

Figure 2. Enthalpy of di-1-norbornyldiazene (**2**) and the transition states for isomerization and decomposition. See caption for Figure 1. ^a Estimated.

strain.^{5,16} Furthermore, it will be noted in Table II that λ_{\max} for **2c** lies between the 380 nm found for *cis*-diisopropylidiazene and the 447 nm for **3c**. It has been proposed that λ_{\max} is a function of N–N–C bond angle,¹⁷ which in turn should govern the strain energy.¹⁶ In fact, the strain energy of **2c** is intermediate between that of *cis*-diisopropylidiazene and **3c**. We therefore have a self-consistent picture in which the lower strain in **2c** relative to **3c** coupled with the higher $\Delta H_{\text{dec}}^{\ddagger}$ of **2t** (lower stability of incipient radical) combine to make decomposition of **2c** energetically inaccessible.

1 resembles **2** in its low quantum yield of nitrogen but the λ_{\max} of **1c**, which is the longest ever found for an acyclic *cis* diazene, is not far from that of **3c**. Its strain energy probably lies in the region of 24 kcal mol⁻¹, which places the transition state for isomerization at 50 kcal mol⁻¹. Since some nitrogen is evolved on heating **1c**, the transition state for decomposition must not be much above 50 kcal mol⁻¹. This figure is considerably lower than the reported $\Delta H_{\text{dec}}^{\ddagger}$ of **1t** (cf. Table I), a value quite possibly in error.¹⁸

A final note concerns the effect of ground state energies of *cis* diazenes on ΔH^{\ddagger} of isomerization. *cis*-Diisopropylidiazene possesses 8 kcal mol⁻¹ of strain and $\Delta H_{\text{isom}}^{\ddagger}$ is 32.3 kcal mol⁻¹. Both *cis* diazenes studied here are more strained than *cis*-diisopropylidiazene and also have lower values of $\Delta H_{\text{isom}}^{\ddagger}$. Although variations in $\Delta S_{\text{isom}}^{\ddagger}$ make quantitative arguments tenuous, it is gratifying to note that the very strained **1c** isomerizes more readily than the less strained **2c**.

These results then, allow one to predict when stable *cis* dialkyldiazene might be isolable, namely, when decomposition is impeded by radical instability and when isomerization is not facilitated by bulky substituted groups.

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- For example, the ΔS^{\ddagger} for **1t** listed in Table I is one of the largest ever reported. If one assumes $\Delta S^{\ddagger} = 10$ eu and $k_{300^\circ} = 6.32 \times 10^{-4}$ s⁻¹,¹⁹ a more reasonable value of $\Delta H^{\ddagger} = 48.4$ kcal mol⁻¹ is obtained.
- C. Rüdhardt, private communication.

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Thermochemistry of Cyclic 1,2-Dialkyldiazene (Azo Compounds). The Effect of Strain Energy on Thermal Lability

Sir:

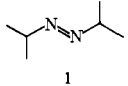
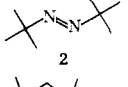
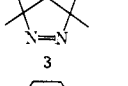
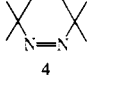
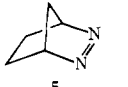
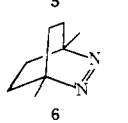
Despite the potential utility of thermochemical data in understanding the decomposition of 1,2-dialkyldiazene,¹ their heats of formation (ΔH_f) have seldom been measured. Prior to 1973, most ΔH_f 's for these compounds were estimated from Coates and Sutton's early study of diisopropylidiazene (**1**);² however, more recent work³ showed their value to be in error by nearly 11 kcal mol⁻¹.

The present report deals mainly with ring strain in cyclic diazenes but it also includes new data⁴ on di-*tert*-butyldiazene (**2**), whose first reported³ ΔH_f was unexpectedly low. Moreover, the present enthalpies of vaporization (ΔH_v) were determined by vaporization calorimetry⁶ and are considerably more accurate than those measured earlier.³

Strain energies are calculated by comparison of specific pairs of compounds. For all cases in which the α -carbon atom is fully substituted, **2** is taken as the reference compound; however, in the case of **5**, diisopropylidiazene (**1**) is a more appropriate model. A sample calculation of the strain energy of **4** is given below, using group contributions taken from the compilation of Benson and O'Neal.⁷ For **2**: $\Delta H_f = -8.51 = 6[\text{C}-(\text{C})(\text{H})_3] + 2[\text{C}-(\text{C})_3(\text{N})] + [-\text{N}=\text{N}-]$. Since $[\text{C}-(\text{C})(\text{H})_3] = -10.08$, it follows that $2[\text{C}-(\text{C})_3(\text{N})] + [-\text{N}=\text{N}-] = 51.97$. For **4**: ΔH_f (calcd) = $2[\text{C}-(\text{C})_3(\text{N})] + [-\text{N}=\text{N}-] + 4[\text{C}-(\text{C})(\text{H})_3] + 2[\text{C}-(\text{C})_2(\text{H})_2] = 51.97 - 40.32 - 9.90 = 1.75$ kcal mol⁻¹. Strain = ΔH_f (obsd) - ΔH_f (calcd) = $10.03 - 1.75 = 8.28$ kcal mol⁻¹.

Table II summarizes the strain energies thus calculated.⁸ Part of the 2.7–15.4 kcal mol⁻¹ strain in these compounds must be due to the energy difference between the *cis* and *trans* diazene linkage. Although it is now clear that the *cis* is normally of higher energy,⁹ the magnitude of the *cis*-*trans* difference remains unmeasured. It is suggested here

Table I. Thermochemical Data for Six 1,2-Dialkyldiazenes^a

Compound	State	$\Delta H_f^\circ(s,1)^{b,c}$	$\Delta H_v^\circ^d$	$\Delta H_f^\circ(g)^c$
	(l)	-0.06 ± 0.84	8.58 ± 0.10	8.52 ± 0.85
	(l)	-17.85 ± 0.86	9.34 ± 0.06	-8.51 ± 0.87
	(s)	-5.34 ± 0.84	14.73 ± 0.05	9.39 ± 0.85
	(l)	-1.93 ± 1.09	11.96 ± 0.10	10.03 ± 1.10
	(s)	36.35 ± 0.62	13.21 ± 0.15	49.56 ± 0.64
	(s)	4.88 ± 1.04	17.20 ± 0.13	22.08 ± 1.05

^a All values in kcal mol⁻¹. ^b Heat of formation of solid or liquid. ^c Tolerances include errors from every conceivable source. ^d Heat of vaporization; tolerances are twice the standard deviation.

Table II. Strain Energies and Activation Enthalpies (ΔH^\ddagger) for Decomposition of Dialkyldiazenes^a

Compound	Strain energy	Obsd ΔH^\ddagger	Calcd transition state energy, E^*
1	(0)	47.3 ^b	47.3
2	(0)	42.2 ^c	42.2
3	2.7	36.9 ^d	39.6
4	8.3	(34.3) ^e	42.6
5	15.4	36.2 ^{d,f}	51.6
6	10.1	42.5 ^g	52.6

^a All entries in kcal mol⁻¹. ^b M. J. Perona, P. C. Beadle, and D. M. Golden, *Int. J. Chem. Kinet.*, 5, 495 (1973). ^c J. C. Martin and J. W. Timberlake, *J. Am. Chem. Soc.*, 92, 978 (1970). ^d Calculated from the data of R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, 88, 3963 (1966). ^e Value for 3,6-dimethyl-3-6-diethyl-1,2-diazacyclohexene-1 from N. A. Porter, Ph.D. Thesis, Harvard University, 1969. ^f S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, 83, 2895 (1961). ^g Preliminary value determined by Lan Shen at Rice University.

that the strain in **4** is representative of this difference in acyclic compounds while the lesser strain in **3** is due to an especially favorable geometry for the diazene linkage. Those familiar with the strain energy in cyclopentene (5.9 kcal mol⁻¹) and cyclohexene (1.4 kcal mol⁻¹)⁷ will have already recognized from Table II that monocyclic diazenes bear little resemblance to olefins. It appears that mutual repulsion of the lone pairs on nitrogen raises the energy of the cis compounds¹⁰ and that this repulsion is reduced by decreasing the N-N-C angle. An acyclic cis diazene cannot achieve the especially favorable geometry found in **3** because of repulsion between cis alkyl groups.

The above suppositions are supported by uv and photoelectron spectroscopy data. Baird et al.¹¹ have suggested that the $n-\pi^*$ excitation energy for diazenes is a sensitive function of N-N-C angle. The uv spectrum of **4** (λ_{\max} 380 nm, ϵ 127) is nearly superimposable on that of *cis*-**1** (λ_{\max} 382 nm, ϵ 140). Similarly, the lowest ionization potential (IP), which reflects the energy of the antibonding combination of nitrogen n orbitals, can be used as an indicator of diazene geometry.¹² When a 0.27 eV correction is made for the in-

ductive effect of two alkyl groups in **4** (IP = 7.89 eV) vs. *cis*-**1** (IP = 8.24 eV), their IP's are found to lie within 0.07 eV of one another, implying similar N-N-C bond angles.^{13,14} The idea that **4** has the same diazene geometry as *cis*-**1** coupled with the assumption that nonbonded interactions are similar in these two compounds allows one to conclude that both possess the same amount of strain energy relative to the model diazene **2**. Independent support for this 8 kcal mol⁻¹ estimate of the *cis*-*trans* energy difference in **1** is found in the inherent 8 kcal mol⁻¹ difference between activation energies for thermolysis of *cis* and *trans* diazenes¹⁶ and in the consistent model generated for the photolysis of *cis*- and *trans*-**1** when 8 kcal mol⁻¹ is taken as the ground state energy difference.¹⁷

Unlike **4**, compound **3** is considered to be a poor model for an acyclic cis diazene. Both its uv spectrum (λ_{\max} 327 nm, ϵ = 204) and lowest IP (8.63 eV) imply that the energy of the HOMO has decreased and therefore that the N-N-C angle has decreased relative to **4**. This geometry change is in accord with its lower total energy than *cis*-**1**, since the interfering hydrogen atoms have been removed to form a ring.

Included in Table II are the experimentally determined activation enthalpies (ΔH^\ddagger) for thermally induced extrusion of nitrogen from diazenes. The transition state energy (E^*) is given in the last column as the sum of ΔH^\ddagger and the ground state strain energy. Although ΔH^\ddagger is known to depend on the stability of the incipient alkyl radicals,¹ comparison of compounds producing the same kind of radicals should reveal other transition state effects. The difference in E^* between **2** and **3**, which is barely outside of experimental error, suggests that the transition state for thermolysis of **3** possesses extra stabilization. This is consistent either with decomposition to a 0,0 trimethylene intermediate whose energy is lowered by interaction between the radical centers, or with concerted loss of nitrogen through a twisted transition state which is stabilized by partial cyclopropane bond formation.¹⁸

The bicyclic diazenes **5** and **6** undergo thermolysis with considerably greater difficulty than expected, suggesting that the transition states still possess considerable strain or that their decomposition mechanism differs from that of **2**. Two-bond cleavage of diazenes may proceed through a geometry which is unattainable in the bicyclic series, forcing **5** and **6** to decompose via the higher energy one-bond mechanism. Indeed there is already stereochemical evidence that thermolysis of **5** proceeds by way of a diazenyl radical.¹⁹ The present results do not require the one-bond mechanism for **3**, in accord with previous studies on pyrazoline decomposition.^{18,20} In the case of **4**, the most expedient explanation for its similar E^* to **2** (cf. Table II) is that all of the ground state destabilization of **4** appears as a lower ΔH^\ddagger , no special effects seem to operate in the tetramethylene biradical and both **2** and **4** decompose by simultaneous two-bond scission.²¹

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- (14) Possible complications introduced by nonplanarity of diazenes are being neglected because theoretical calculations show that even *cis*-di-*tert*-butylethylene is nearly planar¹⁵ and that the potential energy curve for twisting about the N=N bond is similar to that for the same process in olefins.¹¹
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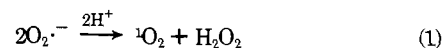
Spectroscopic Evidence for the Generation of Singlet Oxygen in Self-Reaction of *sec*-Peroxy Radicals

Sir:

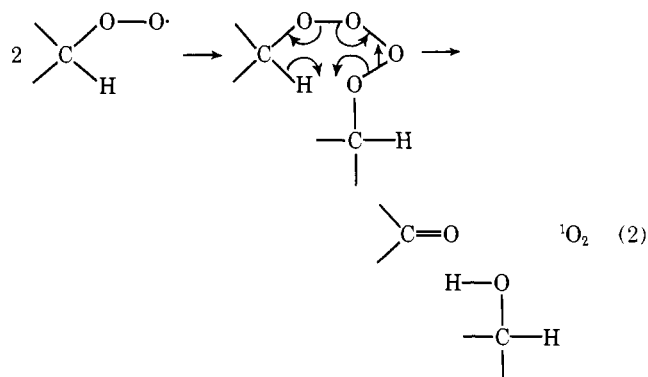
The role of singlet molecular oxygen ($^1\text{O}_2$) in enzyme-mediated peroxidation reactions *in vivo* has been an area of considerable interest in recent years. Howes and Steele have demonstrated chemiluminescence in the system containing rat liver microsomes and NADPH, and postulated the generation of $^1\text{O}_2$ in the process of lipid peroxidation.¹ We have recently succeeded in the direct spectroscopic determination for the generation of $^1\text{O}_2$ in the NADPH-dependent microsomal lipid peroxidation system.²

It has been suggested that dismutation of superoxide anions produces $^1\text{O}_2$ (eq 1).^{3,4} Superoxide dismutase inhibits

the generation of $^1\text{O}_2$ in eq 1 by catalyzing the dismutation of $\text{O}_2^{\cdot-}$ to give ground state molecular oxygen.⁵



The addition of the dismutase to the microsomal lipid peroxidation system, however, did not inhibit the light emission originated from bimol collision of $^1\text{O}_2$, indicating the $^1\text{O}_2$ generation in this system does not involve eq 1.² Thus, we believe that $^1\text{O}_2$ is generated by the interaction of lipid peroxide intermediates (radicals) which might be produced during phospholipid peroxidation. This is supported by the finding that $^1\text{O}_2$ is generated in the self-reaction of *sec*-butyl peroxy radicals (eq 2).⁶



We have now identified $^1\text{O}_2$ spectroscopically in self-reactions of linoleic acid peroxy radicals (possible intermediates in NADPH-dependent microsomal lipid peroxidation) identical with the case of *sec*-butylperoxy radicals, and have proved the generation of two types of $^1\text{O}_2$, both $^1\Sigma_g^+$ and $^1\Delta_g$, during these reactions even in aqueous system.

Peroxy radicals were produced from *sec*-butyl hydroperoxide⁷ or linoleic acid hydroperoxide⁸ by oxidation with ceric ion. Either linoleic acid hydroperoxide (0.127 mmol) or *sec*-butyl hydroperoxide (0.15 mmol) in 15 ml of 0.1 M $\text{NH}_4\text{OH-NH}_4\text{Cl}$ buffer (pH 9.0) was transferred to a quartz cell in a new type of spectrometer⁹ and, in the dark, excess ceric ammonium nitrate (1.27 mmol in 2 ml of water) was slowly added to the solution through a capillary tube to maintain a constant generation of $^1\text{O}_2$ without vigorous bubbling. The solution was not stirred during spectral analysis. The ceric oxidation of *sec*-butyl hydroperoxide (0.15 mmol) in 15 ml of benzene, a well-known $^1\text{O}_2$ generating system, was also carried out according to a modified method of Howard and Ingold.⁶

The data obtained from the spectral analysis of chemiluminescence in the aqueous systems (system 1 and 2 contained *sec*-butyl hydroperoxide and linoleic acid hydroperoxide as the source of *sec*-peroxy radicals, respectively) are summarized in Table I, and the typical emission spectrum

Table I. Emission Spectra Observed during Ceric Oxidation of Hydroperoxides

Vibrational transition of $^1\text{O}_2$	I_{max} obsd, f, nm			I_{max} , nm ref
	System 1	System 2	System 3	
$(^1\Sigma_g^+)(^1\Sigma_g^+)(0,0) \rightarrow 2(^3\Sigma_g^-)(0,0)$	None	None	None	400 ^a
$(^1\Sigma_g^+)(^1\Delta_g)(0,0) \rightarrow 2(^3\Sigma_g^-)(0,0)$	480 (0.45)	470 (0.26)	None	478 ^b 480 ^a
$(^1\Delta_g)(^1\Delta_g)(2,0) \rightarrow 2(^3\Sigma_g^-)(0,0)$	520–530 (1.00)	520–530 (0.43)	512–520 (0.30)	520 ^a
$(^1\Delta_g)(^1\Delta_g)(1,0) \rightarrow 2(^3\Sigma_g^-)(0,0)$	570 (0.62)	570 (0.90)	595 (0.85)	578 ^c 580 ^a
$(^1\Delta_g)(^1\Delta_g)(0,0) \rightarrow 2(^3\Sigma_g^-)(0,0)$	620–640 (0.66)	640 (0.64)	630 (1.00)	633 ^{c,d}
Unspecified transition	670 (0.67)	670 (1.00)	680 (0.80)	670 ^e
$(^1\Delta_g)(^1\Delta_g)(0,1) \rightarrow 2(^3\Sigma_g^-)(0,0)$	—	—	—	703 ^d

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^d A. U. Khan and M. Kasha, *J. Am. Chem. Soc.*, **92**, 3293 (1970). ^e U. Sander and J. Stauff, *An. Soc. Chim. Argent.*, **59**, 149 (1971). ^f Number in parentheses represents the relative intensity in mean value which was obtained by three different runs.