Acid-Catalyzed Thermal Decomposition of 1-Aryl-3,3-dialkyltriazenes in the Presence of Nucleophiles

N. Satyamurthy,* Jorge R. Barrio, Derrick G. Schmidt, Craig Kammerer, Gerald T. Bida, and Michael E. Phelps

Division of Nuclear Medicine and Biophysics, Departments of Radiological Sciences and Pharmacology, UCLA School of Medicine and the Laboratory of Nuclear Medicine, Los Angeles, California 90024

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The acid-catalyzed thermal decompositions of a number of substituted 1-aryl-3,3-dialkyltriazenes (1) in the presence of nucleophiles have been conducted with a view to understanding the underlying mechanisms of these reactions. These reactions parallel the corresponding diazonium ion reactions in that a heterolytic dediazoniation path competes with a homolytic route. The relative proportion of the products arising due to these two competing mechanisms depends upon (a) the electron-transfer efficiency of the nucleophile, (b) the redox potential of the aryl diazonium substrate, and (c) the reaction solvent.

Introduction

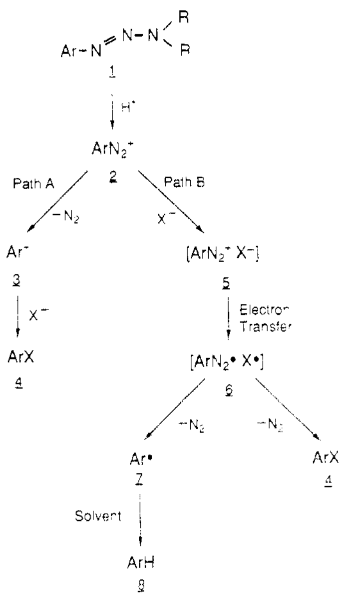
Due to its simplicity, the Sandmeyer reaction is generally the method of choice for the halodeamination of aromatic amines.[1] However, this reaction is often accompanied by several unwanted side reactions,[2] for which from the standpoint of radiohalogenations the Sandmeyer reaction is a rather unattractive choice. On the other hand, 1-aryl-3,3-dialkyltriazenes, a protected form of aryl diazonium ions, are known for more than a century now.[3] However, very little exploration of the chemistry of this interesting system took place until recently. This renewed interest has led to a number of reports highlighting the advantages of 1-aryl-3,3-dialkyltriazenes in various organic transformations.[4]

Unlike their diazonium ion counterparts, 1-aryl-3,3-dialkyltriazenes are (shelf) stable and can be easily purified.[5] Besides, they are soluble in a number of organic solvents and conveniently generate the diazonium ions in situ upon reacting with acids.[6] Hence, triazene reactions could be conducted in nonaqueous solvent systems without the interference of, especially, the hydroxydediazoniation side reaction.[7-9] Recently, we have studied the halodediazoniations of aryltriazenes,[7,9,10] and we now report our results on the mechanistic course of the acid-catalyzed thermal decomposition of 1-aryl-3,3-dialkyltriazenes in the presence of nucleophiles.

Results and Discussion

Decomposition of Aryltriazenes. The acid-catalyzed thermal decomposition of 1-aryl-3,3-dialkyltriazenes (1) in the presence of nucleophiles parallels that of the corresponding diazonium ion reactions. The enormous efforts directed toward the study of the mechanisms underlying the dediazoniation reactions of aryldiazonium ions have now led to the concensus that the diazonium ion can decompose both by radical as well as ionic paths.[2,11] This

Scheme I



a Ar = C_6H_5; R = C_2H_5
b Ar = 4-$CH_3C_6H_4$; R = C_2H_5
c Ar = 4-$CH_3OC_6H_4$; R = C_2H_5
d Ar = 4-$NO_2C_6H_4$; R = C_2H_5
e Ar = 2-$CH_3C_6H_4$; R = C_2H_5
f Ar = 4-CNC_6H_4; R = C_2H_5
g Ar = 4-$CH_3COC_6H_4$; RR = $(CH_2)_5$
h Ar = 4-BrC_6H_4; R = C_2H_5
i Ar = 4-ClC_6H_4; R = C_2H_5
j Ar = 3-$NO_2C_6H_4$; R = C_2H_5

X = Nucleophile

Table I. Redox Potential vs Normal Hydrogen Electrode (NHE) for Halide Ions and Acids[a]

reduced form of the redox couple	$E°$, V: CH_3CN	$E°$, V: H_2O
F^-	2.4	3.6
Br^-	1.2	2.0
I^-	0.7	1.4
CF_3COO^-	1.1	2.2
$CH_3SO_3^-$	1.4[b]	

[a] Reference 13. [b] In CH_2Cl_2 (ref 25). The reported value of $E°$ has been converted to NHE scale.

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Table II. Redox Potentials vs Normal Hydrogen Electrode (NHE) of Selected Diazonium Ions in Sulfolane[a]

aryl group	$ArN_2^{\bullet}/ArN_2^+$ $E_{1/2}$, V	aryl group	$ArN_2^{\bullet}/ArN_2^+$ $E_{1/2}$, V
$2\text{-}CH_3C_6H_4$	0.474	$4\text{-}ClC_6H_4$	0.596
$4\text{-}CH_3OC_6H_4$	0.486[b]	$4\text{-}BrC_6H_4$	0.629
$4\text{-}CH_3C_6H_4$	0.496	$4\text{-}CNC_6H_4$	0.679
C_6H_5	0.541	$4\text{-}NO_2C_6H_4$	0.696

[a] The reported $E_{1/2}$ values vs saturated calomel electrode (SCE) (ref 15) were converted to NHE standard. The corresponding $E_{1/2}$ values in CH_3CN are "somewhat more negative" than those in sulfolane, but exact values are not reported (ref 15). However, these values have been used as such for studies conducted in acetonitrile for quantitative relationships without involving any serious errors (ref 26). [b] Reference 26.

Table III. Methanesulfonic Acid Catalyzed Thermal Decomposition of 1-Aryl-3,3-dialkyltriazenes

triazene 1, Ar	solvent	product, % $ArOSO_2$-CH_3	ArH	other
C_6H_5	CH_3CN			$C_6H_5NHCOCH_3$ (>99)
$4\text{-}NO_2C_6H_4$	THF-d_8		7	$4\text{-}NO_2C_6H_4D$ (93)
$4\text{-}CH_3COC_6H_4$	CH_3CN	74	26	
	CCl_3CN	63	27	$4\text{-}CH_3COC_6H_4Cl$ (10)
	CCl_4	64	32	$4\text{-}CH_3COC_6H_4Cl$ (4)
	THF	21	79	
	DMSO	68	32	
	DMF	21	79	
	PhBr	39	61	

process is outlined in Scheme I. The arenediazonium ion **2** generated by the acid-catalyzed thermal decomposition of **1** could form an intermediate complex **5**, which could undergo a facile reduction via one-electron transfer from the nucleophile X^- leading to the formation of the intermediate **6**.[12] The aryl radical **7** can diffuse from the cage (**6**) and abstract atoms from the solvent to form **8**.[2,11] Also, the intermediate **6** can lead to the product **4** with the rapid loss of a molecule of nitrogen. Alternatively, the diazonium ion **2** can lose dinitrogen in a relatively slow process to give an aryl cation **3**, which could be intercepted by the nucleophile X^- leading to the product **4**.[11] The relative abundance of formation of the aryl cation **3** and the intermediate **6** depends strongly upon (a) the efficiency of the electron transfer by X^- (i.e. its redox potential, Table I),[13,14] (b) the redox potential of the diazonium ion **2** (Table II),[15] and (c) the reaction solvent.[13,14]

The redox potentials of the substituted aryl diazonium ions given in Table II are highly useful in predicting the nature of the dediazoniation reactions. For example, diazonium ions containing electron-releasing groups are reduced at relatively low potentials (<0.5 V). They would undergo one-electron reductions only in the presence of efficient reductants like iodide ion. In the absence of such a reductant, they would preferentially decompose via a heterolytic pathway. On the other hand, diazonium ions having electron-attracting groups could be reduced at higher potentials (>0.6 V) and would generally prefer a homolytic dediazoniation path.

Scheme II

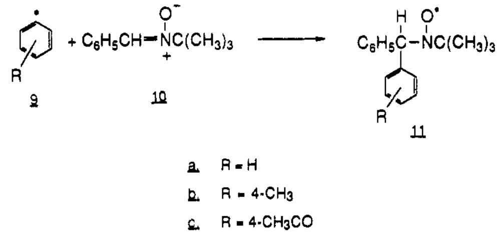

Table IV. Hyperfine Splitting Constants of Nitroxides from α-Phenyl-*N*-*tert*-butylnitrone[a]

spin adduct	${}^{a}N$	${}^{a}H$
11a	14.60	2.68
11b	14.71	2.83
11c	14.69	2.44

[a] In bromobenzene at room temperature. The splittings are in gauss.

Table V. Aryl Iodide Yields

$$1 \xrightarrow{H^+/I^-} ArI$$

triazene 1, Ar	isolated yield,[a] %	triazene 1, Ar	isolated yield,[a] %
C_6H_5	85 (52)	$4\text{-}CNC_6H_4$	92
$4\text{-}CH_3C_6H_4$	90 (51)	$4\text{-}CH_3COC_6H_4$	95
$4\text{-}CH_3OC_6H_4$	85 (63)	$4\text{-}BrC_6H_4$	85
$4\text{-}NO_2C_6H_4$	80 (46)	$4\text{-}ClC_6H_4$	80
$2\text{-}CH_3C_6H_4$	72	$3\text{-}NO_2C_6H_4$	83 (26)

[a] Yields for the reaction in acetonitrile and cation exchange resin (H^+ form) (ref 9). Yields in parentheses are those obtained in aqueous media with HCl or CF_3 COOH (ref 8a).

The acid-catalyzed thermal decomposition of a few selected triazenes in various solvents under argon is reported in Table III. Based on the elegant work by Bunnett et al.,[16] it would be expected that the diazonium ion derived from the triazene **1a** would undergo predominantly a heterolytic decomposition and **1d** would decompose via a radical path. Indeed, the triazene **1a** afforded almost exclusively acetanilide as the product, the formation of which has been recognized as due to the generation of phenyl cation and its subsequent reaction with acetonitrile.[17] In the case of **1d**, the formation of nitrobenzene and nitrobenzene-*4-d*$_1$ suggests that the reaction proceeds exclusively by a radical mechanism. The formation of the sulfonate and the absence of 4-acetylacetanilide in the product mixture (Table III), in the case of **1g** in CH_3CN, strongly suggests homolysis of the diazonium ion in the formation of the sulfonate (path B, Scheme I). If the redox potential of methanesulfonate anion in CH_3CN is close to its value in CH_2Cl_2 (Table I), then it would probably reduce aryl diazonium ions containing electron-attracting groups in a manner analogous to that of bromide ion, as shown later in this discussion. The contribution by the ionic pathway in the formation of the sulfonate, if any, might be small in this case. Differences in the proportions of the sulfonate and acetophenone in different solvents (Table III) may be the consequence of variations in the efficiency of the sulfonate ion to reduce the diazonium ion.[14d]

The formation of aryl radicals in the above reactions was conclusively shown by trapping them with α-phenyl-*N*-*tert*-butylnitrone (**10**)[18] (Scheme II). Due to the high

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Table VI. Yields of Aryl Bromides[a]

triazene 1, Ar	product, % ArBr	ArH	other
C_6H_5	3	4	$C_6H_5NHCOCH_3$ (93)
C_6H_5[b]	17	45	C_6H_5OH (35)
4-$CH_3C_6H_4$			4-$CH_3C_6H_4NHCOCH_3$ (>99)
4-$NO_2C_6H_4$	70	30	
4-CNC_6H_4	>99		
4-$CH_3COC_6H_4$	75	25	
3-$NO_2C_6H_4$	65	35	

[a] The reaction was conducted in acetonitrile and cation exchange resin (H^+ form) (see the Experimental Section). [b] Reaction with 47% HBr.

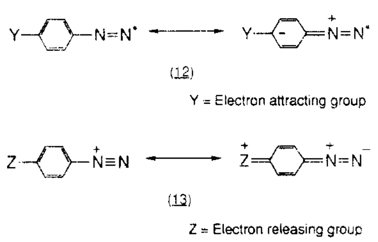
efficiency of the spin trap **10**, even small amounts (~1%) of radicals generated during the acid-catalyzed thermal decompositions of the triazenes **1a** and **1b** were efficiently trapped. The hyperfine splitting constants for the selected spin adducts are reported in Table IV. The small differences of the ^aN and ^aH values among the three adducts given in Table IV are mainly due to the difference in the electronegativity of the aryl rings attached to the adduct **11**.[18]

Iododediazoniation. The results of iododediazoniation of aryl diazonium ions generated from the triazenes 1 in aqueous as well as nonaqueous media are given in Table V. As shown in Scheme I, the diazonium ion **2** could undergo a facile one-electron reduction by iodide ion ($E°$ = 0.7 V in CH_3CN) to produce an aryl and an iodine radical.[14] It has been reported that the iodine radicals undergo a multistep transformation to yield I_2 and I_3^- and postulated that these species, and not I^-, are responsible for the iodination of the aryl radicals.[19] However, facile iododediazoniation of a number of aryl diazonium ions by nanomolar quantities of radioiodide even in aqueous media are known.[20] It is rather unlikely that under such conditions any appreciable concentrations of radiolabeled I_2 or I_3^- would exist.[11,20] While it is possible that these species (I_2 and I_3^-) are the principal iodinating agents at higher concentrations, the ability of I^- to induce iododediazoniation cannot be completely discounted.

The higher yields of aryl iodides obtained in acetonitrile medium could be due to (a) the iodide ion, being a better reducing agent in CH_3CN than in water ($E°$ values are 0.7 and 1.4 V respectively, Table I), would more efficiently reduce the diazonium ions (Table II) via path B (Scheme I), thereby suppressing the competing heterolytic dediazoniation, and (b) in aqueous medium, as I^- is a relatively less efficient reductant it would allow path A leading to solvolysis products.

Bromodediazoniation. The redox potential of bromide ion ($E°$ = 1.2 V in CH_3CN) is higher than that of iodide ion (Table I), indicating that the electron transfer to the diazonium ion by bromide ion would be relatively less efficient. However, aryl diazonium ions having electron-attracting groups are reduced by bromide ion in DMSO medium,[21] suggesting that the redox potential of bromide ion probably represents a borderline case capable of reducing diazonium ions.[14a,22] The results reported in Table VI clearly follow this trend.

Scheme III



It is likely that the diazonium ions derived from triazenes having electron-attracting substituents have a stabilizing influence by resonance on the diazenyl radical (**12**) (Scheme III) and increase the ease of their reduction by a borderline reductant like bromide ion.[14c] On the other hand, electron-releasing groups would stabilize the diazonium cation (**13**), thereby suppressing its tendency to undergo one-electron reduction (Scheme III).[23] Thus, triazenes **1d**, **1f**, **1g**, and **1i** yielded the corresponding bromoaryl derivatives in good yields, whereas the triazenes **1a** and **1b** underwent exclusively heterolytic dediazoniations (Scheme I) leading to the formation of the corresponding acetanilide derivatives due to solvolytic reactions[17] (Table VI).

It is also interesting to note that when the triazene **1a** was reacted with 47% HBr, bromobenzene (17%) along with phenol (35%) and benzene (45%) were formed (Table VI). The dediazoniation of this triazene by aqueous mineral acids would be expected to follow an exclusive ionic pathway,[16] and thus it was surprising that benzene was the predominating product. This could be rationalized by the fact that the diazonium ion could suffer a one-electron reduction by the solvent[11] water generating $PhN_2^\bullet$, which would lead to the formation of benzene.

Fluorodediazoniation. The fluorodediazoniation of a number of 1-aryl-3,3-dialkyltriazenes by hydrogen fluoride has been reported to yield aryl fluorides.[24] Alternatively, aryl fluorides have also been obtained by the reaction of triazenes with fluoride ion in the presence of strong acids.[6] The use of chlorinated solvents to improve the yields of aryl fluorides has also been reported.[10] The use of fluoride ion and an acid for the synthesis of aryl fluorides from the triazenes is an attractive method from the standpoint of radiofluorine labeling techniques.[6,10] Thus, we have studied this reaction in a variety of solvents with a view to understanding the mechanism of the reaction, and the results are summarized in Table VII.

Unlike the iodide and bromide ions, the redox potential of fluoride ion is very high (Table I), and hence no diazonium ion could undergo a one-electron reduction by F^-.[14d] The formation of aryl fluorides in this case is invariably via a heterolytic dediazoniation. However, the conjugate bases of the commonly used acids (CF_3COOH and CH_3SO_3H) for the decomposition of the triazenes would reduce the diazonium ion intermediates efficiently (Table I) and would tend to suppress the ionic pathway, resulting in rather poor yields of aryl fluorides. Addition of radical suppressors[16] such as 2-methyl-2-nitrosopropane, galvinoxyl, or conducting the reaction in an atmosphere

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Table VII. Yields of Aryl Fluorides

				product, %	
triazene 1, Ar	solvent	acid[a]	fluoride source	ArF[b]	other
4-$CH_3C_6H_4$	THF	MSA	Et_4NF	10	ND[c]
4-$CH_3C_6H_4$	CCl_4	TFA	n-Bu_4NF	20	ND[c]
4-CNC_6H_4	CH_3CN	MSA	n-Bu_4NF	9	C_6H_5CN (38) 4-$CNC_6H_4OSO_2CH_3$ (45)
4-$CH_3COC_6H_4$	CH_3CN	MSA	n-Bu_4NF	4	$C_6H_5COCH_3$ (46) 4-$CH_3COC_6H_4OSO_2CH_3$ (45)
	CCl_3CN	MSA	n-Bu_4NF	10	4-$CH_3COC_6H_4Cl$ (36) 4-$CH_3COC_6H_4OSO_2CH_3$ (50)
	CCl_3CN	MSA	CsF	24	4-$CH_3COC_6H_4OSO_2CH_3$ (70) 4-$CH_3COC_6H_4Cl$ (6)
	THF	MSA	CsF	~1	$C_6H_5COCH_3$ (79) 4-$CH_3COC_6H_4OSO_2CH_3$ (20)
	DMSO	MSA	CsF	9	4-$CH_3COC_6H_4OSO_2CH_3$ (91)
	PhBr	MSA	CsF	17	$C_6H_5COCH_3$ (13) 4-$CH_3COC_6H_4OSO_2CH_3$ (70)
	CCl_4	MSA	CsF	22	$C_6H_5COCH_3$ (8) 4-$CH_3COC_6H_4OSO_2CH_3$ (66) 4-$CH_3COC_6H_4Cl$ (4)
	CH_3CN	TFA	CsF	5	$C_6H_5COCH_3$ (20) 4-$CH_3COC_6H_4OCOCF_3$ (75)
	CCl_3CN	TFA	CsF	17	4-$CH_3COC_6H_4OCOCF_3$ (58) 4-$CH_3COC_6H_4Cl$ (25)
	THF	TFA	CsF	0	$C_6H_5COCH_3$ (75) 4-$CH_3COC_6H_4OCOCF_3$ (25)
	DMSO	TFA	CsF	8	$C_6H_5COCH_3$ (32) 4-$CH_3COC_6H_4OCOCF_3$ (60)
	PhBr	TFA	CsF	4	$C_6H_5COCH_3$ (3) 4-$CH_3COC_6H_4OCOCF_3$ (93)
	CCl_4	TFA	CsF	8	$C_6H_5COCH_3$ (19) 4-$CH_3COC_6H_4OCOCF_3$ (47) 4-$CH_3COC_6H_4Cl$ (26)

[a] MSA = methanesulfonic acid. TFA = trifluoroacetic acid. [b] The yields of aryl fluorides obtained from the corresponding diazonium tetrafluoroborates (Balz–Schiemann reaction) range 67–90% (ref 27). However, the triazene method allows the synthesis of high specific activity fluorine-18 radiolabeled aromatic compounds whereas the Schiemann reaction could yield only low specific activity products. For a discussion on this aspect see refs 6, 10, and 24. [c] ND = not determined.

of dry oxygen gas did not improve the yields of aryl fluorides. However, chlorinated solvents such as CCl_4 and CCl_3CN did have a beneficial effect on the aryl fluoride yields, suggesting that these solvents probably enhance the heterolytic dediazoniations (Table VII).

In conclusion, these results strongly suggest that the acid-catalyzed triazene decomposition reactions in the presence of nucleophiles are governed by (a) the one-electron reduction efficiency of the nucleophiles, (b) the $E_{1/2}$ values of the corresponding aryl diazonium ions, and (c) the solvent of reaction. In the case of strong reductants, like iodide ion, the solvent effect is somewhat less pronounced. But in the case of fluorodediazoniation, it was observed that chlorinated solvents like CCl_4 or CCl_3CN markedly increased arylfluoride yields.

Experimental Section

Gas chromatographic analyses were conducted with a Hewlett-Packard 5890 gas chromatograph or Varian Aerograph Model 940 instrument employing a 3% OV-17 column (6 ft × $^1/_8$ in.), FID detection, and a helium flow rate of 40 mL/min. High-pressure liquid chromatography was carried out on a Waters M-45 instrument (Ultrasphere ODS column, 5 μm, 4.6 × 250 mm, 75% CH_3OH and 25% water, flow rate 1.0 mL/min; 254-nm UV detector). In order to obtain quantitative information from the chromatograms, a set of five solutions of known concentrations for each standard were injected. The concentrations ranged over a factor of 250. The peaks were integrated and plotted as a function of the amount of compound injected. The data were used to determine amounts of compounds in the reaction mixtures from the areas of the peaks.

The GC/MS analyses were performed at 70 eV with a Hewlett-Packard 5981A system which was connected via a jet separator to a 6 ft × 2 mm 3% OV-17 column (helium carrier gas, flow rate 30 mL/min). The data were collected with a HP 1000 computer. The ESR spectra were recorded at room temperature on a IBM 200D spectrometer operating at X-band microwave frequencies using a Rectangular Cavity 4102ST.

The 1-aryl-3,3-dialkyltriazenes (1) were prepared as reported in the literature.[7,9]

Acid-Catalyzed Thermal Decomposition of Triazenes. To a boiling solution of the triazene (50 μmol) in 1 mL of the solvent was added dropwise methanesulfonic acid (200 μmol) over a period of 2 min under argon, and reflux was continued for 15 min. The reaction mixture was cooled to room temperature, diluted with ether (20 mL), washed with a saturated solution of sodium bicarbonate and water, and then dried (Na_2SO_4). The crude product was analyzed by GC, HPLC, and GC/MS. The composition of the product mixtures is reported in Table III.

Acid-Catalyzed Thermal Decomposition of Triazenes in the Presence of α-Phenyl-*N*-*tert*-butylnitrone. To a solution of the triazene (100 μmol) in bromobenzene (2 mL) were added the nitrone spin trap (20 mg) and CsF (150 μmol) under argon. The solution was stirred under gentle reflux, and trifluoroacetic acid (400 μmol) was added via a syringe. The reaction mixture was refluxed for a further period of 15 min and cooled to room temperature. The solution was filtered under argon into a 2-mm i.d. quartz ESR cell, and the electron spin resonance spectra were recorded, the details of which are furnished in Table IV.

General Procedures for the Preparation of Aryl Bromides. To a suspension of sulfonic acid resin (H^+ form, Bio-Rad AG 50W-X12, 1.0 g, 5 mequiv) in acetonitrile (5 mL) was added LiBr (4 mmol) under argon. The mixture was stirred under gentle reflux, and a solution of the triazene (1.0 mmol) in acetonitrile (0.5 mL) was added dropwise. The reaction was allowed to proceed for 30 min and filtered. The residue was washed with boiling methanol (3 × 3 mL), and the washings were added to the filtrate. The crude product mixture was analyzed by HPLC and GC/MS, and the results are given in Table VI.

Reaction of Aryltriazenes with Fluoride Ion in the Presence of Acids. The fluoride salt (250 μmol) was dried at ~60 °C under vacuum (1 mm) for 1 h. A solution of the triazene

(50 μmol) in 2 mL of the solvent was added to it under argon and stirred under gentle reflux; 200 μmol of the acid was then added to the reaction mixture, and the reflux was continued for 30 min. The mixture was cooled to room temperature and diluted with ether (20 mL). The ethereal solution was washed with a saturated solution of sodium bicarbonate and water and then dried (Na_2SO_4). The solution was analyzed by GC, HPLC, and GC/MS, and the product compositions are provided in Table VII.

The isolated yields of the crude products in all the reactions were >95%, and the material balance for all the product analyses was >90%.

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cis-Diazenes. Pressure Effects on Their Thermal Deazatization and Isomerization Reactions[1]

Robert C. Neuman, Jr.,* Charles T. Berge,[2a] and Glen Al. Binegar[2b]

Department of Chemistry, University of California, Riverside, Riverside, California 92521

Waldemar Adam and Yoshinori Nishizawa[3]

Institut für Organische Chemie, Universität Würzburg, Würzburg, FDR

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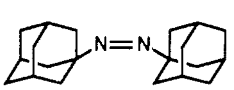
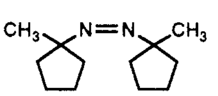
Effects of pressure on solution-phase rates of overall thermal decomposition, deazatization, and isomerization of several symmetric *cis*-diazenes (*cis*-azoalkanes) have been determined in hexane and in ethanol. Increasing pressure decreases all the rates. The large positive activation volumes for deazatization (e.g., +16 to +22 cm^3/mol) have been interpreted in terms of a one-bond scission mechanism and an intermediate diazenyl radical. The smaller positive activation volumes for isomerization (e.g., +5 to +7 cm^3/mol) are consistent with a nonradical inversion mechanism. Dramatic differences in rates between polar and nonpolar solvents are consistent with these mechanisms.

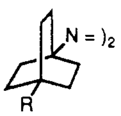
Thermal decomposition of symmetric and unsymmetric *cis*-diazenes via deazatization (loss of molecular nitrogen) and competing isomerization can be explained by Scheme I. Deazatization takes place via one-bond scission and the formation of an intermediate diazenyl radical. Isomerization occurs by nonradical inversion (semilinearization) (k_{inv}) and could also take place through the diazenyl radical intermediate (k_{-1t}). Support for this scheme is derived from a variety of studies[4] including solvent viscosity effects at atmospheric pressure[5] and the effects of high pressure.[6] This paper is a full description of the pressure studies of *cis*-diazenes **1**–**4**, which were partially reported in a communication.[6]



1

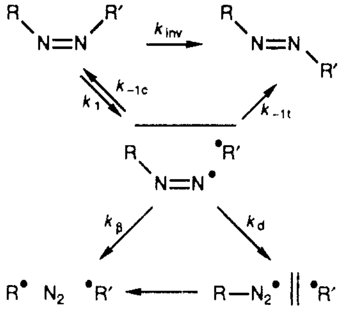


2



3, R = Et
4, R = H

Scheme I



The pressure dependence of a rate constant for a chemical reaction in solution gives an activation parameter ΔV^* called the activation volume (eq 1).[7] For single-step

$$\Delta V^* = -RT(\partial \ln k/\partial P) \qquad (1)$$

reactions, activation volumes correspond to the change in volume of the reacting system as reactants pass from ground to transition states. ΔV^* reflects not only changes in bond making and breaking but also changes in solvation. When rate constants are composite quantities for a sequence of several reactions, their pressure dependence gives an *apparent* ΔV^* which, while not simply interpretable in terms of molecular volume or solvation changes, can be useful in interpreting mechanism.

The values of k(N) for *cis*-diazenes are such composite rate constants.[5,6] Values of k(I), however, are composite

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(3) Alexander von Humboldt Fellow, 1981–1983.

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