

approach those of the simple classical model based on eq 2 and 8.

As shown by Figure 1, the Marcus quadratic equation (eq 3) is a good approximation to eq 8 in the range  $|\Delta G| \leq 4\Delta G^\ddagger(0)$ . The "linear" free-energy relationships (eq 4) can be viewed as tangents to the eq 8 curve.<sup>45</sup> The slopes of such "linear" plots have to be in the range  $0 < \alpha < 1$ , with values lower or higher than 0.5 for exo- or endoergonic reactions, respectively.<sup>46</sup> For values different from 0 and 1, "linear" relationships can only be valid for more or less narrow ranges of  $\Delta G$ , depending on the curvature of the eq 8 plot, i.e., on the  $\Delta G^\ddagger(0)$  value.

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Franco Scandola\*

Centro di Studio sulla Fotochimica e Reattività degli Stati Eccitati dei Composti di Coordinazione del CNR  
University of Ferrara, Ferrara, Italy

Vincenzo Balzani\*

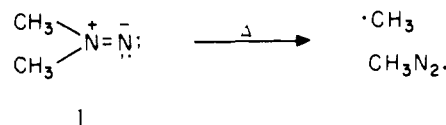
Istituto Chimico "G. Ciamician" dell'Università  
and Laboratorio di Fotochimica e Radiazioni  
d'Alta Energia del CNR, Bologna, Italy

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## Kinetics of the Thermal Decomposition of a 1,1-Dialkyldiazene, N-(2,2,6,6-Tetramethylpiperidyl)nitrene

Sir:

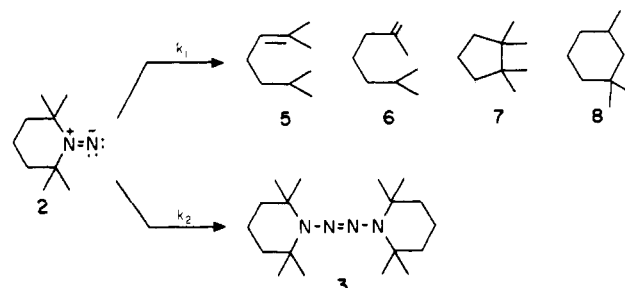
The rates and activation parameters of 1,1-diazene thermal reactions are not known.<sup>1</sup> Recent theoretical studies suggest that the C-N bond strength of the 1,1-dialkyldiazene is substantially lower than that of the trans-1,2 isomer.<sup>2</sup> The homolytic decomposition of *N*-(dimethylamino)nitrene (1) is calculated to be endothermic by 23.5<sup>2a</sup> and 26.2<sup>2b</sup> kcal/mol, respectively.



We report the kinetics of the thermal decomposition of a 1,1-dialkyldiazene. The temperature dependence of the unimolecular rate ( $k_1$ ) of *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (2) fragmentation was examined in three different solvents, and kinetic evidence for a direct bimolecular pathway ( $k_2$ ) for the formation of tetrazene 3 from 1,1-diazene 2 is provided (Scheme 1).

We recently described the direct spectroscopic observation ( $-78^\circ\text{C}$ ) of a 1,1-dialkyldiazene, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (2).<sup>3</sup> Treatment of 1-amino-2,2,6,6-tetramethylpiperidine (4) with *tert*-butyl hypochlorite and triethylamine in dimethyl ether at  $-78^\circ\text{C}$  affords, in addition to an insoluble white precipitate ( $\text{Et}_3\text{NHCl}$ ), an intense purple solution of 2 that is kinetically persistent at  $-78^\circ\text{C}$  but decolorizes rapidly at  $0^\circ\text{C}$ . The visible ( $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) 541 nm) and infrared ( $\nu(\text{N}=\text{N})$  1595  $\text{cm}^{-1}$ ) spectra of 2 provided ex-

### Scheme 1



**Table I.** Decomposition of **2** at  $-10.0\text{ }^{\circ}\text{C}$ 

solvent	$E_T$	$k, \text{s}^{-1}$	$k_{\text{rel}}$	$\Delta G^\ddagger$
<i>n</i> -hexane	30.9	$3.49 \times 10^{-3}$	4.8	18.3
ethyl ether	34.6	$1.23 \times 10^{-3}$	1.7	18.9
tetrahydrofuran	37.4	$0.73 \times 10^{-3}$	1.0	19.1

**Table II<sup>a</sup>**

solvent	$\log A$	$E_a, \text{kcal/mol}$
<i>n</i> -hexane	$11.6 \pm 0.5$	$16.9 \pm 0.7$
ethyl ether	$13.7 \pm 0.3$	$20.0 \pm 0.4$
tetrahydrofuran	$13.6 \pm 0.3$	$20.1 \pm 0.4$

<sup>a</sup> Tolerances are the standard deviation.

perimental evidence on the 1,1-diazene  $n-\pi^*$  electronic transition and the  $\text{N}=\text{N}$  double bond character in the ground state.<sup>3</sup>

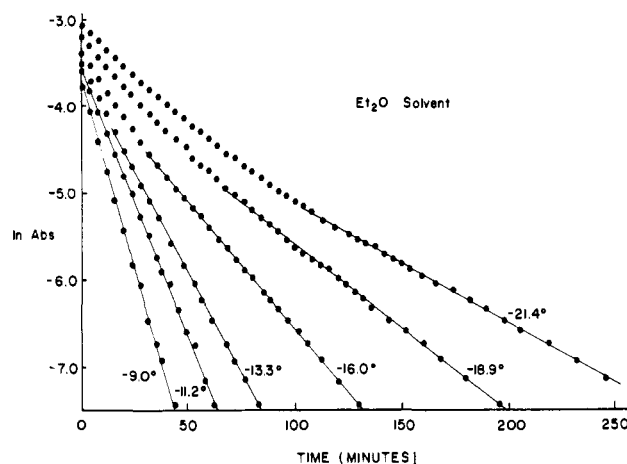
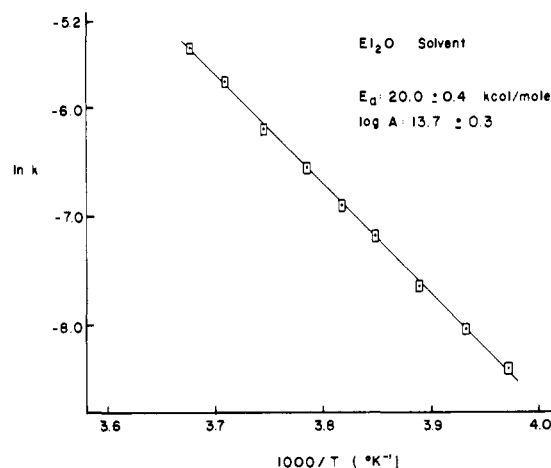
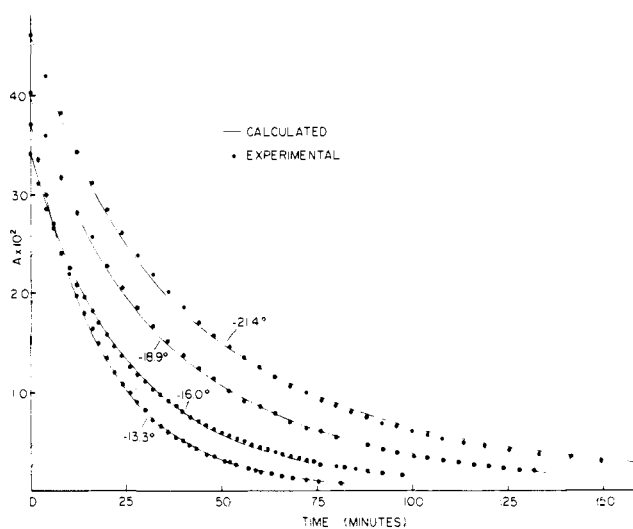
For kinetic studies, the purple 1,1-diazene **2** was chromatographed ( $-82\text{ }^{\circ}\text{C}$ ) on basic alumina, excess triethylamine was added, and the solution was concentrated.<sup>4</sup> Inspection of the chromatographed solution at low temperature by proton NMR ( $\text{CDCl}_3$ ) revealed substantial amounts of the tetrazene **3** and absorptions at  $\delta$  1.15 and 2.15 (2:1 ratio). Warming the sample to  $25\text{ }^{\circ}\text{C}$  results in the disappearance of the 1.15 and 2.15 signals, presumably the 1,1-diazene **2**,<sup>6</sup> while the tetrazene **3** signals increase and new absorptions in the region of the four  $\text{C}_9$  hydrocarbons **5-8** appear.<sup>7</sup> These NMR results indicate that under some conditions the unimolecular and bimolecular processes in Scheme I are competitive.

The decay kinetics of **2** were studied in three different solvents (*n*-hexane, ethyl ether, and tetrahydrofuran) typically in the temperature range of  $+4$  to  $-21.6\text{ }^{\circ}\text{C}$  by monitoring the optical density of the purple solution ( $\sim 10^{-3}\text{ M}$ ) at 541 nm as a function of time.<sup>8</sup> The disappearance of **2** was strictly first order at higher temperatures ( $-1$  to  $-11.2\text{ }^{\circ}\text{C}$  in  $\text{Et}_2\text{O}$ ), becoming a combination of first- and higher-order kinetics as the temperature was lowered ( $-13.3$  to  $-21.4\text{ }^{\circ}\text{C}$  in  $\text{Et}_2\text{O}$ ). Plots of  $\ln \text{Abs}$  vs. time at the lower temperatures ( $-16.0$  to  $-21.4\text{ }^{\circ}\text{C}$  in  $\text{Et}_2\text{O}$ ) afforded a curve segment at short times followed by a linear segment at longer times (Figure 1). First-order rate constants were taken to be the slopes of the linear portions of these plots. The results of nine kinetic runs in ethyl ether ( $-1$  to  $-21.4\text{ }^{\circ}\text{C}$ ) are plotted in Figure 2. The observed activation energy for the unimolecular 1,1-diazene **2** thermal decomposition in  $\text{Et}_2\text{O}$  is  $20.0 \pm 0.4\text{ kcal/mol}$ . This is a substantially lower  $E_a$  than that observed in the decomposition of similarly substituted 1,2-dialkyldiazenes.<sup>10</sup>

The effect of solvent on the unimolecular rate of 1,1-diazene **2** decomposition was examined. We find that the rate of decomposition of **2** is sensitive to solvent, the rate increasing with decreasing solvent polarity (Table I). The activation parameters are listed in Table II.

The observed rate dependence on solvent polarity is consistent with a polar ground state decomposing by a less polar transition state. Such an effect has been observed in the decompositions of 1,2-dialkyldiazenes by Ruchardt and co-workers.<sup>11a</sup> For the three solvents examined,  $\ln k_1$  correlates with  $E_T$  reasonably well.<sup>11b</sup>

We find that the curved portions of the  $\ln \text{Abs}$  vs. time plots may be modelled as competitive unimolecular and bimolecular reactions,  $k_{\text{obsd}} = k_1 + k_2[\mathbf{2}]$ . Using computer simulation, rate constants could be fitted to generate the experimental  $\text{Abs}$  vs. time plots (Figure 3).<sup>12,13</sup> For example, in  $\text{Et}_2\text{O}$  at  $-16\text{ }^{\circ}\text{C}$ ,  $k_1 = 5.03 \times 10^{-4}\text{ s}^{-1}$  and  $k_2 = 5.0 \times 10^{-2}\text{ L}/(\text{mol s})$ . Although there is not sufficient data to derive accurate Arrhenius parameters for the bimolecular reaction  $\mathbf{2} \rightarrow \mathbf{3}$ , the results of the computer simulation indicate that the temperature de-

**Figure 1.****Figure 2.****Figure 3.**

pendence of the dimerization rate is small.<sup>14</sup> This is the first kinetic evidence for a direct bimolecular pathway for the formation of tetrazenes from 1,1-diazenes.

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- (4) Chromatography on deactivated basic alumina at -82 °C using dimethyl ether-propane as solvent removed the *tert*-butyl alcohol and substantial amounts of unreacted 1-amino-2,2,6,6-tetramethylpiperidine (**4**). A 1,1-diazene → tetrazene dimerization (**2** → **3**) on the column resulted in the loss of ~65% of the purple 1,1-diazene **2** upon chromatography. Importantly, the chromatography and subsequent addition of triethylamine<sup>5</sup> were necessary to obtain reproducible kinetics.
- (5) The 1,1-diazene **2** is sensitive to trace acid.
- (6) From the NMR experiment (EM-390) we measured the concentration of **2** against an internal standard (CH<sub>2</sub>Cl<sub>2</sub>). From this we calculate the extinction coefficient for the n-π\* electronic transition of **2**, ε ~ 18 ± 3.
- (7) The tetrazene product **3** was isolated previously and characterized. The ratios of hydrocarbon products are sensitive to both solvent and temperature and will be reported in a full manuscript. At 0 °C in Et<sub>2</sub>O we find hydrocarbons **5-8** in ratios of 6:1:10:24:5, respectively.
- (8) The purple solution is introduced via Teflon tubing connected to sample injection parts into a specially designed copper-jacketed quartz cell attached to a cryogenic unit<sup>9</sup> maintained at -21 to +4 ± 0.2 °C. The optical density was monitored on a Cary Model 14 spectrophotometer.
- (9) Air Products Laboratory cryogenic system, Model LC-1-100 liquid nitrogen Dewar assembly, Model WMX-1A optical shroud with injector ports.
- (10) For *trans*-azo-*tert*-butane the enthalpy of activation ΔH<sup>‡</sup> = 42.2 ± 0.8 kcal/mol. Martin, J. C.; Timberlake, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 978. For a recent discussion of the enthalpies of 1,2-diazene decompositions, see Engel, P. S.; Hayes, R. A.; Keifer, L.; Szilagy, S.; Timberlake, J. W. *ibid.* **1978**, *100*, 1876.
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- (13) Computer simulation performed using the MS1M4 Stochastic Mechanism Simulator developed by F. A. Houle and D. L. Bunker, Quantum Chemistry Program Exchange No. 293.
- (14) On the basis of the computer simulation we estimate an E<sub>a</sub> of ≤ 7 kcal/mol for the bimolecular process **2** → **3**.
- (15) National Science Foundation Predoctoral Fellow, 1975-1978.
- (16) Alfred P. Sloan Research Fellow, 1977-1979; Camille and Henry Dreyfus Teacher-Scholar, 1978-1983.

William D. Hinsberg, III,<sup>15</sup> Peter B. Dervan\*<sup>16</sup>

Contribution No. 6046, Crellin Laboratory of Chemistry  
California Institute of Technology  
Pasadena, California 91125

Received June 11, 1979

## Generation and Thiol Reduction of a "Quinonoid" Dihydropterin and an Oxidized Pyrimidine Analogue

Sir:

In an effort to determine the exact role of the tetrahydropterin cofactor utilized in the formation of tyrosine from phenylalanine and molecular oxygen in the reaction catalyzed by phenylalanine hydroxylase<sup>1</sup> (E.C. 1.14.16.1), we have been investigating the spectral and chemical properties of a "quinonoid" dihydropterin and an analogous "quinonoid" oxidized pyrimidine, the presumed products derived from the respective cofactors during turnover. The quinonoid compounds also may be generated by chemical oxidants including bromine, dichlorophenolindophenol,<sup>2</sup> and ferricyanide<sup>3</sup> as well as peroxidase.<sup>4</sup> These species are rapidly reduced to the parent cofactor by a variety of reagents, including thiols<sup>5</sup> and quinonoid dihydropteridine reductase.<sup>6</sup> Our results for the thiol reduction of the quinonoid compounds implicate the intermediacy of thiol adducts presumably at the 4a, 8a- and 5,6 positions of the oxidized pterin and pyrimidine, respectively, during the reduction process and provide direct evidence for the existence of a hydroxylated derivative at the 5 position of 4-hydroxy-2,5,6-

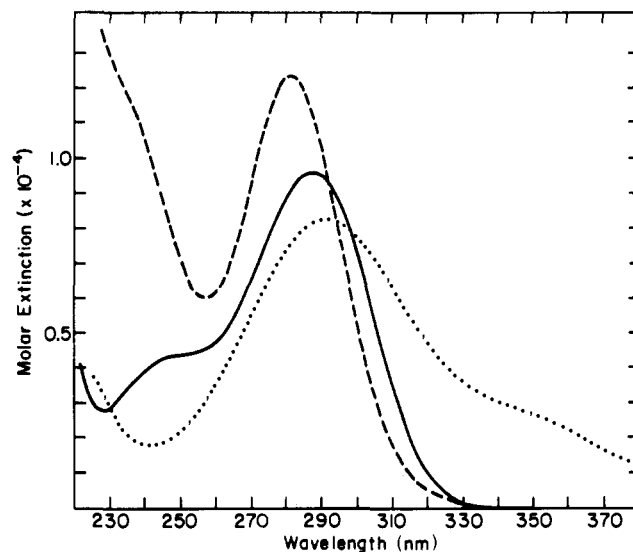
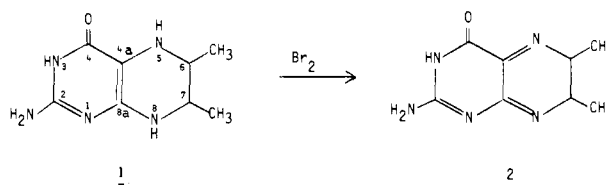


Figure 1. UV spectra of 4-hydroxy-2,5,6-triaminopyrimidine (**5**) (—), the product of bromine oxidation of **5** (···), and 2,6-diamino-4,5-dihydroxypyrimidine (**8**) in the presence of a 20-fold excess of dithiothreitol (---), in 0.2 M Tris-HCl, pH 8.10.

triaminopyrimidine during its oxidation by horseradish peroxidase (E.C. 1.11.1.7).

When 6,7-dimethyltetrahydropterin (**1**) is treated with 1 equiv of bromine, an oxidized pterin species (**2**)<sup>7</sup> is generated whose UV spectral characteristics are consistent with those attributed to the primary oxidation product of **1** in its phenylalanine hydroxylase catalyzed oxidation.<sup>2</sup> The reaction of **2** with excess 2-mercaptoethanol (pH 7.45-8.10, Tris buffer, μ = 0.2 KCl, 25 °C) gives two products, **1** and 7,8-dihydro-6,7-dimethylpterin (**3**). The reaction can be followed by the



decrease in absorbance at 380 nm. The reductive process at a given pH is dependent on the second power of the total thiol concentration, independent of buffer, and gives rise to the following rate law as shown by the dependence of the rate on pH:

$$k_{\text{obsd}} = k_2'[\text{RSH}][\text{RSH}]$$

The kinetics are consistent with the processes outlined in Scheme 1, where  $k_2' = k_1k_2/k_{-1} = 2.2 \times 10^3 \text{ s}^{-1} \text{ M}^{-2}$  and require the intermediacy of an adduct such as **4**, derived from attack by mercaptoethanol at the 8a carbon. We cannot rule out, on the basis of presently available data, formation of an analogous 4a adduct. The intermediate resembles that recently isolated by Sayer et al.<sup>8</sup> in the reaction of 1,3-dimethyl-5-(*p*-nitrophenylimino)barbituric acid with thiols and implicated

### Scheme I

