215 (36.9), 202 (21.5), 91 (22.0). Anal. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 93.11; H, 6.48.

1-Benzyltetralin. α-Tetralone (12.3 g, 84.3 mmol) in ether (70 mL) was added to benzylmagnesium chloride prepared in 100 mL of ether from benzyl chloride (11.7 g, 92.1 mmol) and magnesium (3.00 g, 123 mmol). After 72 h of stirring, the reaction was poured into an ice/HOAC mixture. Extraction (ether), neutralization (Na_2CO_3), and drying (Na_2SO_4) gave the crude product, which was loaded onto an alumina column (neutral, activity I) and eluted sequentially with hexane, 20% (v/v) ether/hexane, and then ether. The combined eluents were concentrated in vacuo to give 12.9 g (64%) of 1-benzyl-1-tetralol. Dehydration of the alcohol (7.2 g, 30 mmol) to 1-benzyl-3,4-dihydronaphthalene was accomplished by stirring in HCO_2H (100 mL, 30 min). The addition of water followed by an extraction (ether) ultimately yielded 6.1 g (92%) of 1-benzyl-3,4-dihydronaphthalene. Catalytic hydrogenation (40 psi H_2, 10% Pd/C) of the olefin (5.0 g, 23 mmol) produced 4.8 g (95%) of 1-benzyltetralin: ^1H NMR ($CDCl_3$) δ 7.25 (m, 9 H), 2.9 (m, 5 H), 1.7 (m, 4 H); MS, *m/e* (relative intensity) 222 (2.1), 132 (11.0), 131 (100.0), 130 (23.4), 129 (9.9), 128 (8.9), 127 (3.4), 116 (8.5), 115 (12.8), 91 (28.4). Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.52; H, 8.74.

General Na–K Reduction Procedure. All reductions were carried out under Ar using Na–K (1:4, w/w) in a 50/50 (v/v) mixture of glyme/triglyme. The ethereal solvents were distilled from Na–K prior to use and stored under an Ar atmosphere. Typically, Na–K (6 mequiv) was added to a cooled (0 °C) mixture of glymes (20 mL). After the deep blue solution formed (1 min of vigorous stirring), the substrate (1 mmol) in 1 mL of solvent was added, and stirring was maintained for 15 min. The reaction was terminated by adding ethanol (10 mL), methyl iodide (6 mmol), or *tert*-butyl bromide (6 mmol). After 5 min, water (50 mL) and an internal GC standard (biphenyl or *o*-xylene) were added, and the concentrated reaction mixture was analyzed by GC (Hewlett-Packard 5880, OV-101 fused silica capillary column, FID detection) and GC/MS (Hewlett-Packard 5995, EI, 70 eV). Product identity was confirmed by comparison of GC and GC/MS properties with authentic standards and yields were calculated by using the appropriate response factors. In the case of Birch products, the response factors were taken to be the same as for the parent hydrocarbon.

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Registry No. $PhCH_3$, 108-88-3; $Ph^{14}CH_3$, 22151-42-4; 1-benzylnaphthalene, 611-45-0; dihydrotoluene, 4313-57-9; dihydrotetralin, 51854-29-6; [*methyl*-^{14}C]-1-benzylnaphthalene, 98577-50-5; tetralin, 119-64-2; 1-bromonapthalene, 90-11-9; benzylzinc bromide, 62673-31-8; tetrakis(triphenylphospine)nickel, 15133-82-1; 1,5-diaminonaphthalene, 2243-62-1; 1,5-dibromonaphthalene, 7351-74-8; 1,5-dibenzylnaphthalene, 54811-17-5; α-tetralone, 529-34-0; 1-benzyl-1-tetralol, 98577-49-2; 1-benzyl-3,4-dihydronaphthalene, 85035-87-6; 1-benzyltetralin, 38899-49-9.

A Theoretical Study of the Decomposition of Alkyldiazenyl Radicals

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The mechanism of the thermal decomposition of azoalkanes continues to be the subject of much attention. The question of whether the reaction generally proceeds as a concerted two-bond cleavage (reaction 1a) or a stepwise mechanism (reaction 1b) has received heightened attention.

$$R{-}N{=}N{-}R' \rightarrow [R{-}N{=}N{-}R']^{\ddagger} \rightarrow R\cdot + N_2 + R'\cdot \tag{1a}$$

$$R{-}N{=}N{-}R' \rightarrow R{-}N{=}N\cdot + R'\cdot \rightarrow R\cdot + N_2 + R'\cdot \tag{1b}$$

In a recent MNDO study of the reaction path for the thermal decompositions of azoethane and 1,1-diethyldiazene,[1] we suggested that the mechanisms involve stepwise cleavage to an intermediate ethyl/ethyldiazenyl radical pair that can either recombine or further decompose to two ethyl radicals and a nitrogen molecule (reactions 2 and 3). We further suggested that reaction 2 could be competitive with reaction 3 under proper reaction conditions. Although the proposed mechanism is capable of explaining most of the existing experimental results, the suggestion that both the decomposition of the ethyldiazenyl radical (reaction 3) and the recombination of the ethyl and ethyldiazenyl radicals (the reverse of reaction 2) have measurable activation energies was surprising to many chemists.

$$CH_3CH_2{-}N{=}N\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_2{-}N{=}N{-}CH_2CH_3 \tag{2}$$

$$CH_3CH_2{-}N{=}N\cdot + CH_3CH_2\cdot \rightarrow 2CH_3CH_2\cdot + N_2 \tag{3}$$

Since our study, two experimental reports that support the mechanism of reactions 2 and 3 have appeared. Using arguments based upon volumes of activation, Neuman has concluded that recombination of the adamantyl/adamantyldiazenyl radical pair formed upon thermolysis of *cis*-azoadamantane must occur.[2] Most recently, Engel has shown that recombination of azoalkanes containing the 1,1-dimethylallyl moiety as one of the alkyl groups can rearrange to form what Engel calls "turnaround azoalkanes" (reaction 4) in some but not all cases.[3] Clearly, the formation of these "turnaround alkanes" will be manifest only when recombination of the alkyl/alkyldiazenyl radical pair competes favorably with either the decomposition of the diazenyl radical or the diffusion of the radicals out of the initial cage.

$$R{-}N{=}N{-}C(CH_3)_2CH{=}CH_2 \rightarrow R{-}N{=}N\cdot + \cdot C(CH_3)_2CH{=}CH_2 \rightarrow R{-}N{=}N{-}CH_2C{=}C(CH_3)_2 \tag{4}$$

We believed it to be of interest to conduct further theoretical studies on the decomposition of diazenyl radicals in order to better understand the factors leading to the calculated activation energies, especially in the context of Engel's recent report.[3] A discussion of the causes of possible activation energies for radical recombination reactions has been reported elsewhere.[4]

Methods

The reaction paths for the decomposition of various alkyldiazenyl radicals were calculated by using the half-electron method in the MNDO approximation of molecular orbital theory.[5] This method has been successful in our previous study of the decomposition of diazenes[1] as well as recent studies of radical recombinations[4] and the thermal rearrangements of several derivatives of semi-

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Table I. Comparison of Calculated and Experimental Activation Parameters for R—N═N•

R	$\Delta H^\ddagger$ (MNDO)	$\Delta G^\ddagger$ expt	$\Delta G^\ddagger$ corr	$\Delta H_{\text{reaction}}$ (MNDO)
CH_3	17.4	6.6	12.6	-6.6
CH_3CH_2	14.0			-13.0
$(CH_3)_2CH$	10.4	4.8	10.8	-21.1
$(CH_3)_3C$	7.6	2.2	8.2	-30.5
CH_2CHCH_2	12.5			-14.8
$CH_2CHC(CH_3)_2$	6.9	0.0	6.0	-32.2
$(CH_3)_2CCHCH_2$	16.7			-19.0

bullvalene.[6] The N–C distance was taken as the reaction coordinate. All other internal coordinates were optimized for each fixed value of the reaction coordinate. In several instances, C–H bonds and HCH angles in methyl groups were constrained to be equal. There were no other constraints imposed upon the optimizations. The true criterion for a transition state is that all the elements of the Hessian matrix be positive except for that corresponding to the reaction coordinate, which should be negative. Performing the complete calculation for open shell systems can be extremely time consuming and expensive. As the reactions under consideration are simple bond cleavages, we believe the use of the C–N separation as the reaction coordinate will provide an adequate approximation to the true transition state.

Results and Discussion

The calculated activation parameters and heats of reaction for the decompositions of the alkyldiazenyl radicals are collected and compared with the experimental free energies of activation reported by Engel[3] in Table I. The geometries and spin densities for these species are collected in Table II. In the half-electron approximation, the spin densities correspond to the electron densities of the singly occupied molecular orbital.

The MNDO $\Delta H^\ddagger$ for the decomposition of the ethyldiazenyl radical has been reported[1] to be in reasonable agreement with experimental observations[7] for H—N═N· and ab initio calculations for the methyldiazenyl radical.[8] The present calculated value for methyldiazenyl radical is about 4 kcal/mol higher than the ab initio value.[8] A recent report of a more elaborate ab initio calculated $\Delta H^\ddagger$ for H—N═N· predicts[9] lower values than the experimental report.[7] MNDO with 3 × 3 CI has been shown to give good dissociation reaction paths for most small molecules, although greater CI was needed in certain cases.[10] More extensive CI (55 × 55) reduced the dissociation energy of NH_2–H by only 0.9 kcal/mol.[10]

The comparison of the calculated and experimentally observed activation energies in Table I indicates a qualitative agreement, especially with respect to those radicals calculated to have low activation energies. Engel uses the difference between the free energies of activation for the decompositions of azo-1,1-dimethylpropene and the appropriate unsymmetrical diazene as the measure of the free energy of activation for the decomposition of the alkyldiazenyl radical. This analysis is based on the assumption that the $\Delta G^\ddagger = 0$ for both the recombination of the radical pair and the breaking of the C–N bond of the (1,1-dimethylallyl)diazenyl radical.

There are three distinctions that will cause the experimental and theoretical values to differ. First, Engel measured $\Delta G^\ddagger$'s while we calculate $\Delta H^\ddagger$'s. Second, he assumes that alkyl/alkyldiazenyl radical pair recombination (reaction 2) has no activation energy. If these $\Delta H^\ddagger$'s of recombination are greater than zero, as we predicted, (and so are the corresponding $\Delta G^\ddagger$'s) the reported free energies of activation should be the difference between the activations for dissociation and recombination. If dissociation of a particular alkyldiazenyl radical requires less activation than does recombination, the radical pair will not recombine competitively. Thus, the $\Delta G^\ddagger$ of the decomposition of the diazene in question will be the same as that for azo-1,1-dimethylpropene, leading to the conclusion that the second bond breaks without activation. If one accepts that an activation barrier exists for the recombination of the radical pair, the $\Delta G^\ddagger$'s reported should be increased by the height of this barrier. Third, recombination can be avoided by diffusion of the radicals out of the solvent cage as well as by dissociation of the alkyldiazenyl radical. This last process will become dominant in the case of the more stable diazenyl radicals. Ultimately, diffusion out of the cage must put an upper limit on the apparent activation energy for diazenyl radicals. This limit can be estimated if one assumes that the free energies of a caged and solvated radical are the same. Then, $\Delta G = 0$ and $K_{\text{eq}} = 1$ for the equilibrium between caged and solvated radicals. In this case the unimolecular rate constant for diffusion apart of two caged radicals must equal the bimolecular rate constant for diffusion of two radicals together. If one further assumes that the specific rate of diffusion (k_d) is 10^9 to 10^{10}/s, the lifetime of the cage is 10^{-10} to 10^{-9} s. With use of an Arrhenius pre-exponential factor of 10^{13}, $\exp(-E_a/RT)$ must equal 10^{-3} to 10^{-4} or E_a must be 5–8 kcal/mol for the temperature range studied by Engel.[3] It is noteworthy that the only major discrepancy between the theoretical and (corrected) experimental activation parameters in Table I is for R = methy, where the reported $\Delta G^\ddagger$ is 6.6 kcal/mol. This value is close to the upper limit predicted by the diffusion model.

In order to better compare the theoretical and experimental results, we have added a correction factor to the experimental $\Delta G^\ddagger$'s which is chosen to give the best fit to the calculated $\Delta H^\ddagger$'s. This correction should reflect both the difference between the actual recombination barrier and the assumed value of zero as well as the differences in the $T\Delta S^\ddagger$ terms for breaking the second bond and recombination. We should expect the activation entropies to be somewhat positive for bond-breaking and negative for recombination, the differences in the free energies for dissociation and recombination could be reasonably large. For example, if we assume $\Delta S^\ddagger$ to be +5 eu for the bond cleavage and −10 eu for the recombination and $\Delta H^\ddagger$ to be the same for both, the $\Delta G^\ddagger$ for bond cleavage will be 5–6 kcal/mol higher for recombination than that for cleavage at the temperature range for the experimental studies (50–140 °C).[11] The $\Delta S^\ddagger$ may be small for the decomposition of the diazenyl radicals since the cleavage of the C–N bond is generally quite exothermic. Therefore, the transition states are expected to be close to the alkyldiazenyl radicals in structure, coming early along the reaction path. While the recombination is also generally quite exothermic, the transition state must require a significant amount of ordering with respect to the caged radical pair. Thus, $\Delta G^\ddagger > \Delta H^\ddagger$ for recombination and $\Delta G^\ddagger < \Delta H^\ddagger$ for cleavage.

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Table II.

$—C_A—N_A{=}N_B$

Geometries and Spin Densities of Radicals and Transition States

radical	R_{NN}	$R_{C\text{-}N}$	CNN angle	spin N_B	spin N_A	spin C_A
$CH_3NN\cdot$	1.156	1.478	133.24	0.552	0.220	0.209
TS	1.115	1.90	129.88	0.233	0.093	0.660
difference	−0.04	0.422	−3.36	−0.319	−0.127	0.451
$CH_3CH_2NN\cdot$	1.154	1.487	133.20	0.539	0.214	0.219
TS	1.121	1.88	129.40	0.236	0.093	0.622
difference	−0.033	0.39	−3.80	−0.303	−0.121	0.403
$(CH_3)_2CHNN\cdot$	1.153	1.497	134.53	0.523	0.211	0.230
TS	1.117	1.85	132.23	0.237	0.097	0.589
difference	−0.036	0.35	−2.30	−0.286	−0.114	0.359
$(CH_3)_3CNN\cdot$	1.151	1.506	134.53	0.514	0.208	0.241
TS	1.121	1.80	132.96	0.269	0.112	0.536
difference	−0.030	0.29	−1.57	−0.245	−0.096	0.295
$CH_2CHCH_2NN\cdot$	1.154	1.489	132.78	0.532	0.209	0.219
TS	1.118	1.85	130.46	0.205	0.082	0.518
difference	−0.036	0.36	−2.32	−0.327	−0.127	0.299
$CH_2CHC(CH_3)_2NN\cdot$	1.151	1.511	134.98	0.508	0.209	0.245
TS	1.121	1.80	133.48	0.267	0.113	0.539
difference	−0.030	0.29	−1.50	−0.241	−0.096	0.294
$(CH_3)_2CCHCH_2NN\cdot$	1.154	1.489	132.74	0.541	0.214	0.221
TS	1.114	1.90	131.05	0.214	0.088	0.657
difference	−0.040	0.41	−1.69	−0.327	−0.126	0.436

One might expect that both the $\Delta S^{\ddagger}$'s for recombination and cleavage should be insensitive to the structure of the alkyl group of the alkyldiazenyl radical, RNN·, since the R– group is remote from the site of recombination.

The fact that the transition states do come early along the reaction paths is illustrated by the calculated $\Delta H^{\ddagger}$'s as well as the calculated transition state properties. One of the obvious conclusions that can be drawn from Table I is that the activation energies seem to be more influenced by the potential relief of steric crowding in the alkyldiazenyl radical than by the stability of the alkyl radical product. This is exactly the behavior that would be predicted by the Hammond Postulate[12] for a reaction that is exoergonic, where the transition state closely resembles the reactant. Thus, the predicted descending order of activation energies for R—N=N· cleavage is the following:

methyl > ethyl > $(CH_3)_2C{=}CHCH_2—$ > allyl >
isopropyl > *tert*-butyl > $CH_2{=}CHC(CH_3)_2—$

Inspection of Table II reveals that, with the exception of methyl and ethyl, the C–N bond lengths in R—N=N· and the differences in the spin densities on C between the alkyldiazenyl radicals and the transition state for decomposition increases, while the corresponding differences in spin densities on N_B decrease in the same order.

The conclusion that the activation energies for the decomposition of alkyldiazenyl radicals is strongly influenced by steric crowding in the radical must be somewhat tempered by the tendency of the MNDO method to overestimate the energies of species containing *tert*-butyl groups.[13] One can compare the two isomeric (dimethylallyl)diazenyl radicals to the isomeric hydrocarbons 2-methyl-2-pentene and 3,3-dimethyl-1-butene, where the diazenyl moiety is replaced by a methyl group. The experimental ΔH_f's for these compounds are −16.0 and −14.5 kcal/mol, respecively.[14] The difference in the ΔH_f's for the hydrocarbons (1.5 kcal/mol) can be compared with the corresponding difference for the diazenyl radicals (13.2 kcal/mol, see Table I). Nevertheless, one should note that the corresponding energies for compounds containing isopropyl groups are normal yet the present calculations suggest that the isopropyldiazenyl radical should decompose more easily than the allyldiazenyl radical. In fact the differences in predicted $\Delta H^{\ddagger}$ upon going from methyl > primary > secondary > tertiary diazenyl radicals are all similar (~3 kcal/mol). It seems likely that the exaggerated repulsions that MNDO seems to predict for *tert*-butyl groups still exists in the transition state for C–N cleavage, resulting in a cancellation of errors. This is consistent with the predicted early transition state, where the bond angles at the α-C of the transition state are only slightly changed from those of the starting radical, indicating little change in the amount of crowding upon going from the radical to the transition state. This interpretation is consistent with studies by Walling[15,16] on the β-scission of alkoxy radicals (reaction 5) where the relative rates follow the order

methyl < ethyl < isopropyl < benzyl < *tert*-butyl

$$R\text{-}C(CH_3)_2O\cdot \rightarrow CH_3COCH_3 + R\cdot \qquad (5)$$

In conclusion, the present calculations predict that the rates of C–N cleavage of alkyldiazenyl radicals is most influenced by the amount of steric crowding in the radical. As these reactions are exoergonic, the transition states strongly resemble the starting radicals.

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Registry No. $CH_3N{=}N\cdot$, 64287-49-6; $CH_3CH_2N{=}N\cdot$, 98577-59-4; $(CH_3)_2CHN{=}N\cdot$, 98577-60-7; $(CH_3)_3CN{=}N\cdot$, 98577-61-8; $CH_2CHCH_2N{=}N\cdot$, 98577-62-9; $CH_2CHC(CH_3)_2N{=}N\cdot$, 98577-63-0; $(CH_3)_2CCHCH_2N{=}N\cdot$, 98577-64-1.

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