important are calculations to determine how the reaction profile is modified by solvation. It is well recognized that the behavior of ionic species, in particular, can be very different in the gas phase and solution, so that care is required in extrapolating from the former to the latter. In the present system, there are important differences between the gas-phase calculations and experimental solution results; e.g., the enthalpy of activation for the basic hydrolysis of dimethyl phosphate is estimated to be 28 kcal/mol,[13] in contrast to the gas-phase 3-21+G* result of about 90 kcal/mol. Use of a Born type model suggests that a dianionic intermediate will be stabilized significantly more than two monoanionic reactants since the solvation free energy and enthalpy depend quadratically on the charge of the ion.[14] Simulations along the reaction path to provide more quantitative evaluations of the relative solvation free energies of the different species are in progress. Their comparison with empirical rules for phosphate ester hydrolysis[6,15,16] will be of great interest.

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Formation of α- and β-Azo Radicals by C–C and C–N Homolysis of Vicinal Bisazoalkanes

Paul S. Engel,* Yanqiu Chen, and Chengrong Wang

Department of Chemistry, Rice University
P.O. Box 1892, Houston, Texas 77251

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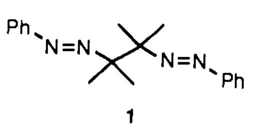
While azoalkanes are well-known precursors of carbon-centered radicals,[1,2] the azo group as a radical-stabilizing substituent[3] has received little attention.[4] Even less is known about azoalkanes whose β-carbon bears a radical center;[5] in fact, such species could lose nitrogen so rapidly as to be undetectable. Our longstanding interest in azoalkanes and more recently in bisazoalkanes[6] prompted us to examine the thermolysis of compounds **1** and **2**.[7]



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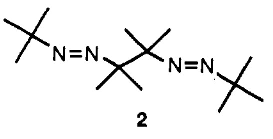

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Although C–N bond cleavage is the normal decomposition mode of azoalkanes,[1] the work of Wintner[8] and others[9] demonstrates that C–C bond homolysis can also occur. Unfortunately, the vicinal bisazoalkanes studied to date[8] are complicated by possible tautomerization and by α-aryl groups that contribute in an unknown way to the lability of the adjacent bonds.

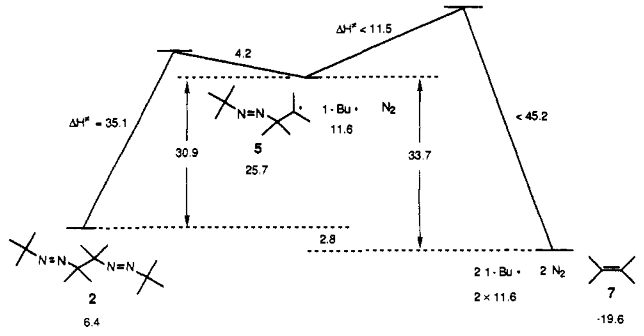
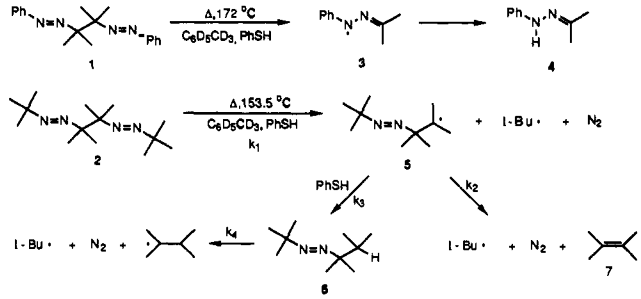


Figure 1. Enthalpy diagram for stepwise fragmentation of **2**. Calculated heats of formation (kcal/mol) are shown below each species. The strain energies of **2** and **5** are estimated while ΔH_f of *t*-Bu• is from ref 16.

We report here that thermolysis of **1** leads exclusively to cleavage of the central C–C bond while **2** undergoes only C–N homolysis via a short-lived β-azo radical. This remarkably different behavior is most readily seen in the nitrogen yield, which is <0.5% for **1** at 171.7 °C and 199% for **2** at 156.6 °C. In the presence of thiophenol, **1** affords exclusively acetone phenylhydrazone (**4**) and diphenyl disulfide while **2** yields isobutane, tetramethylethylene (**7**), and diphenyl disulfide.



Thermolysis kinetics were studied for both vicinal bisazoalkanes. The NMR spectrum of degassed **1** with added PhSH in C_6D_6 or $C_6D_5CD_3$ was monitored with time over the temperature range 133.3–158.1 °C, leading to the activation parameters $\Delta H^{\ddagger} = 30.2 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = -4.3 \pm 1.3$ eu, and $\Delta G^{\ddagger}(150\ °\mathrm{C}) = 32.0$ kcal/mol.[10] UV spectroscopy was used to monitor the disappearance of **2** in toluene over the temperature range 153.5–180.0 °C, providing the activation parameters $\Delta H^{\ddagger} = 35.1 \pm 0.9$ kcal/mol, $\Delta S^{\ddagger} = 2.7 \pm 2.2$ eu, and $\Delta G^{\ddagger}(150\ °\mathrm{C}) = 34.0$ kcal/mol. The 2.0 kcal/mol greater stability of **2** than **1** will be rationalized below.

Similar to the longstanding controversy about stepwise versus simultaneous bond cleavage of simple azoalkanes,[11] the question arises whether **2** breaks four C–N bonds at once or whether β-azo radical **5** is the reaction intermediate. We ignore the possible intervention of *tert*-alkyldiazenyl radicals, whose lifetime is expected to be less than 0.5 ps.[12] In an attempt to trap **5**, a sample

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[7] Spectral data for **1**: ^{1}H NMR (90 MHz, C_6D_6) δ 1.51 (s, 12 H), 7.80 (m, 6 H), 7.10 (m, 4 H); ^{13}C NMR (22.5 MHz, C_6D_6) δ 152.82, 130.28, 129.58, 75.32, 21.55; UV (hexane) $\lambda_{max} = 410$ nm, $\epsilon = 258$; MS (30 eV) *m/e* (relative abundance) 41(31), 51(33), 69(17), 77(100), 105(86), 147(1), 148(1), 182(2), 189(2), 210(1), 294(1). Anal. Calcd for $C_{18}H_{22}N_4$: 294.1844. Found: 294.1845. Spectral data for **2**: ^{1}H NMR (90 MHz, C_6D_6) δ 1.21 (s, 18 H), 1.32 (s, 12 H); ^{13}C NMR (22.5 MHz, C_6D_6) δ 73.15, 66.87, 26.92, 21.01; UV (hexane) $\lambda_{max} = 372$ nm, $\epsilon = 30$. Anal. Calcd for $C_{14}H_{30}N_4$: 254.2470. Found: 254.2468.

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[10] The thermolysis rates of **1**, **2**, and **6** were determined at four or five temperatures. In each kinetic run, the NMR relative peak area or UV absorbance was measured at 7–10 elapsed times. The oil-bath temperature was regulated to ±0.01 °C and was measured to nearly the same precision with a platinum thermometer.

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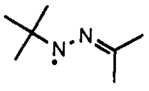
of 0.082 M **2** with 1.67 M thiophenol was thermolyzed at 153.5 °C and subjected to periodic analysis by GC and NMR. As shown by comparison with an authentic sample, a small amount of azoalkane **6** formed and ultimately disappeared. The measured concentration of **2**, **6**, and **7** as a function of time, the independently determined thermolysis rates of **2** and **6**, and the known value of $k_3 = 3.2 \times 10^8$ M^{-1} s^{-1} [13] were fit by computer to a simple kinetic scheme in which k_2 was the only unknown. The best value of k_2 was 3.9×10^9 s^{-1}, corresponding to a 0.26-ns lifetime of **5** at 153.5 °C. Since β-scission of **5** requires coplanarity of the breaking C–N bond with the radical p orbital, ΔS^* for fragmentation of **5** should be less than the 11.7 eu found for **6**. This limit on ΔS^* and the ΔG^*(153.5 °C) = 6.55 kcal/mol corresponding to k_2 lead to $\Delta H^* < 11.5$ kcal/mol for deazatation of **5**. This ΔH^* of **5** is considerably lower than the $\Delta H^* = 40.0 \pm 0.5$ kcal/mol of closed-shell analogue **6**, showing that cleavage of the second azo group is greatly facilitated by the β-azo radical center.

Although the formation of **6** indicates that **5** is involved in the thermolysis of **2**, we have yet to show that this β-azo radical is the major intermediate. The activation parameters for **2** and **6** were used to calculate that **2** decomposed only 3.7 times faster than **6** at 150 °C. Since half of this rate increase is purely statistical while the rest is attributable to steric acceleration of the more hindered **2**,[14,15] we conclude that breaking of the first C–N bond in **2** is not aided by simultaneous cleavage of the second azo group. Thus thermolysis proceeds by stepwise cleavage of the two azo groups, despite the fact that concerted cleavage is roughly 3 kcal/mol exothermic while stepwise cleavage is 31 kcal/mol endothermic. Figure 1 shows the thermochemistry of these pathways based on the values of ΔH^* obtained here and on heats of formation calculated from literature data.[1,16]

The completely different thermolysis behavior of **1** versus **2** suggests that the central C–C bond of **1** is weakened by resonance stabilization of **3** that is lacking in the analogous intermediate **8**. At 150 °C, **1** exhibits $\Delta G^* = 32.0$ kcal/mol while **2** shows $\Delta G^* = 34.0$ kcal/mol. Since no products of C–C homolysis were detected from **2**, let us assume that this reaction is less than 5% as fast as C–N homolysis. We can then calculate that C–N cleavage must have $\Delta G^* > 36.5$ kcal/mol at 150 °C. The resonance stabilization due to phenyl in **3** must therefore be at least $(36.5 - 32.0)/2 = 2.25$ kcal/mol. It is this additional stabilization that makes **1** more labile than **2**. Furthermore, the high stability of (phenylazo)-*tert*-alkanes (ΔG^*(150 °C) ~ 44 kcal/mol)[12,17] versus azo-*tert*-butane (ΔG^*(150 °C) = 35.3 kcal/mol) will surely carry over to **1**, rendering C–N homolysis energetically inaccessible.



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In summary, we have found that thermolysis of diaryl bisazoalkane **1** breaks the central C–C bond while the alkyl analogue (**2**) undergoes exclusive C–N cleavage. The difference between **1** and **2** is attributed to greater resonance stabilization of phenylhydrazonyl radical **3** than its *tert*-butyl analogue **8**. Despite the fact that simultaneous four-bond cleavage of **2** is energetically favored over sequential loss of nitrogen, this vicinal bisazoalkane decomposes via very short lived β-azo radical **5**, which has been trapped for the first time.

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A New Twist on Pseudorotation

Theresa L. Windus and Mark S. Gordon*

North Dakota State University
Fargo, North Dakota 58105

Larry W. Burggraf

Directorate of Chemical and Atmospheric Sciences
Air Force Office of Scientific Research
Bolling AFB, Washington, D.C. 20332

Larry P. Davis

HQAFSC/XTR, Andrews AFB, Washington, D.C. 20334

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For pentacoordinated structures in a trigonal bipyramidal arrangement, Berry[1] proposed a "pseudorotation" mechanism whereby two such isomers can interconvert through a tetragonal transition state (TS). This Berry pseudorotation mechanism was demonstrated explicitly for SiH_5^- by following the MP2[2]/6-31G(d)[3] minimum energy path[4] (MEP).

In the Berry pseudorotation of SiH_4F^-, we expect two minima (trigonal bipyramids with F either axial, **1**, or equatorial, **2**) and two maxima (square pyramids with F either basal, **3**, or apical, **4**). Indeed, these are the results obtained by several investigators.[5-8] We report here that SiH_4F^- has only one minimum on its potential energy surface (PES) and therefore does not appear to follow the usual Berry pseudorotational model (**1** ⇔ **3** ⇔ **2** ⇔ **4**).

Optimized structures and hessians were calculated with use of restricted SCF (RHF) and Møller–Plesset perturbation theory (MP2)[2] wave functions with the 6-31G(d)[3] and 6-31++G(d,p)[9] basis sets. Final energies were determined at the full fourth order Møller–Plesset (MP4)[10] perturbation level. Calculations were performed with the GAUSSIAN86[11] program.

Relative energies of **1**–**4** are given in Table I. At the RHF/6-31G(d) level, we observe the four expected structures, but we also obtain an unexpected result. In the Berry model, **2** should pseudorotate to **1** with **3** as the TS. However, at all correlated levels **2** becomes *higher* in energy than **3**. This suggests that at higher computational levels the hessian of **2** will not be positive definite and that the usual Berry pseudorotation may not be taking place. Indeed, further investigation with the 6-31++G(d,p) basis set reveals that **2** and **3** coalesce into one C_{2v} TS with one imaginary frequency, even at the SCF level! The same result is found when the geometry is optimized at the MP2/6-31++G-

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