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Cage Effects in Dimethylaminyl Radical Formation

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ABSTRACT

The rate of decomposition of 1,1,4,4-tetramethyl-2-tetrazene (TMT) was measured in various unbranched alkanes of varying viscosities. The observed rate constant for the decomposition of TMT decreases with the viscosity of the solvent. A compensating change was found in the enthalpy and entropy of activation. It was also found that the decomposition of TMT occurs by the scission of only one N-N single bond and undergoes cage return in the alkanes by recombination of radicals.

INTRODUCTION

1,1,4,4-Tetramethyl-2-tetrazene (TMT) is able to initiate the radical polymerization of various vinyl monomers, such as ethylene [1-3], styrene [4, 5], and acrylonitrile [5, 6]. It has been demonstrated that the thermal decomposition of TMT is a first-order reaction and that the reaction process involves the homolytic fission of the nitrogen-nitrogen linkage to give two dimethylaminyl radicals with liberation of nitrogen [7]. Furthermore, it was reported that the activation energy of the decomposition of TMT is 31-36 kcal/mole with a corresponding preexponential factor log A of 11.4-14.4 [1, 8-10].

When a pair of dimethylaminyl radicals if produced from TMT in solution, it may either diffuse out of the solvent cage or recombine within the cage. The thermal decomposition of TMT has been thought of as proceeding by two possible mechanistic routes: the synchronous scission of two single N-N bonds to produce two dimethylaminyl radicals or nonconcerted decomposition as a two-step mechanism.

Although there has been great interest in this cage effect on the bond homolysis of various initiator such as peroxides and azoalkanes [11-14], systematic studies of the cage effect on the radical decomposition of TMT have not been reported. Continuing our investigation of the vinyl polymerization initiated by 2-tetrazenes, it was of particular interest to examine the effect of solvent viscosity on the decomposition of 2-tetrazene. The present paper deals with a detailed study on the effect of solvent viscosity on the rate of the decomposition of TMT in various unbranched alkanes.

EXPERIMENTAL

Reagents

1,1,4,4-Tetramethyl-2-tetrazene (TMT) was prepared according to the method of Bull et al. [15]; bp 31.5-32°C/15 Torr; λ_{max} (in hexane) 276 nm (log ϵ = 3.92). The unbranched alkanes hexane, octane, decane, dodecane, tetradecane, and hexadecane were purified by standard methods and then distilled twice under nitrogen before use. Their purities were checked by gas chromatography (GLC). The viscosities of the alkanes were determined at 110, 115, 120, 125, and 130°C by using an Ostwald viscometer.

Thermolysis Procedure

A known amount of TMT in alkane was placed in a glass tube which was cooled in a Dry Ice/methanol bath and sealed. The sealed tube was shaken in a thermostat maintained at a definite temperature. After thermolysis for a given time, the remaining content of TMT in the tube was determined by UV measurement.

UV Measurements

UV spectra were obtained with a Shimadzu UV-200S double-beam spectrophotometer. The rate of thermolysis of TMT in alkanes was determined by measuring the rate of disappearance of the absorption at 276 nm of TMT. The relation of absorbance versus concentration followed Beer's law in alkanes over the concentration range from 0.6 to 2.2×10^{-4} mole/liter. The observed first-order rate constants k_{obsd} were estimated from Eq. (1):

$$k_{obsd} = (1/t) \ln (D_0/D_t) \tag{1}$$

where D_0 and D_t represent the absorbances at zero time and time t, respectively.

Activation Parameters

The Arrhenius energy of activation E_a [16] was calculated from a plot of log k_{obsd} versus 1/T. The enthalpy of activation was obtained from the equation

$$\Delta H^{\ddagger} = E_a + RT$$

$\Delta S^{\ddagger}$ was evaluated from Eyring's equation,

$$k_{obsd} = \kappa T/h \exp \{- \Delta H^{\ddagger}/RT \} \exp \{\Delta S^{\ddagger}/R \}$$

RESULTS AND DISCUSSION

Measurement of the Viscosity of Alkanes

In order to see the effect of viscosity on the rate of the decomposition of TMT, it is necessary to use a solvent in which the viscosity can be varied without sharply changing any other properties of the solvent. In this work, the viscosities of alkanes were measured at

TABLE 1. Activation Parameters and Viscosities of Alkanes at Various Temperatures

n-Alkane	Viscosity (Cpoise) 110°C	115°C	120°C	125°C	130°C	E_{vis} (kcal/mole)	A_{vis}
Hexane	0.182	0.167	0.152	0.136	0.122	2.105	0.0145
Octane	0.346	0.329	0.312	0.295	0.277	2.420	0.0141
Decane	0.460	0.440	0.422	0.402	0.383	2.750	0.0124
Dodecane	0.778	0.757	0.736	0.714	0.695	3.020	0.0115
Tetradecane	0.896	0.872	0.849	0.823	0.802	3.340	0.0098
Hexadecane	0.920	0.883	0.859	0.829	0.803	3.570	0.0092

various temperatures. Arrhenius-like plots of the viscosities gave straight lines, from which the activation parameters E_{vis} and A_{vis} [Eq. (3)] were calculated. They are tabulated in Table 1.

Thermal Decomposition of TMT

The kinetics of decomposition of TMT were measured in alkanes over the temperature range 110-130°C. The reaction rate was strictly first-order with concentration of TMT under these conditions [10]. The observed rate constants k_{obsd} for the decomposition of TMT are listed in Table 2.

As can be seen from Table 2, k_{obsd} decreases with the viscosity of the solvent. It may be concluded that the macroscopic viscosity reflects the resistance to translational motion of dimethylaminyl radicals in alkanes.

Arrhenius plots of the data in Table 2 yielded straight lines, from which the activation 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 solvents on the activation parameters, a compensating change was found in the enthalpy and entropy of activation for the decomposition of TMT, as shown in Fig. 1. In addition, activation free energies are little influenced by any kind of alkanes. These findings suggest that a single mechanism is operative for the thermal decomposition of TMT in alkanes. Accordingly the variation of k_{obsd} with viscosity is not due to different

TABLE 2. First-Order Rate Constants (k_{obsd}) for the Decomposition of TMT in Alkanes at Various Temperatures

	$k_{obsd} \times 10^6$ (sec^{-1})				
n-Alkane	110°C	115°C	120°C	125°C	130°C
Hexane	1.20	2.20	3.31	6.70	11.8
Octane	1.11	2.07	3.25	6.29	10.8
Decane	1.07	2.03	3.18	6.25	10.2
Dodecane	0.89	2.00	3.00	6.11	9.44
Tetradecane	0.87	1.72	2.85	5.67	9.09
Hexadecane	0.75	1.44	2.71	5.32	8.14

TABLE 3. Activation Parameters for the Decomposition of TMT in Various Alkanes at 130°C

n-Alkane	$0.239\Delta H^{\ddagger}$ (kJ/mole)	$0.239\Delta S^{\ddagger}$ (J/mole-deg)	$0.239\Delta G^{\ddagger}$ (kJ/mole)
Hexane	36.0	7.73	32.9
Octane	36.9	9.83	33.0
Decane	37.4	10.9	33.0
Dodecane	39.2	15.2	33.1
Tetradecane	39.7	16.3	33.1
Hexadecane	41.1	19.5	33.2

decomposition mechanism. It is suggested that the variation of $\Delta H^{\ddagger}$ does not depend on the reaction mode, but depends on the change in the apparent rate of decomposition.

Qualitative Viscosity Test

In the reaction (2) k_1, k_{-1}, k_D, 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

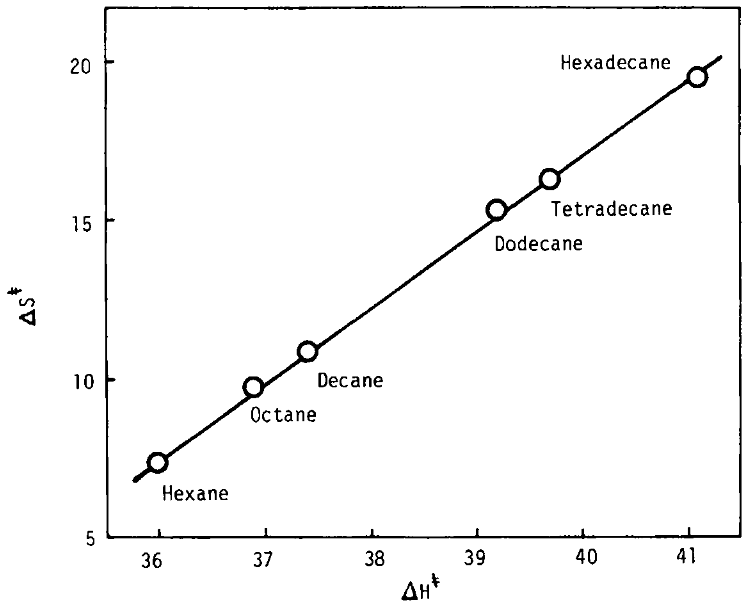
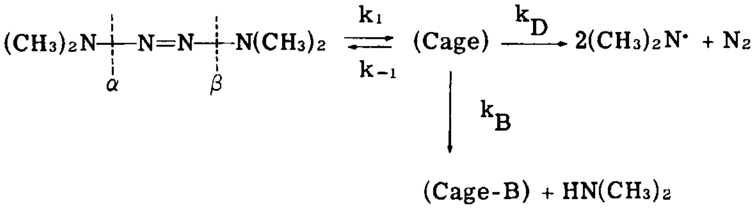


FIG. 1. $\Delta S^{\ddagger}$ vs. $\Delta H^{\ddagger}$ for the decomposition of TMT in various alkanes at 130°C.



$$\begin{array}{l} (CH_3)_2N\underset{\alpha}{\vdots}N{=}N\underset{\beta}{\vdots}N(CH_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{Cage}) \xrightarrow{k_D} 2(CH_3)_2N^{\cdot} + N_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow k_B \\ \qquad\qquad\qquad\qquad\qquad\qquad (\text{Cage-B}) + HN(CH_3)_2 \end{array} \qquad (2)$$

that competes with diffusion and cage return. In this case, k_{obsd} is given as

$$k_{obsd} = k_1(k_D + k_B)/(k_{-1} + k_D + k_B) \qquad (3)$$

The viscosity of alkanes may be written as [16]

$$\eta = A_{vis} \exp \{E_{vis}/RT\} \qquad (4)$$

while the temperature dependence of k_D can be expressed as [14]

$$k_D = A_D \exp \{-E_D/RT\} \tag{5}$$

According to Pryor [14], the following relationship can be obtained for the decomposition of TMT in high viscosity media;

$$1/k_{obsd} = 1/k_1 + (k_{-1}/k_1A_D)(\eta/A_{vis})^{1/2} \tag{6}$$

Equation (6) suggests that the decomposition of TMT may be divided into two classes.

Class I: $k_{-1} = 0$. TMT decomposes by the synchronous scission of both α and β bond. The rate of decomposition may be independent on the solvent viscosity.

Class II: $k_{-1} \neq 0$. TMT decomposes by the scission of the β bond only to give cage return in whichever solvent by radical recombination. In this case, the k_{obsd} decreases as the viscosity of the solvent increases.

In order to check whether TMT decomposes by the initial scission of only one N-N bond (β scission) or the synchronous scission of two single bonds (α,β scission), k_{obsd} was plotted against the viscosity term. As can be seen from Fig. 2, the slopes of the lines are not zero in the decomposition of TMT in various alkanes. Therefore, it is concluded that TMT does not decompose by a concerted mechanism but decomposes by a two step mechanism. That is, TMT decomposes by the scission of only one N-N single bond, and undergoes cage return by recombination of radicals. The same results have been obtained in the decomposition of tetraphenyl-2-tetrazene [17] and 1,4-dimethyl-1,4-diphenyl-2-tetrazene [18]. Accordingly it is generally concluded that the 2-tetrazene does not decompose through a concerted mechanism but decomposes by a two-step one.

Decomposition Mechanism

TMT is expected to act as the combination of three possible mesomeric structures [19] shown in Eq. (7)

$$(CH_3)_2\overline{N}-\overline{N}=\overline{N}-\overline{N}(CH_3)_2 \rightleftarrows (CH_3)_2\overline{N}^{+}=\overline{N}-\underline{\overline{N}}^{-}-N(CH_3)_2 \rightleftarrows$$

$$(CH_3)_2\overline{N}-\underline{\overline{N}}^{-}-\overline{N}=\overline{N}^{+}(CH_3)_2 \tag{7}$$

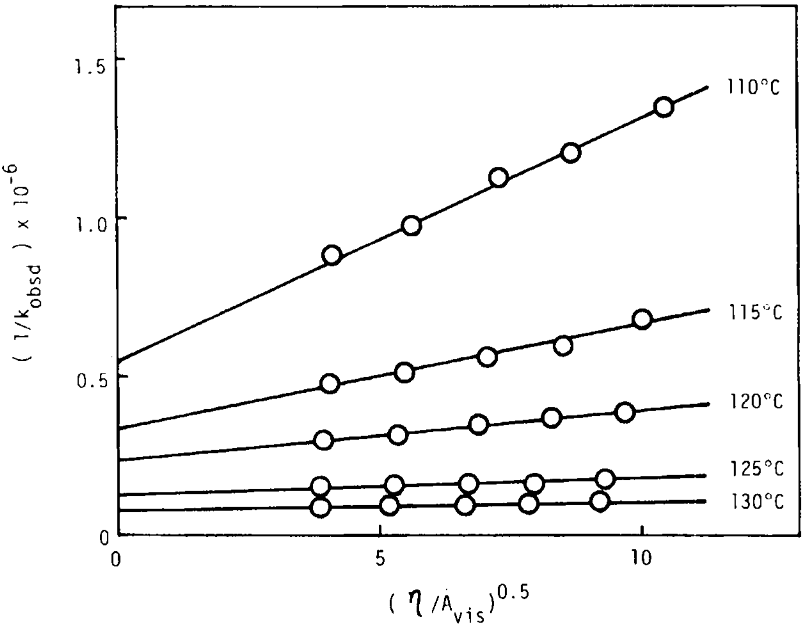
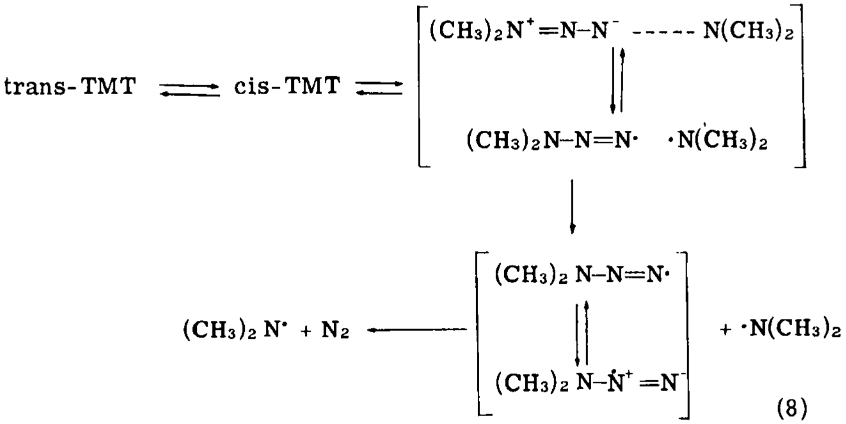


FIG. 2. Viscosity plots for the decomposition of TMT at various temperatures.



$$\text{trans-TMT} \rightleftharpoons \text{cis-TMT} \rightleftharpoons \left[\begin{array}{c} (CH_3)_2N^+{=}N{-}N^- \text{-----} N(CH_3)_2 \\ \updownarrow \\ (CH_3)_2N{-}N{=}N\cdot \quad \cdot N(CH_3)_2 \end{array}\right]$$

$$\downarrow$$

$$(CH_3)_2N^\cdot + N_2 \longleftarrow \left[\begin{array}{c} (CH_3)_2N{-}N{=}N\cdot \\ \updownarrow \\ (CH_3)_2N{-}\dot{N}^+{=}N^- \end{array}\right] + \cdot N(CH_3)_2 \qquad (8)$$

TABLE 4. Values of f_R for Decomposition of TMT at Various Temperatures

	f_R				
n-Alkane	110°C	115°C	120°C	125°C	130°C
Hexane	0.37	0.27	0.24	0.20	0.06
Octane	0.41	0.32	0.25	0.24	0.14
Decane	0.43	0.33	0.27	0.25	0.18
Dodecane	0.53	0.34	0.31	0.27	0.24
Tetradecane	0.54	0.43	0.34	0.32	0.27
Hexadecane	0.60	0.52	0.38	0.36	0.35

Though TMT is in the trans form in the ground state [20], it is possible for TMT to isomerize from trans to cis form in the transition state because of its small dipole moment (1.28 ± 0.01 D) [21]. Such a configuration change was found in the course of the photolysis of tetraisopropyl-2-tetrazene [22]. It was also shown that the steric factor plays an important role in the decomposition of aromatic 2-tetrazene, especially a series of 1.4-dimethyl-1,4-diphenyl-2-tetrazene and its several p-substituted derivatives [23].

The mechanism of the decomposition of TMT shown in Eq. (8) is, thus, proposed to account for the present observations.

Fraction of Cage Return

The fraction of the geminate pairs that give cage return, f_R, may be written as [14]

$$f_R = 1 - k_{obsd}/k_1 \tag{9}$$

We have used Eq. (9) to calculate the value of f_R for TMT. The results are shown in Table 4. The f_R decreases as the solvent viscosity decreases and the temperature increases. The temperature dependence of the f_R suggested the difference between the activation energy for diffusion and for cage recombination.

TABLE 5. k_1 for the Decomposition of TMT at Various Temperatures

Temperature (°C)	$10^6 \times k_1$ (sec^{-1})
110	1.91
115	3.01
120	4.36
125	8.38
130	12.6

Activation Parameter Based on k_1

The value for the decomposition of TMT were obtained from the intercepts in Fig. 2 as tabulated in Table 5. The activation parameters for the decomposition of TMT based on k_1 were estimated to be 31.6 kcal/mole, 0.24 cal/mole-deg, and 31.5 kcal/mole for $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$, respectively. A comparison of these data with those in Table 3 indicates the importance of β scission for the decomposition of TMT.

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