
|                 | M <sup>+.</sup>   |                |              | -267.599277                   |                |  |
| 3b              | М                 | -344.193477    |              | -346.520659                   | 7.85           |  |
|                 | M <sup>+.</sup>   |                |              | -346.232040                   |                |  |
| 3c              | М                 | -422.261779    |              | -425.148009                   | 7.78           |  |
|                 | M <sup>+.</sup>   |                |              | -424.862184                   |                |  |
| 4               | М                 | -266.110128    |              | -267.880043                   | 7.54           |  |
|                 | $\mathbf{M}^{+.}$ |                |              | -267.602857                   |                |  |
|                 |                   |                |              |                               |                |  |

<sup>a</sup>All-anti conformer.

<sup>b</sup>Single point energy calculation for M<sup>+.</sup> on the optimized geometry of the molecule M.

<sup>c</sup>N-H syn to C-Me bond.

rationale for the successful application of the Koopmans' Theory-like interpretation [17] of the orbital energies obtained at the DFT level of theory in a PE spectroscopic study of a series of carbenes has recently been provided by Arduengo and coworkers [18]. Applying a uniform shift to the B3LYP orbital energies has nicely reproduced the PE spectra of numerous compounds [13,15,19] vastly different from the carbenes studied by Arduengo.

We performed similar calculations for 3,4dimethyl-1,2-diazetidine (**3a**), the product of ring closure from a possible 1,4-diradical generated from **1a**. The poor performance of HF/6-31 + G\* for  $IP_vs$  and orbital energies led us to employ only the B3LYP method in the following energy calculations. As the experimental *IP*s are not known for diazetidine **3a**, we 'calibrated' B3LYP calculations using the related 1,2dimethyl-1,2-diazetidine (**4**). Total energies and  $IP_v$ values for **4** (methyl groups *anti*, as this is more stable than the *syn* conformer by 45.11 kJ mol<sup>-1</sup> according to HF/6-31 + G\* (42.30 kJ mol<sup>-1</sup> with B3LYP/6-31 + G\*//HF/6-31 + G\*)) are given in Table 2, the reported first ionization is at 7.95 eV [20] (8.12 eV [21]). The calculated  $IP_v^1$  value of 7.54 eV is acceptably close to the experimental one and a transfer from methyl substituted to N-unsubstituted diazetidine should not alter this result substantially: an error of 0.4 eV has to be admitted for **3a**.

While for **3a** the all-*anti* conformer is most stable, the one formed through a direct ring closure should be with N-H and C-Me bonds in a *syn* position. As can be seen in Table 2, this hardly affects the  $IP_v$ . With a calculated  $IP_v^1$  value of 7.9 eV and considering the 0.4 eV shift, the first ionization of **3a** can be expected around 8.3 eV. As can be seen in the pyrolysis spectrum of **1a** (Fig. 1(a)), the onset of the first band of imine **2a** is at about 9 eV and any ionization on the low energy side of this band should be clearly distinguishable. We can therefore conclude that **3a** is definitely not present in the pyrolysis spectra of **1a** between 450 and 975°C.

# *3.2. Thermolysis of 3,6-diethyl-1,2,3,6-tetrahydro-1,2,4,5-tetrazine* (**1b**)

Nitrogen extrusion from **1b** is observed from 400°C onwards and thermolysis is complete at 575°C. Unlike the pyrolysis of **1a**, formation of HCN at higher

temperatures (up to 850°C, the final temperature recorded; Fig. 1(b)) is not observed for 1b. Other than this, the pyrolysis PE spectrum of **1b** strongly resembles that of 1a with respect to the positions of the first and second ionization bands as well as their fine structures. Bands are shifted slightly (see experimental IPs in Table 1). Since the PE spectrum of the presumed product propanimine (2b) is not known, we performed calculations for the first vertical ionization potential as well as for orbital energies. The results (total energies and  $IP_{v}$  are given in Table 2, orbital energies in Table 1) match those obtained for ethanimine (2a), and B3LYP calculations confirm the presence of **2b** in the pyrolysis spectrum of **1b**. Shifted orbital energies (the B3LYP difference between  $IP_{v}$ and HOMO energy is 2.6 eV) give values of 9.9, 11.3 and 12.4 eV which is in good agreement with the experimental data.

Assuming that energy differences for the all-*anti* conformer of **3b** and its related *syn* conformer are similar to those of the **3a** analogues, we performed calculations for  $IP_v$  and orbital energies only for all-*anti* **3b**. The results are reported in Table 2. Again, if an error of 0.4 eV is accounted for, the first ionization of **3b** should be found around 8.3 eV, and just as in the pyrolysis spectra of **1a** there is no corresponding band in this region in the spectra of **1b** between 575 and 850°C which excludes the presence of diazetidine **3b**.

# 3.3. Thermolysis of 1,2,3,6-tetrahydro-3,6-di-n-propyl-1,2,4,5-tetrazine (**1c**)

In order to get a PE spectrum of 1c, the sample had to be heated to 85°C for sufficient vapour pressure [13]. A trace of nitrogen is already present in this spectrum which announces the beginning of decomposition of 1c. Gas phase thermolysis commences at 275°C, indicated by a more intensive nitrogen band as well as a less intensive first band of 1c. The 500°C spectrum bears resemblance to the pyrolysis spectra of **1a** and **1b** and should belong to butanimine (**2c**): compared with 2a and 2b, both first and second bands are slightly shifted towards a lower IP (Table 1), and the second band is present as a shoulder on the low energy side of the  $\sigma$  region as would be expected due to the longer alkyl chain. As in the thermolysis of 1a, HCN extrusion is observed at higher temperatures  $(750^{\circ}C, Fig. 1(c)).$ 

We again performed calculations for first vertical ionization potential and orbital energies of **2c** to confirm its presence in the thermolysis of **1c** (Table 2 gives total energies and  $IP_v$ , Table 1 orbital energies). As for imines **2a** and **2b**, the calculated  $IP_v$  (B3LYP/6-31 + G\*//HF/6-31 + G\*) is very close to the experimental one and relative orbital energies fit perfectly. The energy difference between  $IP_v$  and HOMO is once more 2.6 eV, giving projected ionization potentials of 9.8, 11.2 and 11.9 eV which is exactly what we find experimentally.

For all-*anti* diazetidine **3c**, the calculated  $IP_v$  (Table 2) is very similar to those of **3a** and **3b**; with a 0.4 eV error (see above), the expected first ionization is at about 8.2 eV. Again, there is no indication of **3c** in the gas phase thermolysis spectra of **1c**.

### 3.4. Formation of products

In the transition state for nitrogen extrusion from a tetrahydrotetrazine, a shortened N-N bond-or one that does not change in length—is a prerequisite for ring closure to a diazetidine while a pronounced lengthening would suggest the start of a fragmentation to give imines. Such a lengthening is found in the transition state for the symmetrical elimination of nitrogen from 1a, which was localized using the standard procedure of the program GAUSSIAN 94 [12]. A graphical representation is depicted in Fig. 2, data are given in Table 3. In fact, a 1,4-diradicaloid transition state for nitrogen extrusion with an intact N-N hydrazine bond could not be located; that for a [2 + 2 + 2]-cycloreversion was found instead. Products from this cycloreversion are nitrogen and imine 2a; a diazetidine 3a cannot be formed.



Fig. 2. Optimized (HF/6-31 + G\*) transition state for the symmetrical nitrogen extrusion from **1a**.

Table 3

Total energies  $E_{\rm T}$  (au) and selected bond lengths r (pm) of **1a** and its transition state TS for symmetrical nitrogen extrusion according to HF/6-31 + G\*

|          | $E_{\mathrm{T}}$           | $r(N^1=N^2)^a$ | $r(N^2-C^3)^a$ | $r(N^4-N^5)^a$ |
|----------|----------------------------|----------------|----------------|----------------|
| 1a<br>TS | -375.000327<br>-374.898283 | 121.2<br>112.9 | 147.5<br>190.1 | 140.2<br>175.2 |
|          |                            |                |                |                |

<sup>a</sup>Atom numbers according to Fig. 2.

### 4. Conclusion

The pyrolyses of 1.2.3,6-tetrahydro-1,2,4,5-tetrazines 1a-1c yielded the imines 2a-2c, respectively. While the presence of ethanimine (2a) was established through a comparison of its literature PE spectrum with the obtained pyrolysis spectrum of 1a, this procedure could not be used for 2b and 2c because their PE spectra were not known. As B3LYP/6-31 + G\*//HF/6-31 + G\* calculated first vertical ionization potential and relative orbital energies for 2a matched the experimental data perfectly, similar calculations were performed for propanimine (2b) as well as butanimine (2c) and correlations with recorded values were found to be excellent. Diazetidines 3a-3c are not products of the pyrolyses as was concluded from the computationally predicted first vertical ionization potential which could not be located in the thermolyses spectra of tetrazines 1a-1c. A rationalization for the formation of imines as opposed to diazetidines in the pyrolyses was possible from a computational study of the thermolysis of 1a. The transition state for nitrogen extrusion is representative of a [2+2+2]-cycloreversion.

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