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Activation Volumes and Volumes of Reaction for the Proton-Transfer Reaction between 4-Nitrophenylnitromethane and 1,1′,3,3′-Tetramethylguanidine in Some Aprotic Solvents

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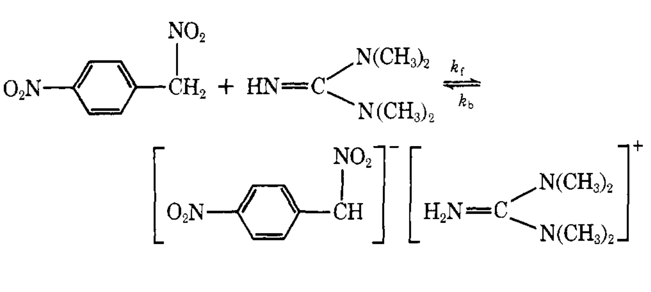
Abstract: Volumes of activation ($\Delta V^{\ddagger}$) and of reaction (ΔV°) have been determined by means of a laser apparatus with a high-pressure cell for the fast proton-transfer reaction between 4-nitrophenylnitromethane and 1,1′,3,3′-tetramethylguanidine in five aprotic solvents (mesitylene, *o*-xylene, toluene, anisole, and chlorobenzene). The values of $\Delta V_f^{\ddagger}$ are around −15 cm^3 mol^{-1} and do not vary by more than twice the standard deviations; those of ΔV° are larger and differ more (−16 to −29 cm^3 mol^{-1}), the ratio $\Delta V_f^{\ddagger}/\Delta V^{\circ}$ ranging from 0.56 to 0.84. An electrostatic treatment is not adequate to explain the results; specific solvation changes are also involved. The near constancy of $\Delta V_f^{\ddagger}$ is consistent with the explanation previously put forward for the large tunneling correction found for the reaction in these solvents; during the proton transfer, the solvation changes involve only electron polarization and not motion of solvent molecules.

The proton-transfer reaction (eq 1) between 4-nitrophenylnitromethane (4-NPNM; $NO_2C_6H_4CH_2NO_2$) and a base B in aprotic solvents produces a yellow solution, with λ_{max} approximately 450 nm, containing an ion pair.[2-5] The observed rate constant k depends on the concentration of base b (in large excess) in the way expected from the reaction scheme of eq 1 (eq 2). The reaction with the strong base, 1,1′,3,3′-tetramethylguanidine [TMG; $HN{=}C(NMe_2)_2$], has recently been studied by the stopped-flow method.[3,4] In solvents of low polarity (dielectric constant <6), the kinetic deuterium isotopic effects and in particular the ratio of the preexponential factors (A^D/A^H) are exceptionally large and indicate a large tunneling correction:[6,7] for instance, in toluene, k^H/k^D at 25 °C is 45 ± 2, ($\Delta H^{\ddagger D} - \Delta H^{\ddagger H}$) is 4.3 ± 0.3 kcal mol^{-1}, and A^D/A^H is 32 ± 14. Application of Bell's equation[8,9] for tunneling through an unsymmetrical parabolic barrier, on the assumption that the mass of the particle transferred is that of the proton or deuteron (m^H = 1, m^D = 2 amu), allows determination of the barrier dimensions that give the best fit to the experimental data; the result is that the barrier height is solvent dependent, but the barrier width is nearly constant. In solvents of higher polarity (dielectric constant >7), the isotopic differences are smaller but still indicative of tunneling. It was found possible to fit the data to Bell's equations either on the assumption that m^H = 1 and m^D = 2 amu, in which case the resulting barrier widths are solvent dependent and larger than for the less polar solvents; or with the assumption only that $m^D - m^H = 1$, in which case the best fit is obtained with barrier widths that are nearly constant and equal to those for the less polar solvents, while the effective mass is increased (m^H = 1.17 to 1.27). Other bases gave similar though smaller effects.[5]

$$NO_2C_6H_4CH_2NO_2 + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NO_2C_6H_4CHNO_2^- \; HB^+ \text{ (ion pair)} \quad (1)$$

$$k = bk_f + k_b \quad (2)$$



The interpretation that was suggested for these solvent-dependent results is as follows. The transfer of the proton leads to a separation of charge and therefore to a strong electrostatic field with which the solvent must interact. In the solvents of higher polarity, the field produces a torque on the polar solvent molecules, whose motion is therefore coupled to that of the proton, thus increasing the effective mass; while in the less polar solvents (which are also the more polarizable), the field produces only electron polarization, so that the effective mass is practically unaltered.

Determination of the activation volume ($\Delta V^{\ddagger}$) in a range of solvents should allow a test of this model. Values of $\Delta V^{\ddagger}$ may be considered[10-13] as made up of two major contributions, one due to changes in bonding as the transition state is formed ($\Delta V^{\ddagger}{}_1$) and the other due to changes in the adjacent solvent ($\Delta V^{\ddagger}{}_2$). For the less polar solvents, the model predicts that $\Delta V^{\ddagger}{}_2$ should be relatively small or zero, and, therefore, from the model we should expect $\Delta V^{\ddagger}$ to be nearly equal to $\Delta V^{\ddagger}{}_1$ and independent of solvent.

We have therefore made measurements of $\Delta V^{\ddagger}$ in some aprotic solvents of low polarity using a pulsed laser in conjunction with a high-pressure cell. The reaction was initiated photochemically by a method similar to photosensitization.

Experimental Section

Materials. 4-Nitrophenylnitromethane, a gift from Dr. S. Mateo, was recrystallized from toluene. 1,1′,3,3′-Tetramethylguanidine, from Koch Light, was dried over NaOH and distilled under nitrogen at reduced pressure. Toluene (AR) and mesitylene (SLR) were dried over sodium and fractionally distilled under nitrogen. *o*-Xylene and anisole (SLR) were washed with aqueous sodium hydroxide (2 M) and water, dried over calcium chloride, and distilled from sodium. Chlorobenzene (AR) was shaken with successive portions of concentrated sulfuric acid until the acid remained colorless and washed with aqueous sodium bicarbonate and finally with distilled water; it was then dried over anhydrous sodium sulfate and distilled from P_2O_5 under nitrogen. Since it has a tendency to produce acid, it was tested before use with the basic indicator Nile Blue.

Stock solutions of TMG were prepared by weight and concentrations determined by titrating aliquots in aqueous methanolic solution with standard hydrochloric acid with bromophenol purple as indicator. Good agreement was found between concentrations by weight and by titration, indicating that TMG had not been pyrolyzed during distillation. Stock solutions both of TMG and 4-NPNM were stored under nitrogen and were stable indefinitely. Concentrations at all pressures are expressed in terms of the molarity at 1 atm (which is proportional to molality), without correction for change of volume.[10-13]

Apparatus. The laser apparatus and the high-pressure vessel have been described.[14-16] The ruby laser emitting at 694 nm was used. Some important improvements to the apparatus are the following. (a) The wavelength of the monitoring light beam is selected by means of a Bausch and Lomb monochromator placed between the lamp and the pressure vessel, instead of an interference filter between the pressure vessel and the photomultiplier. This improves the bandwidth to <10 nm and allows quick and accurate selection of wavelength. (b) The 50-W tungsten lamp has been replaced by a 100-W quartz-halogen lamp, which has a higher color temperature and gives a tenfold increase in light intensity in the spectral region 320 to 450 nm. (c) The solution in the reaction cell inside the pressure vessel is isolated from the hydraulic fluid by a piston sealed with O-rings made from the halogenated rubber Viton EP 101-80 (James Walker and Co.); this material is an improvement on the high-nitrile rubber (PB80) formerly used, which deteriorates rapidly in contact with hydrocarbons. (d) Since the laser flash is used in these experiments to produce reactions photochemically, it is convenient to have a method of attenuating the intensity of the flash by variable amounts. This is done by using a pack of Chance glass neutral-density filters, each having an absorbance of about 0.2 at the laser wavelength in a spectrophotometer. (High-absorbance glass filters may be damaged by the laser flash.) The absorbance of such filters when exposed to a laser flash is less than in a spectrophotometer; experiments with a laser power meter (ITL Model LOMB 102/H101) showed that on passing through a filter pack of absorbance 2.0, the intensity was reduced by a factor of 20 rather than the expected 100. A Unicam SP 8000 spectrophotometer was used for equilibrium measurements at atmospheric pressure.

Range of Solvents. The range of solvents that could be used was restricted to those of lower polarity, because in solvents of higher polarity the laser flash led to some irreversible decomposition, especially at increased pressure. In solvents of relatively low dielectric constant, the decomposition was slight. The products had no effect on the kinetics; experiments on solutions which had been exposed repeatedly to laser flashes gave rate constants identical with those from fresh solutions. When not exposed to the flash, solutions in anisole, toluene, *o*-xylene, and mesitylene were indefinitely stable, and in chlorobenzene they were unchanged for 2–3 h; but in solvents of higher dielectric constant, the rate of thermal decomposition was such that accurate measurements could not be obtained after the time required for pressurizing and thermostating (ca. 30 min).

Photosensitized Flash Initiation of Reaction. Rate measurements have been made by a relaxation method with photosensitized initiation by the laser flash. This is a novel and promising method which merits a special description.

The laser apparatus has hitherto been used either for temperature-jump or for flash-photolysis experiments.[14] Temperature-jump experiments are conveniently carried out by passing a flash from the ruby laser (694 nm) into a reaction solution containing also an inert dye which absorbs the radiation and transmits energy readily to the solvent, raising the temperature by several degrees. For the present reaction, however, no suitable dye could be found which had ideal solubility in all the solvents. Vanadylphthalocyanine, the dye actually used, has the nearest to the required solubility properties though only slightly soluble in mesitylene. From the absorbance at 694 nm (0.3), the temperature jump in this solvent would be expected to be only about 15% of the optimum. When the experiment was carried out, however, at atmospheric pressure, with spectrophotometric monitoring of the concentration of the ion pair at 445 nm, the oscilloscope trace showed a change of concentration of about 50%, many times larger than that corresponding to the temperature rise; and instead of a first-order decrease of concentration with time, there was first a rapid decrease occurring during the laser pulse (<1 ms), followed by a relatively slow (20–50 ms) increase back to the original value. By attenuating the laser flash as described above to <0.1 J and reducing the dye concentration, the concentration change on flashing was reduced to 6%. The oscilloscope traces then obtained were first-order curves and gave rate constants at atmospheric pressure, agreeing within a few percent with those found for the same temperature by the stopped-flow method[3] on mixing the acid and base solutions (the discrepancy is 20% in toluene, 5% in mesitylene, and 7% in chlorobenzene, the last two by extrapolation). Therefore the kinetics experiments have been carried out using a low vanadylphthalocyanine concentration ($\sim 5 \times 10^{-6}$ M), and the rate constants were obtained as described. There is no evidence of dye interaction with reactants or product from absorption spectra, and this is supported by the agreement of the rate constants at the same temperature with those obtained from solutions in the absence of dye by the stopped-flow method. Kinetic parameters determined in this study are those at 30 °C, the temperature of solutions immediately following reaction initiation.

Results

The observed pseudo-first-order rate constants k_{obsd} at various concentrations and pressures are given in Table I. The concentration of 4-NPNM, chosen to give a suitable change of absorbance, was in the range of 2×10^{-5} to 3×10^{-5} M. The concentration of TMG was in the range of 2×10^{-4} to 1.5×10^{-2} M, and pseudo-first-order conditions were maintained. The concentration range in each solvent was chosen to give appropriate values of the amplitude of the relaxation; this depends on the magnitude of the equilibrium constant, which for some solvents had been reported[4] and for the others could be estimated. The relaxation times were in the range of 10 to 200 ms, where the accuracy of the instrument is high and the reproducibility good.

Since the base is in large excess, the observed rate constant is related to k_f and k_b by eq 2. Plots of k_{obsd} against the base concentration (B) were good straight lines; representative plots for data in Table I for toluene are shown in Figure 1. The values of k_f and k_b (and the equilibrium con-

Table I. Kinetic Data for TMG + 4-NPNM at 30 °C[a]

Solvent	10^4 [TMG] M	k_{obsd}(s^{-1}) at pressures (kbars) 0.0010	0.33	0.67	1.00	1.33	1.67
Mesitylene	5.25	7.68	8.33	8.93	8.26	8.94	8.45
	10.5	10.1	9.46	9.70	9.20	9.70	9.76
	21.0	10.6	11.2	11.5	12.2	13.0	14.7
	36.7	12.5	14.7	15.1	17.3	19.1	22.0
	52.5	13.6	15.2	18.1	19.6	23.5	25.5
	68.3	16.2	18.4	23.4	24.7	28.6	28.4
	84.0	21.0	26.3	30.4	36.0	46.7	
Toluene[b]	5.16	10.2	9.28	8.98	8.29	8.87	7.83
	10.3	11.2	11.4	10.6	11.5	12.3	12.5
	20.6	12.9	13.4	13.7	14.7	15.8	17.2
	31.0	14.2	15.4	17.6	20.0		23.5
	41.3	17.0	19.1	22.0	23.6	28.3	
	51.6	18.1	20.6	24.9	28.4	33.7	
o-Xylene	2.67	7.09	6.81	6.62	6.19	6.20	5.98
	5.34	8.52	8.51	7.99	8.25	8.50	8.28
	8.55	11.4	9.79	9.42	9.24	9.38	9.46
	16.0	11.4	10.8	12.1	11.7	12.6	12.6
	21.3	11.5	11.9	12.7	13.3	15.1	17.8
	32.0	12.7	13.5	14.8	17.1	21.0	22.3
	42.6	14.1	15.9	17.6	22.2	24.2	30.0
	53.4	16.5	20.1	27.4	29.3	37.0	40.4
Anisole	1.94[c]	5.14	4.68	4.67	4.42	4.22	
	2.90[c]	5.51	5.19	5.65	5.62	6.03	
	3.79	6.12	5.88	5.83	5.91	7.05	
	5.32	6.83	7.10	7.41	7.71	8.85	
	6.77	6.60	6.00	6.55	9.48	10.7	
	8.23	8.67	9.06	9.90	10.4	13.1	
	9.68	9.28	9.73	11.5	11.6	14.1	
	11.6	10.1	11.0	12.3	15.2	15.9	
Chlorobenzene[c]	1.48[d]	5.03	4.33	4.45	4.64	4.98	4.97
	2.97	4.07	4.50	4.83	4.74	4.81	4.67
	4.44	6.97	7.34	9.03	9.14	9.98	9.89
	5.95[e]	7.33	7.02	8.68	11.1	11.4	13.6
	7.40	11.4	11.7	12.0	13.5	13.1	
	8.93	10.3	10.2	13.5	16.2	17.8	22.0
	10.4	11.3	11.8	13.6	17.2		21.4
	11.9	13.2	14.2	20.1	17.9	20.8	24.3
	14.9	15.0	19.0	19.9			

[a] [4-NPNM] = 3.0 × 10^{-5} M except as indicated. [b] We are indebted to Dr. T. Altinata for obtaining these results. [c] [4-NPNM] = 2.0 × 10^{-5} M. [d] [4-NPNM] = 1.0 × 10^{-5} M. [e] 4-NPNM concentrations of 1.0 × 10^{-5} and 2.0 × 10^{-5} M were used in these runs.

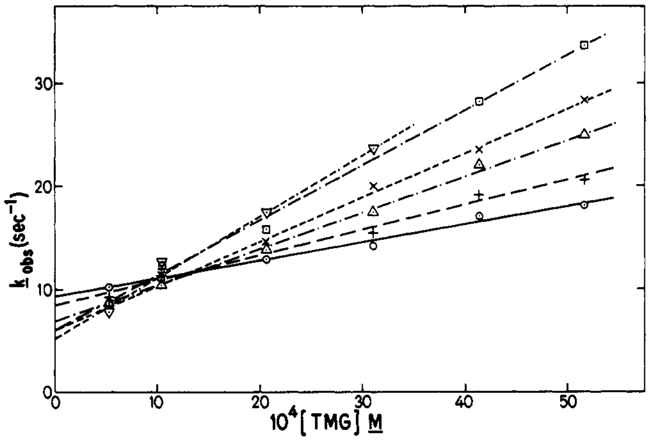


Figure 1. Plot of k_{obsd} vs. [TMG] for TMG + 4-NPNM in toluene at various pressures. The concentration of 4-NPNM is 3.0 × 10^{-5} M, reaction temperature is 30 °C, and vanadylphthalocyanine is present (see text). The lines drawn are the least-mean-squares fit lines for each set of data points: (⊙, —) atmospheric pressure; (+, —) 0.33; (△, —·—) 0.67; (×, - - -) 1.00; (□, —·—) 1.33; (▽, - ·· -) 1.67 (all pressures in kbars).

stant $K = k_f/k_b$) were determined from the slopes and intercepts of the plots, by a weighted least-mean-squares treatment; they are given, with their standard deviations, in Table II. The values of k_f at 1 atm increase with dielectric constant; in each solvent the values increase with pressure.

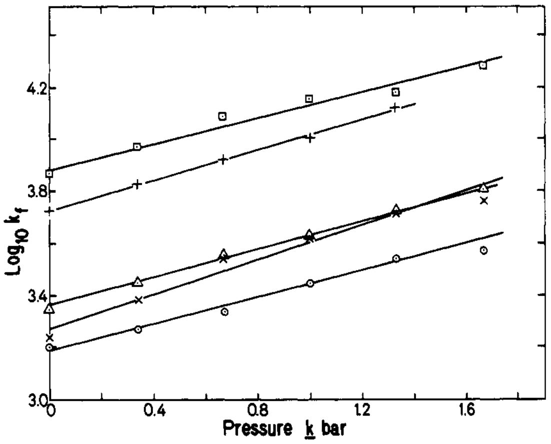


Figure 2. Plot of log k_f vs. pressure (kbars) for 4-NPNM + TMG at 30 °C in different solvents. The lines drawn are the least-mean-squares fit for each set of data points: (⊙) mesitylene; (×) toluene; (△) *o*-xylene; (+) anisole; (□) chlorobenzene.

In the more polar solvents, anisole and chlorobenzene, k_b shows a slight increase with pressure and in the less polar solvents shows changes which are hardly distinguishable from the experimental error. Since no specific interpretation will be made from these trends, individual values of k_b are not reported.

The plots of log k_f against pressure are essentially linear for all five solvents, as shown in Figure 2; so also are those

Table II. Kinetic and Equilibrium Data for 4-NPNM + TMG at 30 °C at Pressures to 1.67 kbars[a, b]

Pressure, kbars	Log k_f	Log K	Log k_f	Log K
	Mesitylene		Toluene	
0.001	3.204 ± 0.080	2.350 ± 0.103	3.242 ± 0.042	2.275 ± 0.051
0.33	3.267 ± 0.034	2.398 ± 0.045	3.387 ± 0.003	2.464 ± 0.013
0.67	3.332 ± 0.035	2.447 ± 0.047	3.55 ± 0.05	2.707 ± 0.078
1.00	3.446 ± 0.033	2.620 ± 0.050	3.625 ± 0.02	2.813 ± 0.032
1.33	3.532 ± 0.048	2.693 ± 0.078	3.73 ± 0.02	2.945 ± 0.012
1.67	3.564 ± 0.032	2.754 ± 0.053	3.77 ± 0.05	3.03 ± 0.06
	o-Xylene		Anisole	
0.001	3.352 ± 0.070	2.529 ± 0.085	3.726 ± 0.012	3.114 ± 0.020
0.33	3.452 ± 0.063	2.652 ± 0.062	3.829 ± 0.012	3.303 ± 0.021
0.67	3.553 ± 0.036	2.791 ± 0.052	3.913 ± 0.021	3.423 ± 0.044
1.00	3.627 ± 0.037	2.908 ± 0.056	3.999 ± 0.021	3.602 ± 0.053
1.33	3.720 ± 0.032	3.027 ± 0.049	4.115 ± 0.019	3.840 ± 0.065
1.67	3.794 ± 0.024	3.152 ± 0.046		
	Chlorobenzene			
0.001	3.867 ± 0.074	3.310 ± 0.129		
0.33	3.969 ± 0.047	3.530 ± 0.107		
0.67	4.084 ± 0.038	3.693 ± 0.087		
1.00	4.149 ± 0.045	3.793 ± 0.106		
1.33	4.175 ± 0.059	3.790 ± 0.133		
1.67	4.274 ± 0.059	4.049 ± 0.194		

[a] k_f units of M^{-1} s^{-1} and K units of M^{-1}. [b] Errors quoted are least-mean-squares deviations from plots of data in Table I.

Table III. Kinetic, Activation, and Thermodynamic Data for 4-NPNM + TMG at 30 °C

Solvent	k_f, M^{-1} s^{-1} (1 atm)	$\Delta V_f^{\ddagger}$, cm^3 mol^{-1}	ΔV°, cm^3 mol^{-1}	$\Delta S_f^{\ddagger}$,[a] cal mol^{-1} K^{-1}
Mesitylene	1.60×10^3	−13.2 ± 1.0	−15.9 ± 1.7	−31.3 ± 0.1
Toluene	1.74×10^3	−17.8 ± 1.2	−25.5 ± 1.6	−31.0 ± 0.2
o-Xylene	2.24×10^3	−14.6 ± 0.4	−21.3 ± 0.3	
Anisole	5.32×10^3	−16.3 ± 0.5	−29.3 ± 1.7	
Chlorobenzene	7.36×10^3	−13.0 ± 1.4	−21.9 ± 3.5	−28.9 ± 0.5

[a] At 25 °C, from kinetic data of E. F. Caldin and S. Mateo (ref 4, 5).

Table IV. Physical Properties of Solvents[a]

	Mesitylene	Toluene	*o*-Xylene	Anisole	Chlorobenzene
D[b] (25°C)	2.28 (20°C)	2.38	2.57	4.33	5.62
q[c] (30 °C)		0.240	0.251	0.343	0.378
$10^5 (\delta q/\delta P)_T$[d] ($J^{-1}$ cm^2) (30 °C)	>10[e]	10.8 ± 0.5	10.9 ± 0.5	6.8 ± 0.5	6.3 ± 0.5
n	1.497	1.494	1.506	1.518	1.523
a (cm^3 mol^{-1})	40	30	35	33	31
μ (D)	0.0	0.38	0.6	1.30	1.56
V° (cm^3 mol^{-1})	140	106	118	109	102

[a] D, dielectric constant; q, $(D - 1)/(2D + 1)$; n, refractive index; α, molar polarizability; μ, dipole moment; V°, molar volume. [b] National Bureau of Standards Circular, No. 514 (1951). [c] Reference 17. [d] Calculated from data in ref 17. [e] See text.

of log K. The slopes of the plots which gave $\Delta V^{\ddagger}$ were therefore assumed independent of pressure and the best values were determined by a weighted least-mean-squares treatment. The values are collected, with other relevant data, in Table III. Relevant solvent properties are summarized in Table IV.

Discussion

Photosensitized Flash Initiation of Reaction. The traces observed on flashing a solution containing the reactants and a small concentration of the dye vanadylphthalocyanine are taken to refer to the proton-transfer reaction $AH + B \rightarrow A^-HB^+$.

The initial rapid decrease of the concentration of the ion pair cannot be attributed to dissociation of the ion pair ($A^-HB^+ \rightarrow A^- + HB^+$); this process would not give the considerable change of absorbance observed since the molar absorbances of A^-HB^+ and A^- are not greatly different. Moreover, the amplitude decreases with increase of solvent polarity and increase of pressure, both of which would favor the formation of free ions. The alternative possibility is proton transfer ($A^-HB^+ \rightarrow AH + B$), and the fact that the observed rate constants agree with those determined by a rapid-mixing method for the reverse of this reaction ($AH + B \rightarrow A^-HB^+$) leaves little doubt that the fast initial change is a disturbance of the acid-base equilibrium toward AH + B, and the subsequent relaxation is the re-establishment of equilibrium. There is no indication of an excited state of reactants or of the ion pair, and these would in any case be expected to be short lived (<1 μs). The observed relaxation time is independent of the concentration of the dye, while the amplitude increases with its absorbance.

It appears therefore that the sequence is as follows. The dye molecules absorb energy from the laser flash and transmit energy selectively to the ion pairs, which then react in the endothermic direction ($A^-HB^+ \rightarrow AH + B$). The products are deactivated rapidly by solvent molecules, and the result is a solution with uniform temperature in which the chemical equilibrium has been displaced in favor of AH + B. The reaction AH + B → A^-HB^+ then occurs to re-establish chemical equilibrium; this is the process giving rise to the observed traces. It is a relaxation process initiated neither by the temperature jump nor directly by the flash, but by photosensitization, i.e., the species that react are not the ones that absorb the radiation. This phenomenon may be termed "photosensitized relaxation". It promises to provide a useful method of studying fast reactions.

Rate and Equilibrium Constants in Various Solvents. The rate constants and equilibrium constants (K) at 30 °C determined here are in reasonably good agreement with those determined earlier[4] directly or by extrapolation in the same solvents and with those determined in other aprotic solvents of comparable dielectric constant (D). Thus the trends in dependence of k_f and K against $1/D$ and $(D-1)/(2D+1)$ are confirmed, and there is a fairly good linear relation between log K and the empirical solvent polarity parameter, E_T, especially away from the extremes of the range of solvents investigated (Table V). The general behavior of the reaction corresponds with that of an ionogenic reaction in which specific solvation plays some part as well as electrostatic effects.

Table V. Solvent Polarity Parameters and Equilibrium Constants for 4-NPNM + TMG

Solvent	E_T	$K = k_f/k_b$, M at 30 °C
Cyclohexane	32.5	127[b]
Toluene	33.9	188
Mesitylene	33.5[a]	224
o-Xylene	33.7[a]	338
n-Butyl ether	35.0	545[b]
Anisole	37.2	1300
Chlorobenzene	37.5	2040
Tetrahydrofuran	37.4	4100[b]
Methylene dichloride	41.1	5170[b]
Acetonitrile	46.0	6170[b]

[a] Estimated value. [b] Extrapolated from data in ref 4.

The Volumes of Activation and Reaction. General. The values of the activation volume $\Delta V^{\neq}$ for the forward reaction in the various solvents (Table III) are in the range of −13 to −18 cm^3 mol^{-1}. The standard deviations are consistent either with a nearly constant value of about −15 cm^3 mol^{-1} (none of the values differ from this by more than twice its standard deviation) or with slight variations from solvent to solvent. The values of the overall volume change for reaction $\Delta V°$ are all larger than $\Delta V^{\neq}$ by 3-13 cm^3 mol^{-1} and vary considerably more; the ratio $\Delta V^{\neq}/\Delta V°$ varies from 0.56 to 0.84. The values of $\Delta V^{\neq}$ are smaller than those reported for Menschutkin reactions,[17,18] which being ionogenic might be compared with the present reaction; in aprotic solvents, these reactions yield $\Delta V^{\neq}$ in the range of −20 to −50 cm^3 mol^{-1}.

Electrostatic Considerations. The volume change ΔV, whether for activation or for the overall reaction, may be regarded as the sum of the change in volume (ΔV_1) of the reacting acid-base pair CH···N and the change in volume (ΔV_2) due to movements of adjacent solvent molecules. If ΔV_2 is due entirely to electrostriction, it will be related to the pressure dependence of the electrostatic work done in forming the transition complex. A calculation based on the Kirkwood model of a point dipole in a spherical cavity of radius a in an isotropic medium of dielectric constant D gives for the electrostatic contribution to ΔV_2:[10,11,13,19]

$$\Delta V_2^{\mathrm{ES}} = -A(\delta q/\delta P)_T \tag{3}$$

where $q = (D-1)/(2D+1)$, and A depends on the dipole moments and radii of the initial and final states [$A = N^0\Sigma(\mu^2/a^3)$], which may be assumed independent of solvent. (There is also a term for compression of the cavity, but for these solvents it is only a few percent of $\Delta V^{\neq}{}_2^{\mathrm{ES}}$ and will be omitted.) A linear plot of $\Delta V^{\neq}$ or $\Delta V°$ against $(\delta q/\delta P)_T$ would indicate that electrostatic influences are predominant; the intercept would give ΔV_1 and the slope $\Sigma(\mu^2/a^3)$. Measured values of $(\delta q/\delta P)_T$ are available for four of our solvents, but not for mesitylene (Table IV); however, the values for other solvents[17,20] indicate that solvents of low dielectric constant (D <3) all have high values of $(\delta q/\delta P)_T$ (>10), and from the values for toluene, o-xylene, and p-xylene we can therefore confidently expect that for mesitylene the value of $(\delta q/\delta P)_T$ will be high. It is therefore anomalous, from the electrostatic point of view, that the values of $\Delta V^{\neq}$ are about equal for mesitylene and chlorobenzene and about equal for o-xylene and anisole; and, similarly, the values of $\Delta V°$ are about equal for o-xylene and chlorobenzene and for toluene and anisole. The simple electrostatic model is evidently unsatisfactory. The only correlation with electrostatic properties is a rough inverse parallelism between the variations of $\Delta V^{\neq}$ and the polarizability of the solvent (Table IV), but even here chlorobenzene is an exception.

Interpretation in Terms of Constant $\Delta V^{\neq}$ ($=\Delta V^{\neq}{}_1$). An interpretation in line with the model put forward to explain the isotopic effects for this reaction in solvents of low polarity[4] (cf. the Introduction) is that, in these solvents, $\Delta V_f^{\neq}$ is nearly constant, and $\Delta V°$ depends on specific solvation effects as well as on electrostatic interactions. The suggested reason why $\Delta V^{\neq}$ is effectively constant is that it represents the contraction in volume of the reacting acid-base pair alone, without appreciable motion of solvent molecules, because the effect of the field due to the charge separation in the transition state is to bring about electron polarization, rather than motion of solvent molecules. It is of interest that the values of $\Delta S_f^{\neq}$ for the three solvents for which they are available are also fairly constant (Table III). We note, however, that while the values of $\Delta S_f^{\neq}$ (the temperature coefficient of $\Delta G_f^{\neq}$) reflect solvation effects,[4] they do not tell us whether they involve motions of solvent molecules or only electron polarization, because they depend on the energies of molecules as well as configurations; whereas the values of $\Delta V_f^{\neq}$ (the pressure coefficient of $\Delta G_f^{\neq}$) give an indication that solvent molecules do not move during the formation of the transition state.

A corollary of this interpretation is that the change in volume of the reacting pair, $\Delta V^{\neq}{}_1$, is about −15 cm^3 mol^{-1}. The following rough estimate of $\Delta V^{\neq}{}_1$ from molecular properties gives some support to this view. It may be supposed that in the initial state (CH···N), the acid and base molecules have approached without change of volume until the H and N atoms are at their van der Waals distance and that they then approach closer, with C, H, and N collinear, until the C-N distance is approximately that for a hydrogen bond (CH···N), at which point the proton moves from C to N without appreciable movement of the heavier atoms ($^-$C···HN$^+$). (The effect of a charge on hydrogen-bond lengths is usually only a few hundredths of an ångström.)[21,22] The initial C-N distance is the sum of the C-H bond length (1.1 Å) and the van der Waals radii of H and N (1.20 and 1.55 Å),[23] i.e., 3.85 Å; while the transition-state C-N distance may be taken as approximately the hydrogen-bonded distance in solid HCN, namely, 3.18 Å.[23,24] (This is the only available measured value for a CH···N hydrogen bond.) The shortening of the C-N distance on forming the transition state is thus about 0.67 Å. To obtain ΔV_1, this must be multiplied by the cross section of the area swept out.[13] The molecular volumes of the acid and base molecules may be estimated by Edward's method[25] as 143 and 124 Å^3 mol^{-1}, respectively; treating these as spheres, one obtains radii of 3.2 and 3.1 Å, respectively. Hence we obtain $-\Delta V^{\ddagger}_1$ = 12–13 cm^3 mol^{-1}. The agreement with the experimental value is satisfactory, given the uncertainties in the calculation.

The values of $\Delta V^{\ddagger}_2$ ($=\Delta V^\circ - \Delta V_f^{\ddagger}$), representing the volume change due to electrostriction, do not follow the trend expected from electrostatic theory and shown by Menschutkin reactions,[17] namely, more negative values in the less polar solvents. The electrostatic model is evidently inadequate, as was indeed suggested by the trends in k_f and K at 1 atm.

Conclusion

We conclude that the pressure dependence of the rate constants is consistent with a nearly constant volume of activation in the several solvents, in accordance with the model proposed earlier to account for the large tunneling corrections. The new technique of photosensitized initiation of fast reactions in solution by laser flashes appears promising.

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The Mechanism of Allene Cycloaddition. III. Thermal and Photochemical Generation of 2,2′-Bis(1,1-dimethylallyl) Biradical from an Azocyclane Precursor[1]

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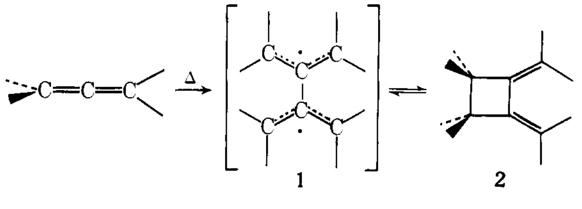
Abstract: Thermal dimerization of 1,1-dimethylallene in triglyme solution for short times at 151 °C gives 1,2-diisopropylidenecyclobutane, 1-isopropylidene-2-methylene-3,3-dimethylcyclobutane, and 1,2-dimethylene-3,3,4,4-tetramethylcyclobutane (DMTM) in relative yields of 46, 36, and 18%. Thermal decomposition of 4,5-dimethylene-3,3,6,6-tetramethyl-3,4,5,6-tetrahydropyridazine gives the same products in the same ratio at 151 °C. Extrapolation of the latter thermolysis results at five other temperatures to 35 °C gives a product ratio (53, 33, and 14%, respectively), which is the same as that obtained from direct photolysis at 35 °C of the same compound for short times. The results are interpreted in terms of the title species being a common intermediate for all three reactions. Although accurate product ratios could not be obtained from the triplet sensitized photolysis of the same azo compound, nor from the thermal rearrangement of DMTM, it is proposed that the same intermediate is also involved in these cases.

The possible intermediacy of a 2,2′-bisallyl, or tetramethyleneethane, biradical **1** in the thermal dimerization of allenes (eq 1) has been widely debated since the suggestion was first popularized by Roberts and Sharts in 1962.[3] Our own interest in the mechanism of this reaction dates from the same period, when we were using the reaction for synthetic purposes.[4] The question of the allene cycloaddition mechanism gained considerable currency during the period in which the original series of Woodward–Hoffmann orbital symmetry papers were appearing in 1965. By coincidence, two very convincing and apparently contradictory documents relating to this question were received by one of us (E.F.K.) on the same day: a student research report in



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