(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%.

Acknowledgment. This work was supported in part by Department of Energy Grant DE-FC0387-ER60615, NIH Grant P01-NS-15654, NIMH Grant R01-MH-37916, and donations from the Hereditary Disease Foundation and the Jennifer Jones Simon Foundation.

---

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

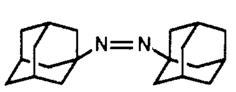
Waldemar Adam and Yoshinori Nishizawa[3]

Institut für Organische Chemie, Universität Würzburg, Würzburg, FDR

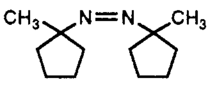
Received February 12, 1990

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.

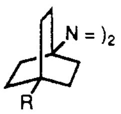
Thermal decomposition of symmetric and unsymmetric *cis*-diazenes via deazatization (loss of molecular nitrogen) and competing isomerization can be explained by Scheme I. Deazatization takes place via one-bond scission and the formation of an intermediate diazenyl radical. Isomerization occurs by nonradical 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

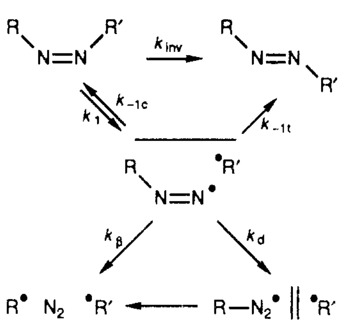


2



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

---

[1] (a) High-Pressure Studies. 28. Part 27: Neuman, R. C., Jr.; Frink, M. E. *J. Org. Chem.* **1983**, *48*, 2430. (b) This work was supported by grants from the National Science Foundation.

[2] (a) Berge, C. Ph.D. Dissertation, University of California, Riverside, March 1979. (b) Binegar, G. A. Ph.D. Dissertation, University of California, Riverside, Dec 1984.

[3] Alexander von Humboldt Fellow, 1981–1983.

[4] Two major papers that include references to previous work are: (a) Chae, W.-K.; Baughman, S. A.; Engel, P. S.; Bruch, M.; Özmeral, C.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824. (b) Schmittel, M.; Rüchardt, C. *Ibid.* **1987**, *109*, 2750.

[5] Neuman, R. C., Jr.; Grow, R. H.; Binegar, G. Al.; Gunderson, H. J. *J. Org. Chem.* **1990**, *55*, 2682.

[6] Neuman, R. C., Jr.; Binegar, G. Al. *J. Am. Chem. Soc.* **1983**, *105*, 134.

[7] Neuman, R. C., Jr. *Acc. Chem. Res.* **1972**, *5*, 381 and references therein.

0022-3263/90/1955-4564$02.50/0 © 1990 American Chemical Society

Table I. Pressure Dependence of the Decomposition Rate Constants of *cis*-Diazenes 1–4

diazene[a]	P,[b] atm	k(O)[c] × 10^4	k(N)[c] × 10^4	k(I)[c] × 10^4	k(I)/k(N)[d]	[k(I)/k(N)]$_{\mathrm{rel}}$[d]
1 (21, hexane)	1	6.25 (0.10)	3.98 (0.08)	2.27 (0.04)	0.6	1
	670	3.98 (0.12)	2.24 (0.07)	1.74 (0.05)	0.8	1.4
	1000	3.47 (0.11)	1.92 (0.06)	1.54 (0.05)	0.8	1.4
	1390	2.92 (0.11)	1.37 (0.05)	1.55 (0.06)	1.1	2.0
	1700	2.48 (0.09)	1.17 (0.05)	1.33 (0.06)	1.1	2.0
	1990	2.19 (0.09)	0.94 (0.03)	1.24 (0.01)	1.3	2.3
1 (35.7, EtOH)	1	10.73 (0.47)	1.42 (0.06)	9.31 (0.40)	7	1
	720	7.93 (0.11)	0.74 (0.01)	7.19 (0.10)	10	1.5
	950	7.35 (0.08)	0.78 (0.01)	6.57 (0.07)	8	1.3
	1420	6.97 (0.13)	0.43 (0.01)	6.54 (0.08)	15	2.3
	1700	6.40 (0.21)	0.30 (0.01)	6.09 (0.20)	20	3.1
	2040	5.87 (0.04)	0	5.87 (0.04)		
2 (9, EtOH)	1	8.00 (0.34)	6.98 (0.49)	1.02 (0.23)	0.2	1
	670	4.93 (0.06)	4.06 (0.25)	0.87 (0.26)	0.2	1.5
	910	4.08 (0.19)	3.43 (0.07)	0.64 (0.26)	0.2	1.3
	1010	4.06 (0.10)	3.44 (0.34)	0.62 (0.24)	0.2	1.2
	1290	3.20 (0.01)	2.61 (0.02)	0.59 (0.02)	0.2	1.6
	1340	3.22 (0.07)	2.68 (0.17)	0.54 (0.10)	0.2	1.4
	1570	2.78 (0.06)	2.60 (0.29)	0.47	0.2	1.2
	1650	2.61 (0.06)	2.17 (0.17)	0.43 (0.07)	0.2	1.4
	1880	2.34 (0.01)	1.83 (0.09)	0.50 (0.08)	0.3	1.9
	1950	2.07 (0.09)	1.56 (0.09)	0.50 (0.01)	0.3	2.2
3 (35.7, hexane)	1	4.23 (0.14)	0.24 (0.01)	3.99 (0.13)	17	1
	350	3.78 (0.10)	0.32 (0.01)	3.46 (0.09)	11	0.7
	710	3.39 (0.05)	0.24 (0.01)	3.14 (0.05)	13	0.8
	990	3.07 (0.07)	0.19 (0.01)	2.88 (0.06)	15	0.9
	1340	2.87 (0.06)	0.16 (0.01)	2.71 (0.06)	17	1.0
	1660	2.63 (0.04)	0.09 (0.01)	2.53 (0.04)	28	1.7
	2170	2.35 (0.03)	0.08 (0.01)	2.28 (0.03)	29	1.7
4 (35.7, hexane)	1	6.22 (0.46)	0.65 (0.05)	5.57 (0.41)	9	1
	260	5.67 (0.24)	0.55 (0.02)	5.12 (0.22)	9	1.1
	650	4.35 (0.20)	0.50 (0.02)	3.85 (0.18)	8	0.9
	1030	3.94 (0.08)	0.26 (0.01)	3.68 (0.07)	14	1.7
	1400	3.22 (0.31)	0.28 (0.01)	2.76 (0.12)	10	1.2
	1680	3.10 (0.09)	0.27 (0.01)	2.84 (0.09)	11	1.2
	2030	3.30 (0.15)	0.25 (0.01)	3.05 (0.14)	12	1.4
4 (45.9, EtOH)	1	9.28 (0.37)	[0.1][e]	9.15 (0.37)	*e*	*e*
	380	7.53 (0.04)	[0.1]	7.42 (0.04)		
	660	7.63 (0.33)	[0.5]	7.17 (0.31)		
	1060	5.84 (0.25)	[0.2]	5.63 (0.24)		
	1390	6.34	[0.7]	5.69		
	1760	5.32 (0.12)	[0.2]	5.09 (0.11)		
	2140	4.75 (0.03)	[0]	4.75 (0.03)		

[a] Diazene (T (°C), solvent). [b] P variation generally <1%. [c] In s^{-1}. Numbers in parentheses are standard deviations. See the Experimental Section. [d] Some values of k(I)/k(N) have been rounded off; values of [k(I)/k(N)]$_{\mathrm{rel}}$ were calculated from values of k(I)/k(N) before they were rounded off. [e] The very small values of k(N) for **4** in ethanol contain substantial experimental error precluding calculation of meaningful values of k(I)/k(N) and [k(I)/k(N)]$_{\mathrm{rel}}$.

Table II. Activation Volumes for Deazatization and Isomerization of *cis*-Diazenes 1–4

diazene	solvent	temp, °C	$\Delta V(\mathrm{N})^{*}$[a,b]	$\Delta V(\mathrm{I})^{*}$[a,b]
1	hexane	21.0	+17 (1)	+7 (1)
1	ethanol	35.7	+22 (3)	+5 (1)
2	ethanol	9.0	+16 (1)	+10 (2)
3	hexane	35.7	+16 (3)	+6 (1)
4	hexane	35.7	+13 (3)	+9 (2)
4	ethanol	45.9	[+9][c] (12)	+7 (1)

[a] Units cm^3/mol. [b] Numbers in parentheses are standard deviations. [c] Large uncertainty in this value.

quantities only if isomerization occurs via the diazenyl radical (k_{-1t}). When isomerization proceeds by inversion, k(I) equals the rate constant k_{inv} for the single-step nonradical reaction. The rate constant k(O) is a composite quantity equal to k(I) + k(N) independent of the respective mechanisms.

Results

Values of k(O), k(N), and k(I) for **1**–**4** are given in Table I. The corresponding activation volumes are summarized in Table II. Plots of k(N) and k(I) versus pressure for *cis*-1,2-bis(1-adamantyl)diazene (**1**) in hexane are shown in Figure 1.

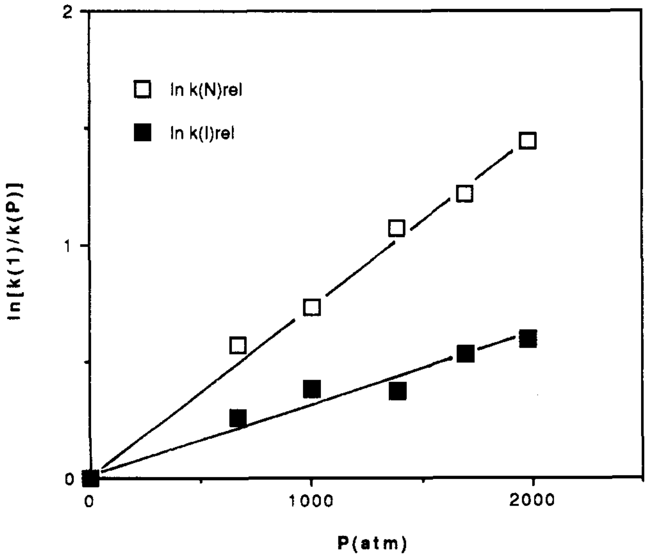


Figure 1. ln [k(1 atm)/k(P atm)] versus pressure for **1** in hexane.

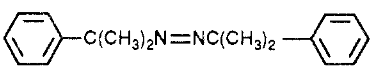
Oxygen was excluded from the reaction mixtures because spectral data from nondeoxygenated samples gave nonlinear kinetic plots showing rate accelerations with increasing time. In addition, weak UV absorbances developed that partially masked the spectra of the diazenes. These effects are attributed to the formation of hydroperoxides. They are weakly acidic and might have caused acid-catalyzed isomerization[4a] of the diazenes. Trace quantities of *tert*-butylamine were added to all reaction mixtures to eliminate acid catalysis.

Thermal decomposition rates were derived from changes in UV spectra of *cis*-diazene reaction mixtures thermostated and pressurized in a high-pressure optical cell. Values of $k(\mathrm{O})$ were determined from the decrease in the intensity of the cis absorption band at the UV $\lambda_{\max}$. The ratios $k(\mathrm{I})/k(\mathrm{O})$ were determined by monitoring the fraction of *cis*-diazene that isomerized to *trans*-diazene. Values of $k(\mathrm{N})$ and $k(\mathrm{I})$ were calculated from the relationship $k(\mathrm{O}) = k(\mathrm{N}) + k(\mathrm{I})$.[8]

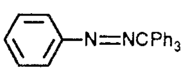
Discussion

Deazatization. The large positive values of $\Delta V(\mathrm{N})^*$ for 1–4 lead us to conclude that they lose molecular nitrogen via one-bond scission and the formation of an intermediate diazenyl radical (Scheme I). On the basis of previous studies of other radical initiators,[7,9] we proposed that activation volumes for homolysis of single bonds are small and positive (ca. +5 cm^3/mol),[7,9a–f] while radical initiators that give intermediates that can return to the starting initiator give much larger positive activation volumes (+10 to +20 cm^3/mol).[7,9a,f,g]

For example, $\Delta V(\mathrm{N})^*$ for azocumene (**5**) is about +5 cm^3/mol,[9f] while $\Delta V(\mathrm{N})^*$ for phenylazotriphenylmethane (PAT) (**6**) ranges from +16 to +19 cm^3/mol depending on the solvent.[9g] Decomposition of **6** is accompanied by the formation of a phenyldiazenyl radical that recombines with the geminate trityl radical to re-form PAT in competition with separative diffusion and β-scission analogous to the mechanism outlined in Scheme I. The effect of pressure on all of these competing reactions for PAT causes the apparent activation volume to be much larger than those observed for systems where the first formed radicals do not recombine to regenerate the starting initiator (e.g., azocumene (**5**)).



5



6

The composite rate constant $k(\mathrm{N})$ depends on the fundamental rate constants (Scheme I) as shown in eq 2. *The possibility of isomerization via a radical mechanism* (k_{-1t}) *has not been included.* The resulting $\Delta V(\mathrm{N})^*$ is then given by the expression in eq 3. Since pressure should cause k_{-1c} to increase, and both k_β and k_d to decrease,[7,9] the differential term of eq 3 would be positive[10] and $\Delta V(\mathrm{N})^*$ is predicted to be *greater* than ΔV_1^* (which is expected to be about +5 cm^3/mol (vide supra)).

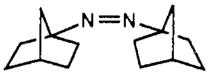
$$k(\mathrm{N}) = k_1/[1 + k_{-1c}/(k_\beta + k_d)] \qquad (2)$$

$$\Delta V(\mathrm{N})^* = \Delta V_1^* + RT(\partial \ln [1 + k_{-1c}/(k_\beta + k_d)]/\partial P) \qquad (3)$$

We would have preferred to measure all ΔV^* values in the nonpolar solvent hexane. However, the rate of decomposition of **2** in hexane was too rapid at the lowest available temperature. Since *cis*-diazene decompositions are slower in polar solvents,[4a] we used ethanol as the solvent for **2**.

As a control, we measured the kinetics for decomposition of **1** in both hexane and ethanol. Table I shows that the solvent effect (vide infra) was dramatic; it was necessary to increase the reaction temperature by 15 °C in order to have an overall decomposition rate in ethanol comparable to that in hexane. The major effect was on $k(\mathrm{N})$; it became much smaller in ethanol while the values for $k(\mathrm{I})$ were relatively similar in the two solvents.[11] Although values of $\Delta V(\mathrm{N})^*$ for **1** are different in the two solvents, we do not believe that this is due to a change in mechanism. Both large values of $\Delta V(\mathrm{N})^*$ are consistent with one-bond scission and an intermediate diazenyl radical. Their differences could arise from solvent effects on k_1 and $k_{-1c}/(k_\beta + k_d)$ (eq 3).

Isomerization. The activation volume for isomerization of *cis*-1,2-bis(1-norbornyl)diazene (**7**) has been determined to be +6 cm^3/mol by Rüchardt and Kelm.[12] Since **7** must isomerize via inversion,[4b,12a,13] this $\Delta V(\mathrm{I})^*$ corresponds to that mechanism. Rüchardt and Kelm also determined[12b] that *trans*-**7** was 12 cm^3/mol larger than *cis*-**7**, suggesting that the transition state for nonradical inversion lies midway along the reaction coordinate.[4b,12]



7

Our values of $\Delta V(\mathrm{I})^*$ for 1–4 (Table II) are generally comparable to that for **7**. Earlier, we suggested that our $\Delta V(\mathrm{I})^*$ values for **1** and **2** supported a diazenyl radical mechanism.[6] We now agree that inversion appears to be the dominant mechanism for **1** and other symmetric *cis*-diazenes studied[5] and also believe that $\Delta V(\mathrm{I})^*$ for a radical mechanism may be impossible to reliably predict.

On the basis of Scheme I, $k(\mathrm{I})$ and $\Delta V(\mathrm{I})^*$ for such a radical mechanism would be given by eqs 4 and 5, respectively. A prediction of $\Delta V(\mathrm{I})^*$ requires an estimation of both the pressure dependence and relative magnitude of each of the ratios k_{-1c}/k_{-1t}, k_β/k_{-1t}, and k_d/k_{-1t}. While the rate constant k_{-1c} should increase with increasing pressure and both k_d and k_β should decrease, it is difficult to predict the pressure dependence of k_{-1t}. Recombination of the two radicals to give *trans*-diazene should be favored

$$k(\mathrm{I}) = k_1[k_{-1t}/(k_{-1c} + k_{-1t} + k_\beta + k_d)] \qquad (4)$$

$$\Delta V(\mathrm{I})^* = \Delta V_1^* + RT(\partial \ln [1 + (k_{-1c} + k_\beta + k_d)/k_{-1t}]/\partial P) \qquad (5)$$

---

[8] Values of $k(\mathrm{O})$, $k(\mathrm{I})$, and $k(\mathrm{N})$ (Table I) are typically averages from three separate kinetic runs. The errors are standard deviations. Although values of $k(\mathrm{N})$ were calculated from the equation $k(\mathrm{N}) = k(\mathrm{O}) - k(\mathrm{I})$, the errors shown for $k(\mathrm{N})$ are not the sum of those for $k(\mathrm{O})$ and $k(\mathrm{I})$; they are standard deviations of values of $k(\mathrm{N})$ that were averaged to give the reported $k(\mathrm{N})$ values.

[9] (a) Neuman, R. C., Jr.; Behar, J. V. *J. Am. Chem. Soc.* **1969**, *91*, 6024. (b) Neuman, R. C., Jr.; Bussey, R. J. *Ibid.* **1970**, *92*, 2440. (c) Neuman, R. C., Jr.; Pankratz, R. P. *Ibid.* **1973**, *95*, 8372. (d) Neuman, R. C., Jr.; Ertley, E. W. *Ibid.* **1975**, *97*, 3130. (e) Neuman, R. C., Jr.; Wolfe, R. *J. Org. Chem.* **1975**, *40*, 3147. (f) Neuman, R. C., Jr.; Amrich, M. J., Jr. *Ibid.* **1980**, *45*, 4629. (g) Neuman, R. C., Jr.; Lockyer, G. D., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3982.

[10] If k_{-1t} is nonzero, the equation will be $k(\mathrm{N}) = k_1/[1 + k_{-1c}/(k_\beta + k_d) + k_{-1t}/(k_\beta + k_d)]$. Discussion later in the paper suggests that the latter term in this equation would also be expected to increase with increasing pressure leading to no qualitative change in the expected pressure dependence of $k(\mathrm{N})$ or the sign and general magnitude of $\Delta V(\mathrm{N})^*$.

[11] Taking into consideration the 15 °C higher temperature in ethanol compared to hexane.

[12] (a) Van Eldik, R.; Kelm, H.; Schmittel, M.; Rüchardt, C. *J. Org. Chem.* **1985**, *50*, 2998. (b) *cis*-**7** is one of the few *cis*-diazenes sufficiently stable to permit determination of its partial molar volume.

[13] (a) No deazatization of **7** has ever been observed. This is strong evidence that the norbornyldiazenyl radical is not formed during its thermal decomposition.[13b] (b) Porter, N. A.; Dubay, G. R.; Green, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 920 and references therein.

by pressure, but the rotational diffusion process required for the radicals to achieve the proper orientation for combination should be pressure retarded.[7] If the *overall* pressure dependence of k_{-1t} is small due to partial compensation of these effects, the ratios k_β/k_{-1t} and k_d/k_{-1t} might both decrease and k_{-1c}/k_{-1t} might increase with increasing pressure. The net effect on $\Delta V(I)^*$ (eq 5) would then depend on the relative magnitudes of these various ratios and whether their sum was substantially greater, or less, than 1. Clearly, an a priori prediction of $\Delta V(I)^*$ for a radical mechanism would be very speculative.

It is interesting to note, however, that a radical mechanism (excluding nonradical inversion, k_{inv}) leads to the prediction that the ratio $k(N)/k(I)$ is given by eq 6 and that this leads to eq 7. Thus, experimental values of

$$k(N)/k(I) = (k_\beta + k_d)/k_{-1t} \qquad (6)$$

$$\Delta V(I)^* = \Delta V_1^* + RT(\partial \ln [1 + k_{-1c}/k_{-1t} + k(N)/k(I)]/\partial P) \qquad (7)$$

$\Delta V(I)^*$ and $k(N)/k(I)$, for a *cis*-diazene whose isomerization had been documented to proceed via a radical mechanism, might give information about the ratio k_{-1c}/k_{-1t}.

In this regard it should be noted that values of $k(I)/k(N)$ for these diazenes differ but their *pressure dependences* are all about the same. The comparable increases in the values of $[k(I)/k(N)]_{rel}$ for 1–4 (Table I) support a common decomposition mechanism for each of them.

Solvent Effects. The dramatic decrease in $k(N)$ for 1 and 4 on changing solvent from a nonpolar hydrocarbon (hexane) to a hydroxylic solvent (ethanol), and the virtual insensitvity of $k(I)$ to the same solvent variation,[11] has been previously noted.[4] We suggest that the one-bond scission deazatization mechanism together with previous rationales more completely explains the deazatization results.

The higher viscosity (and internal pressure[14]) of ethanol and other hydroxylic solvents should give a more highly structured solvent cage around the initially formed radicals. This could dramatically reduce k_d, leading to increased return to the original *cis*-diazene. If polar *cis*-diazene is specifically solvated by ethanol (perhaps via hydrogen bonding), such solvation might stabilize the ground state compared to the scission transition state, reducing the magnitude of k_1. Alternatively, the ground and deazatization transition states may be similarly solvated, and this solvation remains in the intermediate diazenyl radical leading to its stabilization and a decrease in k_β. Each of these effects would cause a decrease in $k(N)$.

The virtual absence of solvent effect on $k(I)$ may also be consistent with specific solvation by ethanol. Isomerization of *cis*-diazenes is catalyzed by acids, and we have suggested above that adventitious ROOH can serve as such a catalyst. Perhaps hydrogen bonding of *cis*-diazenes by hydroxylic solvents also increases their isomerization rates, offsetting expected reductions in those rates by increased solvent viscosity.[5]

Experimental Section[2b]

Synthesis of *trans*-Diazenes. *cis*-Diazenes 1–4 were synthesized in situ by photoisomerization[4a] of their corresponding trans isomers 1′–4′ (vide infra).

***trans*-*N*,*N*′-Bis(1-adamantyl)diazene (1′).** This diazene was synthesized according to known procedures that have been extensively reported.[2,4,5] From 11.4 g (0.075 mol) of 1-adamantylamine was obtained 2.05 g (0.0069 mol; 18.4%) of 1′: mp 280–284 °C (lit.[15] mp 280–284 °C); ^{1}H NMR (CDCl$_3$) δ 2.10 (s), 1.70 (d), 1.50 (s); UV, λ_{max} 368 nm (lit.[4a] λ_{max} 368 nm).

***trans*-*N*,*N*′-Bis(1-methylcyclopent-1-yl)diazene (2′).** A mixture of 40.1 g (0.48 mol) of cyclopentanone, 12.4 g (0.25 mole) of 85% hydrazine hydrate, and a catalytic amount (3 drops) of concentrated hydrochloric acid was reacted to give 15.7 g (0.096 mol, 40%) of *N*,*N*′-dicyclopentylimine (pale yellow liquid): bp 95 °C (6 mm) (lit.[16] bp 92 °C (10 mm)); ^{1}H NMR (CDCl$_3$) δ 2.29 (m), 1.70 (m).

A cooled petroleum ether solution of 20.1 g (0.13 mol) of *N*,*N*′-dicyclopentylimine was reacted with chlorine gas to give 11.7 g (0.052 mol, 40%) of *N*,*N*′-bis(1-chlorocyclopentyl)diazene: pale yellow crystals; mp 43 °C (lit.[16] mp 43 °C); ^{1}H NMR (CDCl$_3$) δ 2.40 (m), 2.20 (m), 2.08 (s).

A petroleum ether solution of 9.8 g (0.040 mol) of *N*,*N*′-bis(1-chlorocyclopentyl)diazene was slowly reacted with a cooled petroleum ether solution of 6.0 g (0.083 mol) of trimethylaluminum to give 6.7 g (0.036 mol, 90%) of *trans*-bis(1-methylcyclopentyl)diazene; HPLC purification yielded a yellow liquid: bp 79 °C (7 mm) (lit.[16] bp 92 °C (15 mm)); ^{1}H NMR (CDCl$_3$) δ 2.00 (d), 1.50 (m), 1.13 (s); UV, λ_{max} 369 nm (lit.[16] λ_{max} 369 nm).

***trans*-*N*,*N*′-Bis(4-ethylbicyclo[2.2.2]oct-1-yl)diazene (3′).** This compound was synthesized from 4-ethylbicyclo[2.2.2]octylamine by procedures analogous to those for the synthesis of 1′: ^{1}H NMR (CDCl$_3$) δ 1.53 (m), 1.18 (q), 0.78 (t); mass spectrum, 302 (2%, M$^+$), 137 (100%, 4-ethylbicyclooctyl ion); UV, λ_{max} 368 nm.

***trans*-*N*,*N*′-Bis(bicyclo[2.2.2]oct-1-yl)diazene (4′).** A 50.0 g (0.42 mol) sample of 2-norbornanecarbonitrile was hydrolyzed to give 42.4 g (0.31 mol, 74%) of 2-norbornanecarboxylic acid: pale yellow liquid; ^{1}H NMR (CDCl$_3$) δ 10.88 (s), 2.78 (m), 2.53 (m), 2.28 (s), 1.40 (m); IR, 3000, 1615, 1420, 1310, 1230, 925 cm^{-1}.

A mixture of 44.1 g (0.33 mol) of 2-norbornanecarboxylic acid, 54.0 g (0.34 mol) of bromine, and 1.5 mL of phosphorus trichloride was reacted to give 20.8 g (0.095 mol, 28%) of 2-bromonorbornane-1-carboxylic acid: mp 144–148 °C (lit.[5,17] mp 147–148, 151 °C); ^{1}H NMR (CDCl$_3$) δ 10.66 (s), 4.16 (m), 2.30 (m), 1.71 (m); IR, 3700, 2910, 1700, 1400, 1310, 1020 cm^{-1}.

A 4.3-g (0.020-mol) sample of 2-bromonorbornane-1-carboxylic acid was reacted with 6.3 g (0.022 mol) of tri-*n*-butyltin hydride to give 2.4 g (0.017 mol, 87% yield) of norbornane-1-carboxylic acid: mp 102–105 °C (lit.[5,17] mp 105–107, 111–112 °C); ^{1}H NMR (CDCl$_3$) δ 10.44 (s), 2.30 (s), 1.60 (m); ^{13}C NMR (CDCl$_3$) δ 183.6, 52.1, 42.4, 37.8, 32.9, 30.0; IR, 2940, 1435, 1395, 1290, 1215 cm^{-1}.

An ethyl ether solution of 5.0 g (0.036 mol) of 1-norbornanecarboxylic acid was slowly reacted with 7.0 g (0.18 mol) of lithium aluminum hydride to yield 4.2 g (0.033 mol, 92%) of bicyclo[2.2.1]heptyl-1-carbinol (pale yellow solid), which was further purified by flash chromatography, yielding a white solid: mp 40–45 °C (lit.[4a] mp 60–62 °C); ^{1}H NMR (CDCl$_3$) δ 3.57 (s), 2.13 (s), 1.14 (m); ^{13}C NMR (CDCl$_3$) δ 66.4, 79.9, 40.4, 36.9, 31.5, 30.2.

An acetonitrile solution of 6.1 g (0.048 mol) of bicyclo[2.2.1]heptyl-1-carbinol was cautiously reacted with a *carefully* prepared and cooled mixture of 70 mL of fuming sulfuric acid, 23 mL of concentrated sulfuric acid, and 3 mL of acetonitrile to give 5.7 g (0.034 mol) of *N*-bicyclo[2.2.2]oct-1-ylacetamide: small white needles; mp 124–126 °C (lit.[4a] mp 130–131 °C); ^{1}H NMR (CDCl$_3$) δ 5.75 (s), 1.77 (s), 1.65 (m); ^{13}C NMR (CDCl$_3$) δ 169.4, 50.4, 30.0, 25.9, 24.0, 23.6.

A concentrated hydrochloric acid solution of 12.1 g (0.073 mol) of *N*-bicyclo[2.2.2]oct-1-ylacetamide was refluxed for 16 h, evaporatively distilled, and heated to 150 °C in vacuo, yielding 11.6 g (0.072 mol, 99%) of 1-bicyclo[2.2.2]octylammonium chloride, mp >308 °C (lit.[4a] mp >350 °C).

A 5.5-g (0.35-mol) sample of 1-bicyclo[2.2.2]octylammonium chloride was neutralized in aqueous base and reacted with 1.4 g (0.010 mol) of sulfuryl chloride to yield 1.3 g (0.0042 mol, 40%) of *N*,*N*′-bis(1-bicyclo[2.2.2]octyl)sulfamide, mp 186–187 °C (lit.[15] mp 188 °C).

A mixture of 1.3 g (0.0042 mol) of *N*,*N*′-bis(1-bicyclo[2.2.2]octyl)sulfamide and 100 mL of 5% sodium hypochlorite (house-

---

(14) See for example: Neuman, R. C., Jr. *J. Org. Chem.* **1972**, *37*, 495.

(15) Glozke, V.; Groeger, F.; Oberlinner, A.; Rüchardt, C. *J. Chim.* **1978**, 2, 169.

(16) Beckhaus, H.; Duismann, W.; Rüchardt, C. *Justus Liebigs Ann. Chem.* **1974**, *8*, 1348.

(17) Kwart, H.; Null, G. *J. Am. Chem. Soc.* **1959**, *81*, 2765.

hold bleach) was reacted by procedures analogous to those used for 1′, yielding 0.42 g (0.0017 mol, 40%) of *trans-N,N′*-bis(1-bicyclo[2.2.2]octyl)diazene (4′): mp 130–131 °C (lit.[15] mp 132–134 °C); ^{1}H NMR ($CDCl_3$) δ 1.60 (m), 1.49 (m), 0.82 (m); ^{13}C NMR ($CDCl_3$) δ 67.5, 33.4, 32.2, 30.8, 29.8, 8.2; UV, λ_{max} 368 nm (lit.[4a] λ_{max} 369 nm).

Solvents. The alkane solvents were purified by stirring over sulfuric acid for 24–48 h, washed with water and 10% aqueous sodium bicarbonate, and then distilled from phosphorus pentoxide and stored over potassium carbonate. Ethanol (95%) was used as supplied; its UV spectrum was free of interfering absorbances between 330 and 700 nm. *tert*-Butylamine and triethylamine, used to eliminate traces of acid in the reaction mixtures,[2b,4a] were stirred over potassium hydroxide for 12 h, distilled in vacuo, and stored in brown bottles.

Kinetics. General Procedures. All glassware, reaction cells, droppers, and syringes that came in contact with the diazene reaction mixtures were carefully washed with dilute ammonium hydroxide and air-dried.

Pressure Apparatus. Kinetic studies were conducted in a thermostated optical high-pressure bomb that has been described.[2a,18] Degassed solutions of reactants were transferred to the high-pressure sample cell with use of a glovebag with a nitrogen atmosphere.

Photolysis of *trans*-Diazenes. The photolysis apparatus has been described.[5] Solutions of *trans*-diazenes were photolyzed in the thermostated high-pressure optical cell that was then transferred to the UV–vis spectrometer for kinetic measurements.

Kinetic Studies of *cis*-Diazene Decompositions. The procedures used were essentially the same as those recently reported by us for a viscosity study of a series of *cis*-diazenes.[5] Values of k(O) were calculated from the decrease with time in the *cis*-diazene absorbance at λ_{max} by standard procedures and appropriate base-line corrections. Values of k(I)/k(O) were obtained from eq 8 as previously described.[5]

$$k(\mathrm{I})/k(\mathrm{O}) = [A_{\mathrm{trans}(t=\infty)} - A_{\mathrm{trans}(t=0)}]/[A_{\mathrm{trans}(\text{pre-}h\nu)} - A_{\mathrm{trans}(t=0)}] \quad (8)$$

---

[18] (a) Ertley, E. Ph.D. Dissertation, University of California, Riverside, 1973. (b) Lockyer, G. Ph.D. Dissertation, University of California, Riverside, 1975.

Kinetics of Reactions of Amines with α-Nitro-β-substituted-stilbenes in 50% Me_2SO–50% Water. Search for the Intermediate in Nucleophilic Vinylic Substitution Reactions

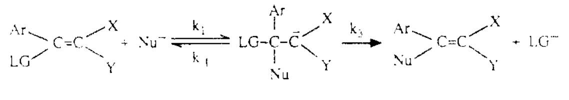
Claude F. Bernasconi,*[†] Julianne Fassberg,[†] Robert B. Killion, Jr.,[†] and Zvi Rappoport[‡]

Thimann Laboratories of the University of California, Santa Cruz, California 95064, and the Department of Organic Chemistry, The Hebrew University, Jerusalem 91904, Israel

Received March 9, 1990

The kinetics of the reaction of Ph(OMe)C=CPh(NO_2) with piperidine, morpholine, pyrrolidine, and *n*-butylamine, and of the reactions of piperidine with Ph(Cl)C=CPh(NO_2), Ph(I)C=CPh(NO_2), and Ph(SEt)C=CPh(NO_2) where measured in 50% Me_2SO–50% water at 20 °C. The reactions are discussed within the framework of the multistep mechanism of nucleophilic vinylic substitutions with amines. Nucleophilic attack is rate limiting in the reactions of piperidine with Ph(LG)C=CPh(NO_2) when LG = Cl, I, EtS, and in the reactions of Ph(OMe)C=CPh(NO_2) with all the amines at high pH. At low pH, methoxide departure becomes partially rate limiting in the reactions with piperidine, morpholine, and pyrrolidine. The intermediate Ph(OMe)(NRR′)CCPh(NO_2)$^-$ could not be directly observed. The failure to detect the intermediate is not caused by a thermodynamic stability of the intermediate with respect to reactants that is too low, but by a rate of conversion to products that is too fast compared to its rate of formation.

Over the last 25 years a large body of evidence has accumulated in favor of the addition–elimination mechanism of nucleophilic vinylic substitution with strongly activated substrates.[1] Equation 1 shows this mechanism for the reaction of a benzylidene type vinylic substrate with an anionic nucleophile:



(1)

1 2 3

X and Y are the activating (electron-withdrawing) groups, while LG is the nucleofuge. For consistency with Scheme I (see below) we shall use the symbol k_3 for leaving-group departure from an anionic intermediate and reserve the symbol k_2 for the breakdown of a zwitterionic intermediate.

The evidence in support of the two-step nature of the mechanism has been mainly indirect and has been based on ratios of rate constants for different leaving groups,[1a,d,e] rate laws showing a change in rate-limiting step in base-catalyzed reactions with amine nucleophiles,[2] stereochemical arguments,[1d,3] and analogies with systems without a leaving group in which adducts of the type **2** (LG = H) could be detected.[4]

In recent papers we reported the first examples of reactions in which intermediates such as **2** could be *directly* observed spectrophotometrically and whose rates of formation and of transformation to products could be measured separately.[5] The successful systems were the re-

---

[†] University of California.

[‡] The Hebrew University.

[1] For reviews, see: (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (d) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (e) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (f) Shainyan, B. A. *Usp. Khim.* **1986**, *55*, 942.

[2] (a) Rappoport, Z.; Ladkani, D. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1045. (b) Rappoport, Z.; Peled, P. *J. Am. Chem. Soc.* **1979**, *101*, 2682. (c) Rappoport, Z.; Topol, A. *J. Org. Chem.* **1989**, *54*, 5967.

[3] (a) Rappoport, Z.; Avramovitch, B. *J. Am. Chem. Soc.* **1988**, *110*, 911. (b) Lodder, G.; van Dorp, J. W. J.; Avramovitch, B.; Rappoport, Z. *J. Org. Chem.* **1989**, *54*, 2574.

[4] For reviews, see: (a) Patai, S.; Rappoport, Z. In *The Chemistry of the Alkenes*; Patai, S., Eds.; Wiley-Interscience: New York, 1964; p 469. (b) Rappoport, Z.; Ladkani, D. *Chem. Scr.* **1974**, *5*, 124. (c) Bernasconi, C. F. *Tetrahedron* **1989**, *45*, 4017.

0022-3263/90/1955-4568$02.50/0