Available online at www.sciencedirect.com

SCIENCE DIRECT®

Mendeleev Commun., 2007, **17**, 204–206

Mendeleev
Communications

Formation of thiazyl radicals by the thermolysis and photolysis of sulfur–nitrogen bicycles RCN_5S_3

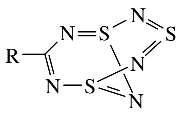
Nina P. Gritsan,*[a,b] Konstantin V. Shuvaev,[c,d] Stanislav N. Kim,[a,d] Carsten Knapp,[e]
Rüdiger Mews,*[e] Victor A. Bagryansky[a] and Andrey V. Zibarev*[b,c]

[a] *Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 330 7350; e-mail: gritsan@ns.kinetics.nsc.ru*
[b] *Department of Physics, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[c] *N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 330 9752; e-mail: zibarev@nioch.nsc.ru*
[d] *Department of Natural Sciences, Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[e] *Institute for Inorganic and Physical Chemistry, University of Bremen, 28359 Bremen, Germany. Fax: +49 421 218 4267; e-mail: mews@chemie.uni-bremen.de*

DOI: 10.1016/j.mencom.2007.06.005

4-R-1,2,3,5-dithiadiazolyl radicals are identified by EPR spectroscopy upon thermal and photochemical decomposition of 7-R-1,3,5-trithia-2,4,6,8,9-pentaazabicyclo[3.3.1]nona-1(9),2,3,5,7-pentaenes in hydrocarbon solutions.

Thiazyl radicals are of fundamental interest, but they are especially fascinating due to their unusual physical properties and potential applications as molecular magnets, molecular conductors and magnetic switches.[1] Recently, we demonstrated that the thermal and photochemical degradation of sulfur–nitrogen heterocycles (isomeric 1,2,4,3,5- and 1,3,5,2,4-benzotrithiadiazepines and 1,3,2,4-benzodithiadiazines) under mild conditions afforded thiazyl radicals in nearly quantitative yields.[2] Previously, the only route to these species was the reduction of corresponding salts,[1] whereas our findings indicated that stable thiazyl radicals can be generated from neutral precursors. To explore the generality of this phenomenon, we explored a series of bicyclic compounds RCN_5S_3 (**1**)[3] as possible precursors for the formation of thiazyl radicals (Scheme 1).[†]

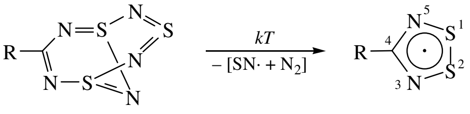


1a R = Ph
1b R = 4-MeC_6H_4
1c R = 4-FC_6H_4
1d R = 4-PhC_6H_4
1e R = 2,6-$F_2C_6H_3$
1f R = CF_3
1g R = NMe_2

Scheme 1

A previous study showed compounds **1** to be prone to thermal degradation in an acetonitrile solution, although only benzonitrile and S_4N_4 were identified as decomposition products in the case of **1a**.[4] Herein, we report that this process is more complex than that described hitherto, and the mild thermolysis of compounds **1** in hydrocarbon solutions results in the formation of thiazyl radicals, which were monitored by *in situ* EPR spectroscopy.[‡]

Figure 1(*a*) shows, as a representative example, the EPR spectrum of derivative **1b** recorded after heating in squalane at 363 K. *A priori*, one would expect the exclusive formation of radicals **2**[†] accompanied by loss of $SN^\cdot$ and N_2 from the RCN_5S_3 molecule (Scheme 2). Note that a series of radicals **2** obtained by other methods has previously been isolated and revealed interesting magnetic and electrical properties.[1]



1a–g **2a–g**

Scheme 2

However, the complex nature of the spectrum (Figure 1) suggested the presence of more than one radical species, since the EPR spectrum of **2b** would only contain a five line pattern from the coupling of an unpaired electron with two equivalent ^{14}N nuclei ($I = 1$). A simulation of the entire EPR spectrum [Figure 1(*b*)] indicated that the mixture actually represents a superposition of resonance lines from two different kinds of thiazyl radicals: a major radical with two equivalent nitrogen nuclei (**2b**), and a minor one with three equivalent nitrogen nuclei (**3b**).[†] However, the spectral features of minor radical **3b** are not so evident since the line-widths of the higher field resonance components of both radical species are much larger than those at a low field. This is explained by the very high

---

[†] *Compounds names and numbering.* **1**: 7-R-1,3,5-trithia-2,4,6,8,9-pentaazabicyclo[3.3.1]nona-1(9),2,3,5,7-pentaenes. **2**: 4-R-1,2,3,5-dithiadiazolyls. **3**: 3,5-R_2-1,2,4,6-thiatriazinyls. **4**: 3,7-R_2-1,5,2,4,6-dithiatetrazocines.

[‡] Compounds **1a**–**g** were prepared as described previously.[3(*a*)–(*c*)] All the experiments were performed in dodecane and squalane (2,6,10,15,19,23-hexamethyltetracosane), photolysis was also performed in CS_2 solutions ($c = 10^{-4}$–10^{-3} mol dm^{-3}) degassed by five freeze-pump-thaw cycles, in quartz tubes fitted with valves. Compounds **1a**–**e** have low solubility in hydrocarbons; therefore, the samples were prepared under mild heating (~40 °C) in an ultrasonic bath.

The thermolysis of **1a**–**g** was carried out using a glycerol thermostat in the temperature range 363–403 K with an accuracy of ±1 K.

The UV-visible spectra of aryl-substituted compounds **1** are characterised by a long-wavelength shoulder at ~400 nm,[3] those of aryl-substituted compounds **4**, by a peak at ~410 nm,[7] while CS_2 is only transparent to visible light (> 400 nm). Therefore, photolysis of **1b** was performed using a selected 436 nm line of a DRSh-500 mercury lamp equipped with a water filter and a combination of glass filters.

The EPR spectra were recorded on a Bruker EMX spectrometer (MW power of 0.64 mW, modulation frequency of 100 kHz and modulation amplitude of 0.1 G). Spectral integration and simulation were performed using the Win-EPR and Win-Sim programs, respectively. The radical yields were determined by comparison of the integral intensities of radicals with the integral intensity of a $CuCl_2 \cdot 2H_2O$ standard with an accuracy of ±15%.

Quantum-chemical calculations at the UB3LYP/6-31G(d) level of theory were performed using the GAUSSIAN 98 suite of programs.[9]

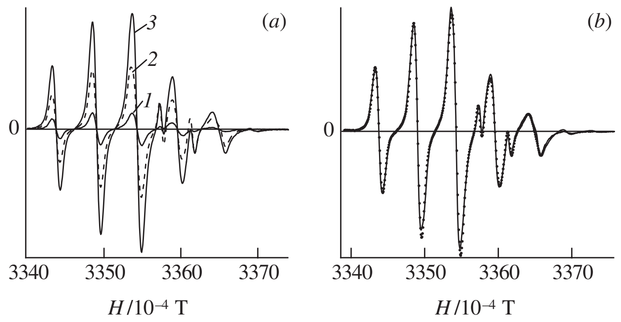
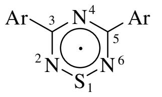


Figure 1 (*a*) EPR spectra recorded after (*1*) 5, (*2*) 40 and (*3*) 320 min thermolysis of **1b** in squalane ($c = 0.9\times10^{-3}$ mol dm^{-3}) at 363 K. (*b*) Experimental EPR spectrum after 320 min thermolysis (dots) and its simulation assuming the presence of two types of radicals (solid line): a radical with 2 N atoms (94.2%, $a_N = 5.21$ G) and a radical with 3 N atoms ($\Delta g = -0.0043$, $a_N = 3.91$ G).

viscosity of squalane solvent resulting in too slow molecular tumbling to average out the partial anisotropy.[6]

In less viscous dodecane, the line broadening is not so substantial and the spectrum detected after 5 min of heating **1a** very clearly demonstrates formation of the second radical with three equivalent nitrogen atoms [Figure 2(*a*), 7 lines marked by asterisks]. The *g*-factor and hyperfine coupling constant ($g = 2.0104$, $a_N = 5.2$ G) for radical **2a** are almost identical to those published for this radical ($g = 2.0102$, $a_N = 5.17$ G).[5(*a*)] The *g*-factor and hyperfine coupling constant obtained for the second radical ($g = 2.0060$, $a_N = 3.96$ G) coincide well with the data reported for **3a**[†] ($g = 2.0059$, $a_N = 3.97$ G; Scheme 3).[5(*b*)]



3a Ar = Ph
3b Ar = 4-MeC$_6$H$_4$

Scheme 3

Nitrogen hyperfine coupling constants for **2a** ($a_{N3} = a_{N5} = 6.1$ G) and **3a** ($a_{N2} = a_{N6} = 4.8$ G; $a_{N4} = 4.9$ G) predicted at the UB3LYP/6-31G(d) level of theory are in a good agreement with the experimental data. The calculated non-equivalence of nitrogen atoms in radical **3a** is not observed given the similarity of their a_N values, and hence yielding the experimental seven line EPR pattern.[5(*b*)]

The lowest-field components of the EPR spectra of major radicals **2** do not overlap with the components of minor radicals **3**. Therefore, the kinetics of formation of radicals **2** could be monitored by measuring the intensity of these components. The relative concentrations of radicals **2** and **3** in the sample were estimated by the spectral simulation [Figures 1(*b*) and 2(*b*)]. Figure 3 displays the typical kinetics of formation of radicals **2b** and **3b** upon thermolysis of **1b**. The formation of radical **2b** is well fitted by the exponential time dependence (Figure 3) yielding the first-order-reaction rate constant $k = (2.7\pm0.5)\times10^{-4}$ s^{-1} at 363 K. It is evident from the kinetic data (Figure 3) that minor radical **3b** is formed much faster than major radical **2b** and its amount remains constant on further thermolysis. The only explanation is the formation of **3b** from an impurity. Unfortunately, additional recrystallization of **1a** from acetonitrile did not lead to the reduction of radical **3a** formation on thermolysis.

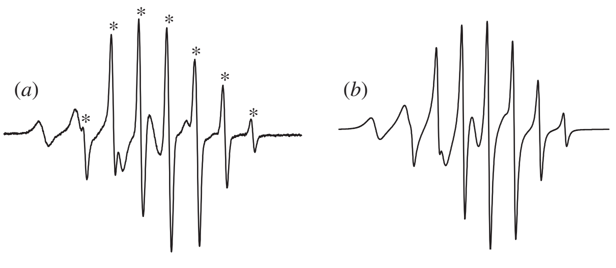


Figure 2 (*a*) Experimental EPR spectrum after heating **1a** in dodecane ($c = 5\times10^{-3}$ mol dm^{-3}) for 5 min at $T = 388$ K. The resonance lines of **3a** are designated by asterisks. (*b*) Simulated spectrum assuming the presence of radicals **2a** ($g = 2.0104$, $a_N = 5.15$ G) and **3a** ($g = 2.0060$, $a_N = 3.96$).

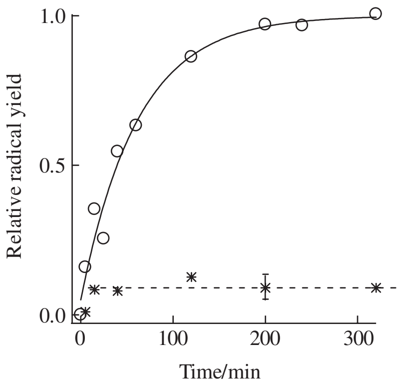


Figure 3 Kinetics of formation of radicals **2b** (circles) and **3b** (asterisks) upon the thermolysis of **1b** in squalane at 363 K and fitting of the data by exponential time dependence (solid curve). A dashed line is given to emphasize a constant amount of radical **3b**.

The overall yield of radicals **2a** (and **2b**) was close to quantitative (to within ±15%). Small amounts (< 5%) of radicals **3** were also detected upon thermolysis of derivatives **1c**–**e**, while only radicals **2f** and **2g** were detected for **1f** and **1g**.[†]

The irradiation of hydrocarbon solutions of **1a**–**g** at ambient temperature with UV (313 nm) or visible (436 nm) light produced EPR spectra similar to those obtained from the thermolysis experiments. However, the solubility of bicycles RCN$_5$S$_3$ was too poor in hydrocarbons for quantitative estimations of the radical yield. Therefore, we studied the photochemistry of **1b** in CS$_2$.

Figure 4(*a*) shows the EPR spectra recorded upon the progressive photolysis of **1b** in CS$_2$. These spectra are very similar

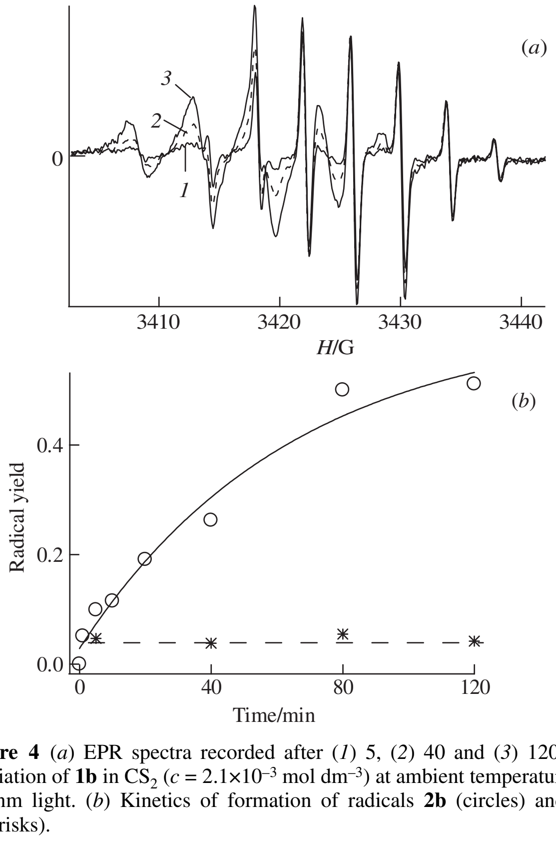
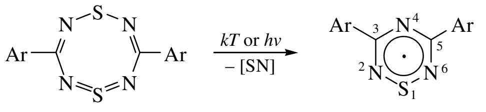


Figure 4 (*a*) EPR spectra recorded after (*1*) 5, (*2*) 40 and (*3*) 120 min irradiation of **1b** in CS$_2$ ($c = 2.1\times10^{-3}$ mol dm^{-3}) at ambient temperature by 436 nm light. (*b*) Kinetics of formation of radicals **2b** (circles) and **3b** (asterisks).

to those recorded upon thermolysis in dodecane (Figure 2) and were simulated as a superposition of resonance lines from radicals **2b** and **3b**, as discussed above. The same hyperfine coupling constants (a_N = 5.2 G and a_N = 3.96 G) were extracted for radicals **2b** and **3b**. Unlike the situation in squalane and dodecane, the spectra of individual radicals were symmetrical due to the very low viscosity of CS_2. Peak-to-peak widths (ΔH_{pp}) for radicals **2b** and **3b** [Figure 4(*a*)] are equal to 0.168 and 0.052 mT, respectively [Figure 4(*a*)]. The difference in ΔH_{pp} is due to the much smaller hyperfine coupling constants with protons of aryl substituents in **3b** (~0.01–0.03 mT) comparing to **2b** (0.03–0.07 mT). The a_H values were taken from UB3LYP/6-31G(d) calculations.

Figure 4 shows the formation of radical **3b** in the first minutes of photolysis (its amount does not depend on further irradiation, while the amount of radical **2b** continues to grow). Therefore, it is clear from kinetic data (Figures 3 and 4) that radicals **3** are formed upon the thermolysis or photolysis of corresponding minor impurities in **1**. Typical (and practically non-removable) impurities in **1a**–**e**[3] are correspondingly substituted compounds **4**,[7] which can formally be transformed into radicals **3** by loss of a $SN^{\cdot}$ fragment (Scheme 4).[†] It should be noted that radicals **3** are generated much faster than radicals **2** on both thermolysis and photolysis [Figures 3 and 4(*b*)].



4 **3**

Scheme 4

Interestingly, corresponding cations **2a**–**e**$^+$ and **3a**–**e**$^+$ were detected by mass spectrometry (EI, 70 eV) of **1a**–**e**,[3(*c*)] and salts of **3a**$^+$ and **3c**$^+$ were identified by XRD as by-products of the reaction between **1a**,**c** and $[M(SO_2)_x][AsF_6]_2$ (M = Co, Hg).[8] To the best of our knowledge, however, the formation of radicals **3** from precursors **4** has never been observed. This reaction will be the topic of further research.

This work was supported by the Russian Foundation for Basic Research (project nos. 04-03-32259 and 07-03-00467), Deutsche Forschungsgemeinschaft (project no. 436 RUS 113/486/0-3 R), the Siberian Branch of the Russian Academy of Sciences (interdisciplinary project no. 25). C.K. acknowledges the support of the BFK NaWi, University of Bremen.

References

1 (*a*) K. Awaga, T. Tanaka, T. Shirai, Y. Umezono and W. Fujita, *C. R. Chimie*, 2007, **10**, 52; (*b*) K. Awaga, T. Tanaka, T. Shirai, M. Fujimori, Y. Suzuki, H. Yoshikawa and W. Fujita, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 25; (*c*) J. M. Rawson, A. Alberola and A. Whalley, *J. Mater. Chem.*, 2006, **16**, 2560; (*d*) J. M. Rawson and F. Palacio, *Struct. Bond.*, 2001, **100**, 93.

2 (*a*) I. V. Vlasiuk, V. A. Bagryansky, N. P. Gritsan, Yu. N. Molin, A. Yu. Makarov, Yu. V. Gatilov, V. V. Shcherbukhin and A. V. Zibarev, *Phys. Chem. Chem. Phys.*, 2001, **3**, 409; (*b*) N. P. Gritsan, V. A. Bagryansky, I. V. Vlasyuk, Yu. N. Molin, A. Yu. Makarov, M. S. Platz and A. V. Zibarev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 1973 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2064); (*c*) K. V. Shuvaev, V. A. Bagryansky, N. P. Gritsan, A. Yu. Makarov, Yu. N. Molin and A. V. Zibarev, *Mendeleev Commun.*, 2003, 178; (*d*) N. P. Gritsan, S. N. Kim, A. Yu. Makarov, E. N. Chesnokov and A. V. Zibarev, *Photochem. Photobiol. Sci.*, 2006, **5**, 95; (*e*) N. P. Gritsan, E. A. Pritchina, T. Bally, A. Yu. Makarov and A. V. Zibarev, *J. Phys. Chem. A*, 2007, **111**, 817.

3 (*a*) T. Chivers, J. F. Richardson and N. R. M. Smith, *Inorg. Chem.*, 1986, **25**, 272; (*b*) R. T. Boere, J. Fait, K. Larsen and J. Yip, *Inorg. Chem.*, 1992, **31**, 1417; (*c*) C. Knapp, E. Lork, T. Borrmann, W.-D. Stohrer and R. Mews, *Eur. J. Inorg. Chem.*, 2003, 3211; (*d*) C. Knapp, E. Lork, R. Mews and A. V. Zibarev, *Eur. J. Inorg. Chem.*, 2004, 2446; (*e*) C. Knapp, E. Lork, R. Maggiulli, P. G. Watson, R. Mews, T. Borrmann, W.-D. Stohrer and U. Behrens, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1235; (*f*) C. Knapp and R. Mews, *Eur. J. Inorg. Chem.*, 2005, 3536.

4 K. T. Bestari, R. T. Boere and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, **111**, 1579.

5 (*a*) S. A. Fairhurst, K. M. Johnson, L. H. Sutcliffe, K. F. Preston, A. J. Banister, Z. V. Hauptman and J. Passmore, *J. Chem. Soc., Dalton Trans.*, 1986, 1465; (*b*) P. J. Hayes, R. T. Oakley, A. W. Cordes and W. T. Pennington, *J. Am. Chem. Soc.*, 1985, **107**, 1346.

6 (*a*) A. Carrington and A. D. MacLachlan, *Introduction to Magnetic Resonance*, Harper and Row, New York, Evanston, London, 1967; (*b*) P. W. Atkins and D. Kivelson, *J. Chem. Soc.*, 1966, **44**, 169.

7 (*a*) A. D. Bond, D. A. Haynes and J. M. Rawson, *Can. J. Chem.*, 2002, **80**, 1507 and references therein; (*b*) I. Ernst, W. Holick, G. Rihs, D. Schomburg, D. Shoham, D. Wenkert and R. B. Woodward, *J. Am. Chem. Soc.*, 1981, **103**, 1540.

8 C. Knapp, *Doctoral Thesis*, Universität Bremen, Bremen, Germany, 2002.

9 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *Gaussian 98, Revision A.6*, Gaussian Inc., Pittsburgh, PA, 1998.

Received: 26th December 2006; Com. 06/2851