Effect of Solvent Viscosity on the Decomposition of 1,1,4,4-Tetraphenyl-2-tetrazene

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The rate of decomposition of 1,1,4,4-tetraphenyl-2-tetrazene (TPT) was measured in the polyethylene glycol (PEG) thickened dimethylformamide (DMF) of varying viscosities. The observed rate constant for the decomposition of TPT decreases with the viscosity of the DMF/PEG solvent system. A compensating change was found in the enthalpy and entropy of activation. It was also found that the decomposition of TPT occurs by the scission of only one N–N single bond, and undergoes cage return in the solvent system by recombination of radicals.

2-Tetrazenes decompose thermally and photochemically to form two neutral amino radicals and nitrogen.[1] The basic nature of 2-tetrazenes and their reactions with electrophilic reagents have been extensively investigated.[2–4] Nelsen *et al.*[1e] prepared 1,4-dimethyl-1,4-diphenyl-2-tetrazene and several of its bis-*p*-substituted derivatives to obtain information about electronic and thermodynamic factors of the decomposition of 2-tetrazenes. With electron withdrawing substituents, it was found that the decrease in the rate of decomposition is not due to the $\Delta H^{\neq}$ term, but to the $\Delta S^{\neq}$ term. However, the rate of decomposition increases with the polarity of the solvent in the radical decomposition of 1,4-dimethoxycarbonyl-1,4-diphenyl-2-tetrazene.[5] The enthalpy of activation is a linear function of the entropy of activation over quite a wide range in various solvents.

There has also been some interest in the effect of viscosity on the rate of bond homolysis.[6] Herk *et al.*[6a] studied the cage reaction of acetyl peroxide and azomethane. Pryor *et al.*[6d] have also investigated the decomposition of a wide variety of free radical initiators in a series of alkane solvents of varying viscosities. However, there has been no systematic investigation of the effect of viscosity on the decomposition of 2-tetrazene.

In earlier works,[1h] we reported that 1,1,4,4-tetraphenyl-2-tetrazene (TPT) acts as an effective inhibitor for the radical polymerization of vinyl monomers. As an extension of our study of the decomposition of TPT, our interests were directed to the effect of solvent viscosity on the decomposition. The present paper is mainly concerned with a detailed study on the decomposition of TPT in polyethylene glycol (PEG) thickened dimethylformamide (DMF) of varying viscosities.

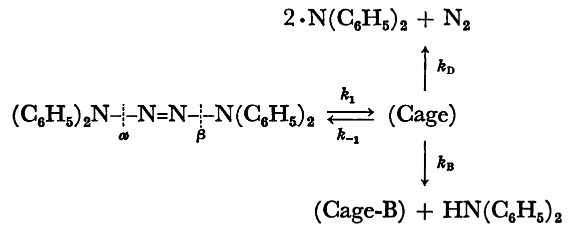
Experimental

Materials. TPT was prepared by oxidizing 1,1-diphenylhydrazine with manganese dioxide, according to the method of Bhatnagar.[8] DMF and PEG were purified in the usual manner.

Viscosity Studies. The stock PEG thickened DMF solution were prepared by dissolving 10 g of PEG of various degrees of polymerization in 100 ml of DMF. The degrees of polymerization of PEG used in this work were 200, 1000, 2000, 4000, 6000, and 20000. The viscosities of the solvent systems, DMF/PEG, were determined at 65, 70, 75, and 80 °C by using an Ostwald viscometer. The rates of decomposition of TPT in DMF and in the six DMF/PEG systems were determined by measuring the amount of nitrogen evolved, according to Overberger *et al.*[9]

Thermodynamic Parameters.[10] The Arrhenius energy of activation E_a, was calculated from a plot of log k_{obsd} *vs.* $1/T$. The enthalpy of activation was obtained from the equation $\Delta H^{\neq}=E_a+RT$. $\Delta S^{\neq}$ was evaluated from the Eyring's equation, $k_{obsd}=T/h\ \exp(-\Delta H^{\neq}/RT)\exp(\Delta S^{\neq}/R)$.

Theory for Qualititative Viscosity Test. The mechanism for the decomposition of TPT has been given as follows.[6d]



$$\begin{tikzcd} & 2\cdot \mathrm{N(C_6H_5)_2} + \mathrm{N_2} \\ \mathrm{(C_6H_5)_2N{-}\underset{\alpha}{\vdots}{-}N{=}N{-}\underset{\beta}{\vdots}{-}N(C_6H_5)_2} \arrow[r, shift left, "k_1"] & \text{(Cage)} \arrow[l, shift left, "k_{-1}"] \arrow[u, "k_D"'] \arrow[d, "k_B"'] \\ & \text{(Cage-B)} + \mathrm{HN(C_6H_5)_2} \end{tikzcd}$$

where k_1, k_{-1}, k_D, and k_B represent the rate constants for the bond homolysis, recombination of original geminate radicals, diffusive separation of the geminate radicals, and any other scission that competes with diffusion and cage return. In this case, the observed rate constant for the decomposition of TPT is given as

$$k_{obsd} = k_1(k_D+k_B)/(k_{-1}+k_D+k_B) \tag{1}$$

The viscosity of DMF/PEG may be written as[10]

$$\eta = A_{vis}\exp(E_{vis}/RT) \tag{2}$$

while the temperature dependence of the rate constant for the diffusion, k_D, can be expressed as[6d]

$$k_D = A_D\exp(-E_D/RT) \tag{3}$$

According to Pryor,[6d] the following relationship can be obtained for the decomposition of TPT in high viscosity media

$$1/k_{obsd} = 1/k_1 + (k_{-1}/k_1A_D)(\eta/A_{vis})^{1/2} \tag{4}$$

Equation 4 suggests that the decomposition of TPT maybe divided into two classes.[6d] i) $k_{-1}=0$, TPT decomposes by the synchronous scission of both α- and β-bonds to produce two diphenylamino radicals. The rate of decomposition may be independent of the solvent viscosity. ii) $k_{-1}\neq 0$, TPT decomposes by the scission of the α-bond only to give cage return in whichever solvent system by radical recombination. In this case, the k_{obsd} decreases as the viscosity of the solvent system increases.

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Results and Discussion

In order to use the viscosity test, it is necessary to adopt a solvent system in which the viscosity can be varied without sharply changing any other properties of the solvent. In this work, we chose DMF/PEG. There is no serious difficulty in using DMF/PEG in the application of the viscosity test to TPT, as discussed below.

Measurements of the Viscosity of DMF/PEG. The viscosities of DMF/PEG were measured over a temperature from 60 to 80 °C, and are listed in Table 1.

Arrhenius-like plots of the relative viscosity gave straight lines, from which the activation parameters, E_{vis} and A_{vis}, in Eq. (2) were calculated: they are also listed in Table 1.

Table 1. Activation parameters and relative viscosities of DMF/PEG at various temperatures

Pn of PEG^a)	Temperature				E_{vis} (kcal/mol)	A_{vis}
	80 °C	75 °C	70 °C	65 °C		
DMF alone	1.000^b)	1.045	1.075	1.128	2.30	0.0189
200(a)	1.022	1.264	1.325	1.406	2.58	0.0146
1000(b)	1.454	1.533	1.617	1.712	2.65	0.0158
2000(c)	1.722	1.817	1.911	2.037	2.79	0.0162
4000(d)	1.994	2.107	2.233	2.359	2.69	0.0220
6000(e)	3.223	3.484	3.669	3.895	3.22	0.0168
20000(f)	7.990	8.525	9.134	9.783	3.47	0.0285

a) Degree of polymerization of PEG as the high viscosity component in DMF. (See Experimental Section)
b) Absolute viscosity 0.507 cps.

Measurements of the Rate of Decomposition of TPT. The kinetics of decomposition of TPT were measured in DMF/PEG at various temperatures. The reaction rate was strictly first-order in TPT-concentration under our conditions.[11] The first-order rate constants are listed in Table 2.

Table 2. First-order rate constants (k_{obsd}) for the decomposition of TPT in DMF and DMF/PEG at various temperatures

Solvent^a)	$k_{\mathrm{obsd}} \times 10^5$ (s^{-1})			
	80 °C	75 °C	70 °C	65 °C
DMF alone	119	115	102	66.4
(a)	24.3	17.7	16.3	12.6
(b)	19.3	16.7	13.2	10.4
(c)	18.7	15.0	11.9	9.23
(d)	16.3	12.8	11.8	7.91
(e)	15.9	12.4	9.89	8.00
(f)	12.6	10.7	—	7.67

a) See Table 1.

As can be seen from Tables 1 and 2, the observed rate constant for the decomposition of TPT decreases with the viscosity of the solvent system. It may be concluded that the macroscopic viscosity reflects the resistance to translational motion of monomeric radicals in this solvent system.

Table 3. Thermodynamic parameters for the decomposition of TPT in various solvent systems

Solvent^a)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)
DMF alone	5.40	−58.9	26.2
(a)	8.85	−52.3	27.3
(b)	9.24	−51.7	27.5
(c)	10.1	−49.2	27.5
(d)	10.7	−47.8	27.6
(e)	11.0	−47.2	27.6
(f)	12.5	−43.3	27.8

a) see Table 1.

Arrhenius plots of the data in Table 2 yielded straight lines, from which the thermodynamic parameters were calculated by the method described in the Experimental Section. The results are shown in Table 3.

From the effect of the viscosity of the solvent system on the activation parameters, a compensating change[12] was found in the enthalpy and entropy of activation for the decomposition of TPT, as shown in Fig. 1.

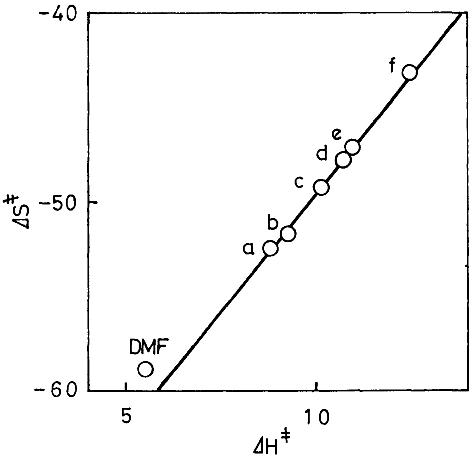
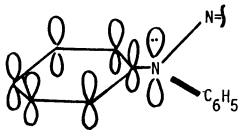


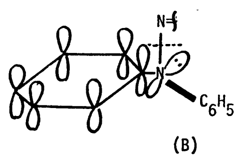
Fig. 1. Relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the decomposition of TPT
The solvent system are DMF, (a), (b), (c), (d), (e), and (f). (See Table 1.)

This finding suggests that a single mechanism is operative for the thermal decomposition of TPT in the DMF/PEG. Accordingly the variation in k_{obsd} with viscosity is not due to different decomposition mechanisms. It is suggested that the variation in $\Delta H^{\ddagger}$ does not depend on the different reaction mode, but depends on the change in apparent rate of decomposition, k_{obsd}.

On the other hand, the factor favoring the dissociation of the N–N single bonds of TPT is mainly responsible for the stability of the nitrogen radical. Large negative entropies of activation were observed in the decomposition of 2-tetrazenes. Nelsen[1e] reported that some 1,4-diaryl-1,4-dimethyl-2-tetrazenes decompose thermally in cumene with negative entropies. In the decomposition of 1,4-dimethoxycarbonyl-1,4-diphenyl-2-tetrazene the entropies were −14.2 cal/K in acetonitrile and −30.5 cal/K in dioxane.[5] It is considered that the delocalization of an odd electron on nitrogen should compete with that of a lone pair on the diphenylamino group at the time of decomposition of TPT. According to Nelsen,[1e] TPT is in conformation A with the lone pair electrons in a p orbital which overlaps with π system of phenyl ring. But the conformation B is needed for maximum stabilization of the odd electron of the diphenylamino radicals in the decomposition of TPT



(A)



(B)

It is obvious that the steric factor plays an important role in the bond homolysis of TPT. The change in $\Delta H^{\neq}$ is balanced by a corresponding change in $\Delta S^{\neq}$.

Viscosity Test. In order to check whether TPT decomposes by the initial scission of only one N–N bond (α-scission) or the synchronous scission of two single N–N bond (α,β-scission), k_{obsd} was plotted against the viscosity term.

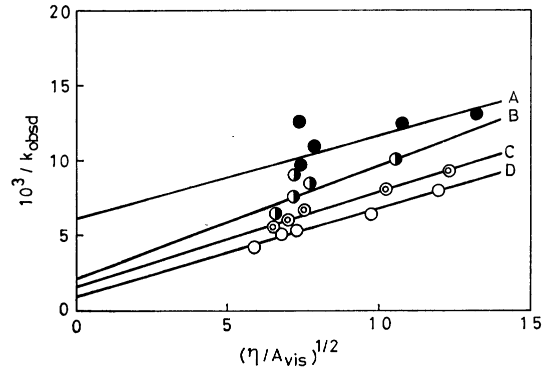


Fig. 2. Relationship between $1/k_{\text{obsd}}$ and $(\eta/A_{\text{vis}})^{1/2}$ for the decomposition of TPT in DMF/PEG at various temperatures. A; 65, B; 70, C; 75, D; 80 °C.

It was found that k_{obsd} decreased regularly as the solvent changed from low viscosity to high viscosity, as shown in Table 2. As can be seen from Fig. 2, the slopes of the lines are not zero in the decomposition of TPT in DMF/PEG. From Eq. (4), it may be concluded that TPT does not decompose by a concerted mechanism but decomposes by a two step mechanism. That is, TPT decomposes by the scission of only one N–N single bond, and undergoes cage return by recombination of radicals. The following mechanism of the decomposition is proposed to account for our observations:

$$\begin{tikzcd} (C_6H_5)_2N\text{-}N{=}N\text{-}N(C_6H_5)_2 \arrow[r, shift left] & {[(C_6H_5)_2N\text{-}N{=}N\cdot\ \cdot N(C_6H_5)_2]} \arrow[l, shift left] \arrow[d] \\ (C_6H_5)_2N\cdot + N_2 & (C_6H_5)_2N\text{-}N{=}N\cdot + \cdot N(C_6H_5)_2 \arrow[l] \end{tikzcd}$$

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