Kinetics of the Thermal Decomposition of Tetrakis(dimethylamino)ethylene in the Vapor Phase

Chas. E. Waring* and Raymond A. Berard

Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268 *(Received October 20, 1975)*

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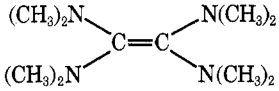
The thermal decomposition of the chemiluminescent compound tetrakis(dimethylamino)ethylene (TMAE) has been investigated in a static system between 283 and 323 °C over initial pressures from 6.0 to 45 mmHg. The order of the reaction was first, as was the order for the formation of methane and dimethylamine, the major decomposition products. The Arrhenius parameters for the TMAE decomposition are given as $k_i = 9.0(\pm 1.0) \times 10^{11}e^{-39\,900(\pm 2000)/RT}$ s^{-1} while those for CH_4 and DMA are $k_{CH_4} = 4.3(\pm 0.03) \times 10^{11}e^{-39\,300(\pm 300)/RT}$ s^{-1} and $k_{DMA} = 2.5(\pm 0.01) \times 10^{10}e^{-36\,500(\pm 200)/RT}$ s^{-1}, respectively. The effect of certain foreign gases indicated that the decomposition was free radical in nature. A mechanism is suggested which accounts for the predominant gaseous products and calculations from experimental data are offered in support of the proposed mechanism.

Introduction

Tetrakis(dimethylamino)ethylene (TMAE) was first reported by Pruett et al.[1] and its structure is given as



This molecule has many interesting characteristics. When exposed to air at ambient temperatures, it chemiluminesces strongly in the visible region. Winberg, Downing, and Coffman[2] report that the fluorescence and chemiluminescence spectra of TMAE are essentially equivalent and without fine-line structure, with the maxima at 5150 Å. Since the known oxidation products[3] do not fluoresce under these conditions, they conclude that an electronically activated TMAE molecule is the emitting species. From the overall chemiluminescence quantum yield, there appears to be only about three photons emitted for 10 000 molecules of TMAE oxidized. It is further reported[2] that the presence of protonic material is essential for chemiluminescence.

Fletcher and Heller[4,5] studied the kinetics of the oxidation of TMAE in decane using octanol as a catalyst. They found the rate of disappearance of TMAE to be first order and the chemiluminescence to be second. They conclude that the oxidation mechanism is not free radical in nature. Urry and Sheets,[6] on the other hand, investigated the autoxidation of TMAE in various solvents and give evidence for a free-radical mechanism. Paris,[7] however, proposes an oxidation process which depends upon carbene formation and subsequent recombination of two carbenes to form an electronically excited TMAE. The TMAE* then decays to the ground state with the emission of light.

It is clear from the literature that the mechanism of the oxidation of TMAE in solution is a complicated process. Because of this, various investigators have been unable to agree on the initial step, the products, or the mechanism of light emission. The purpose of this investigation is to examine first the high-temperature pyrolysis of TMAE vapor for unusual thermal reactions and to see if there is any correlation between these reaction products with those reported for the oxidation of TMAE at ambient temperatures. A subsequent paper will report on the kinetics of the gas phase oxidation of this unusual molecule.

Experimental Section

A. *Apparatus.* The thermal decomposition of TMAE was studied in a static manometric system. The reaction chamber was a 200-ml round-bottom Pyrex flask. This was centered in the furnace well and surrounded with asbestos. The furnace temperature was maintained to within ±0.5 °C by a Leeds and Northrup Electromax control unit. Temperatures were measured with a chromel–alumel thermocouple in conjunction with an automatic recording potentiometer.

The system was evacuated by the usual techniques and no run was made unless the pressure (as measured with an NRC ion gauge) was 10^{-5} mmHg or less. Due to the low vapor pressure of TMAE, samples were introduced into the reaction chamber from a large expansion flask. All external lines and the expansion flask were maintained at 120 °C by asbestos heating tape. The pressure change in the reaction chamber was followed by means of a Consolidated Electrodynamics Corp. absolute pressure transducer. Gaseous reaction products were withdrawn by an automatically controlled Toepler pump and transferred to a sample bulb.

B. *Materials.* The TMAE employed was obtained through the courtesy of the Naval Weapons Center, China Lake, Calif. It was placed in an I^2R drybag which had previously been purged with nitrogen and dried for 12 h with P_2O_5. The TMAE was then stirred with alumina to remove any polar products of oxidation, siphoned into an evacuated flask, removed from the drybag, and attached to the vacuum line through a Teflon connector.

Nitric oxide was obtained from the Matheson Co. and purified by methods previously described.[8]

Propylene was also furnished by the Matheson Co. It was vacuum distilled until a 99% purity was obtained.

The argon employed was from the Air Reduction Co. and the oxygen supplied by the Allstate Gas Co. Because of the high stated purity of these gases, they were used directly.

C. *Analyses.* Analyses of the gaseous reaction products were made on a Perkin-Elmer Model 154A gas chromatograph. The absolute identification of the components was checked on three different columns.

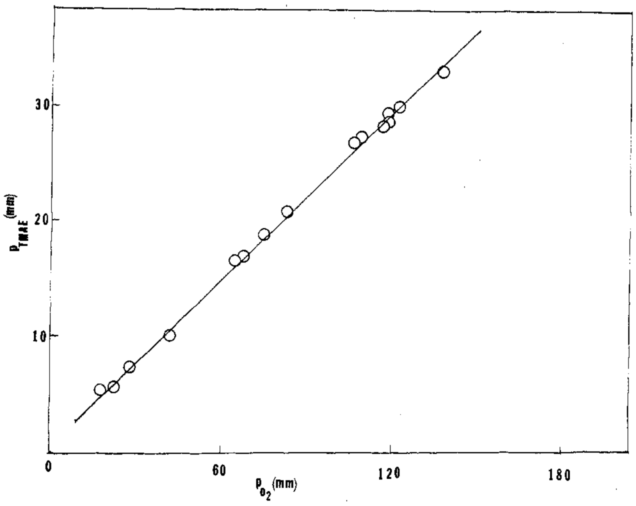


Figure 1. Calibration of the pressure of TMAE in the reaction vessel per mm of oxygen consumed in the special collector (slope = 0.242).

In order to determine the rates of disappearance of TMAE it was necessary to devise an analytical technique for measuring the amount of unreacted TMAE remaining. This was accomplished by adding an excess of oxygen to known amounts of TMAE and measuring the decrease in oxygen pressure which corresponded to the amount of TMAE consumed. Figure 1 shows the calibration curve in which the amount (mmHg) of TMAE in the reaction vessel is plotted against the corresponding amount (mmHg) of oxygen consumed. The slope of the line, which gives the ratio of the pressure of TMAE to the oxygen consumed, was 0.242. Thus, for each mmHg of TMAE present, 4.1 mmHg of O_2 are consumed.

Further, in order to determine if the products had any effect on the oxygen take-up, a sample of TMAE was pyrolyzed for 5 h, or until decomposition was complete. Upon addition of oxygen, no significant change in pressure was observed. It was concluded, therefore, that the products did not affect the TMAE analysis.

Results

1. *Nature of the Decomposition.* The thermal decomposition of TMAE vapor was found to be homogeneous over the temperature range 283–323 °C and over an initial pressure range of 6.0–45.0 mmHg. The ratio of the final to the initial pressure at five different temperatures was approximately 3.

2. *Order of Reaction.* For the decomposition of TMAE, the changes in pressure with time for ten different initial pressures were determined at five different temperatures. These data were programmed on an IBM 1620 computer to solve for k_i, the initial rate constant, and n, the order of reaction, in the equation

$$\log (dp/dt)_0 = \log k_i + n \log p_i \qquad (1)$$

The values of n varied from 0.9 to 1.1 over the five temperatures and the average value was 1.02, indicating that the order of the decomposition is unquestionably first.

Using the calibration curve in Figure 1, the order of reaction, based upon the measured rate of disappearance of TMAE, was also determined. As before, the initial rate of disappearance was evaluated at each initial pressure and the data programmed to obtain k_i and n by eq 1. These data are presented in Table I. A plot of log $(dp/dt)_0$ vs. p_i was also linear, giving a slope, n = 1.0.

TABLE I: Variation of the Initial Rate of Disappearance of TMAE with Initial Pressures at 310 °C

p_i, mm	8.7	15.4	19.3	27.3	32.0
$(dp/dt)_0 \times 10^3$	8.4	14.9	17.0	24.0	32.0
$k_i \times 10^4$ s^{-1}	9.61	9.67	8.82	8.80	10.0 (Av = 9.38)

TABLE II: Variation of Initial Rate Constants of TMAE, CH_4, and DMA with Temperature

t, °C	283	294	304	310	313	323
$k_{TMAE} \times 10^4$	1.89	3.38	5.15	9.56	11.9	20.9
$k_{CH_4} \times 10^4$			4.97		8.42	14.8
$k_{DMA} \times 10^4$			3.75		6.26	10.3

TABLE III: Mole Percent of Gaseous Products at 10 min from the Decomposition of 28 mm of TMAE at 323 °C

Product	CH_4	$(CH_3)_2NH$	$(CH_3)_3N$	CH_3NH_2	C_2H_6	$(CH_3)_2N$–CH_2–$N(CH_3)_2$
Mol %	63	35	<1	<1	<1	<1

Since methane and dimethylamine (DMA) were the only predominant products from the decomposition of TMAE, their initial rates of formation were also determined at various initial pressures of TMAE. Again, by use of eq 1, n and k_i were evaluated for each compound at three different temperatures. The order of reaction, n, was found to be 1.1 for CH_4 and 0.9 for DMA.

3. *Activation Energies.* The activation energies and frequency factors for the thermal decomposition of TMAE, and for the formation of CH_4 and DMA, were determined by the method of least squares from the data in Table II.

The Arrhenius parameters for the decomposition of TMAE are given by

$$k_i = 9.0(\pm 1.0) \times 10^{11} e^{-39\,900(\pm 2000)/RT} \text{ s}^{-1} \qquad (2)$$

The analogous expressions obtained for the formation of CH_4 and DMA are

$$k_{CH_4} = 4.3(\pm 0.03) \times 10^{11} e^{-39\,300(\pm 300)/RT} \text{ s}^{-1} \qquad (3)$$

and

$$k_{DMA} = 2.5(\pm 0.01) \times 10^{10} e^{-36\,500(\pm 200)/RT} \text{ s}^{-1} \qquad (4)$$

4. *Products of Reaction.* The thermal decomposition of TMAE produced only two major gaseous reaction products: methane and dimethylamine. Table III presents all the gaseous products that were formed. The identity of bis(dimethylamino)methane is somewhat uncertain since a known sample of the material could not be obtained. However, a mass spectrum of a chromatographic separation agrees well with the mass spectrum Urry[9] obtained for this compound.

Two condensable products were also obtained. One was a volatile, clear liquid and the other a dark brown, nonvolatile, viscous liquid. The infrared spectra of the two liquids show they are not very different. A further indication that they may be the same is the fact that, on standing, the clear liquid becomes dark brown and viscous, apparently due to polymerization. Attempts to identify this material further were unsuccessful. The spectra indicate the presence of C–H, C=C without associated olefin C–H stretching, and C≡N. The

TABLE IV: Partial Pressures (mm) of CH_4 and DMA from the Decomposition of 28 mm of TMAE at Various Temperatures

	304 °C		313 °C		323 °C	
Time, min	p_{CH_4}, mm	p_{DMA}, mm	p_{CH_4}, mm	p_{DMA}, mm	p_{CH_4}, mm	p_{DMA}, mm
1	0.8	0.5	1.4	0.7	2.6	1.8
2	1.6	1.1	2.7	1.4	4.7	3.2
4	2.8	1.9	5.0	2.6	8.6	5.3
6	4.1	2.6	6.7	3.6	11.2	6.8
8	5.2	3.0	8.1	4.3	13.2	7.9
10	6.1	3.4	9.4	4.9	15.2	8.8
12	7.0	3.8	10.6	5.5	16.7	9.7
15	7.8	4.2	12.1	6.4	18.6	11.2
					Av CH_4/DMA = 1.6	

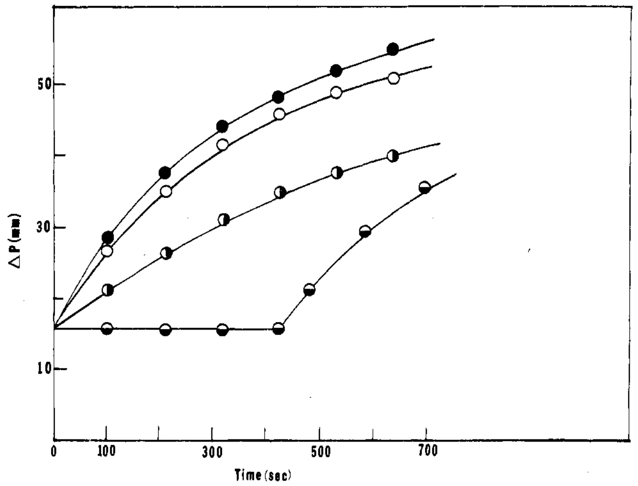


Figure 2. Variation of pressure with time for the decomposition of 28 mm of TMAE in the presence of various foreign gases at 317 °C: (○) 0 mm foreign gas; (◑) 30 mm of propylene; (●) 100 mm of argon; (⊖) 0.3 mm of nitric oxide.

presence of a conjugated system, C=C–N, is possible but difficult to determine with any certainty.

The change in the partial pressures of the major products of reaction with time at several different temperatures are given in Table IV.

5. *Effect of Foreign Gases.* A. *Propylene.* The addition of propylene significantly decreases the initial rate of decomposition of TMAE. Relatively large amounts of propylene are required to produce maximum inhibition. For example, 80 mm of this inhibitor are required to reduce 28 mm of TMAE to a limiting rate of one-quarter of that of the uninhibited reaction. Figure 2 compares the effect of propylene with the uninhibited decomposition of TMAE.

B. *Argon.* It was suspected that the inhibition by propylene might be due to a mass action effect rather than to an actual chain termination process. To resolve this, the rate of pressure increase for the decomposition of TMAE was determined in the presence of various partial pressures of argon. In Figure 2, it can be seen that 100 mm of argon in the presence of 28 mm of TMA produces only a slight increase in the rate of decomposition. This result clearly indicates that the propylene inhibition is not a mass action phenomenon. It does suggest, however, that the effect of argon may be to reduce chain termination at the walls.

C. *Nitric Oxide.* The effect of NO on the pyrolysis of TMAE was unusual. With the addition of 1.0 mm or less of NO to 28.0 mm of TMAE, there was an induction period of approximately 400 s. During this time, very little TMAE reacted. Throughout the induction period, the only gaseous decomposition products were methane, nitrogen, and small amounts of carbon monoxide. This is in sharp contrast to the products obtained from the uninhibited reaction. Table V gives the comparison between the rates of formation of CH_4 in the NO inhibited and uninhibited reactions. It is of interest to mention that rate of formation of CH_4 throughout the induction periods was always roughly inversely proportional to the rate of disappearance of NO.

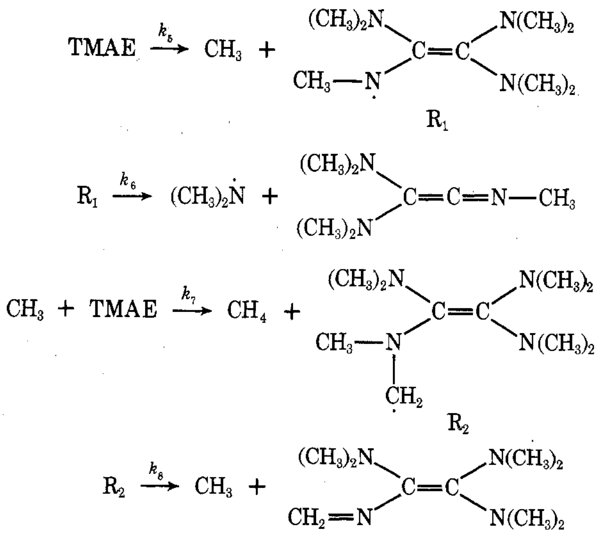
TABLE V: Comparison of the Rates of Formation of CH_4 from the Inhibited and Uninhibited Decompositions of 28 mm of TMAE at 313 °C (p_{NO} = 2.0 mm)

Time, s	100	200	300	400	500	600	700	800
$CH_{4(un)}$, mm	2.3	4.3	5.8	7.0	8.2	9.4	10.1	11.2
$CH_{4(in)}$, mm	0.13	0.24	0.34	0.43	0.50	0.56	0.61	0.65

A number of runs were made pyrolyzing a fixed partial pressure of TMAE in the presence of different initial pressures of NO. Under these conditions, the length of the induction period was a linear function of the partial pressure of NO. At the end of the induction period, mass spectrographic analyses showed no nitric oxide to be present. At this point, the rate of pressure increase is slightly greater than that in the absence of NO, as seen in Figure 2. In this latter pressure increase region, the proportion of the major gaseous products are the same as in the uninhibited reaction, namely, 63% CH_4 and 37% DMA.

Discussion

The inhibiting effects of propylene and nitric oxide indicate that the decomposition of TMAE vapor is undoubtedly free radical in nature. It is also reasonably certain that the overall mechanism of the reaction is more complicated than the detected products reported in Table III suggest. A plausible mechanism can be written, however, to account for the predominant products of the pyrolysis:



$$\mathrm{TMAE} \xrightarrow{k_5} \mathrm{CH_3} + \underset{\mathrm{R_1}}{(\mathrm{CH_3})_2\mathrm{N}(\mathrm{CH_3{-}\dot{N}})\mathrm{C{=}C}(\mathrm{N(CH_3)_2})_2} \qquad (5)$$

$$\mathrm{R_1} \xrightarrow{k_6} (\mathrm{CH_3})_2\dot{\mathrm{N}} + ((\mathrm{CH_3})_2\mathrm{N})_2\mathrm{C{=}C{=}N{-}CH_3} \qquad (6)$$

$$\mathrm{CH_3} + \mathrm{TMAE} \xrightarrow{k_7} \mathrm{CH_4} + \underset{\mathrm{R_2}}{(\mathrm{CH_3})_2\mathrm{N}(\mathrm{CH_3{-}N(\dot{C}H_2)})\mathrm{C{=}C}(\mathrm{N(CH_3)_2})_2} \qquad (7)$$

$$\mathrm{R_2} \xrightarrow{k_8} \mathrm{CH_3} + (\mathrm{CH_3})_2\mathrm{N}(\mathrm{CH_2{=}N})\mathrm{C{=}C}(\mathrm{N(CH_3)_2})_2 \qquad (8)$$

$$(\mathrm{CH_3})_2\dot{\mathrm{N}} + \mathrm{TMAE} \xrightarrow{k_9} (\mathrm{CH_3})_2\mathrm{NH} + \mathrm{R_2} \qquad (9)$$

$$\mathrm{CH_3} + \mathrm{R_2} \xrightarrow{k_{10}} \text{end} \qquad (10)$$

The justifications for the proposed mechanisms are as follows. If one compares the bond dissociation energies of various amines,[10] it is seen that the energy of the CH_3–N bond is decreased when the nitrogen is also bonded to a π-bonded system. In TMAE, where all the nitrogens are partially involved in the π bond of ethylene, the CH_3–N bonds are undoubtedly the weakest. This would tend to favor reaction 5 as the initial step over the elimination of a DMA radical. From an energetics standpoint, reactions 6–9 appear to be the most plausible ones to account for the formation of the two major products, CH_4 and DMA. The postulated product molecules in steps 6 and 8 are admittedly somewhat speculative and must be highly transitive. The compounds indicated, however, have been postulated by Urry,[9] based on NMR analyses, as intermediates in the reaction of TMAE with methyl iodide in dioxane.

If one applies the usual steady-state approximations to the postulated mechanism it can be readily shown that

$$[CH_3]_{ss} = (k_5 k_8/k_7 k_{10})^{1/2} \qquad (11)$$

and

$$[(CH_3)_2\dot{N}]_{ss} = k_5/k_9 \qquad (12)$$

The rate of disappearance of TMAE is then found to be

$$-d[\mathrm{TMAE}]/dt = \left[2k_5 + \left(\frac{k_5 k_7 k_8}{k_{10}}\right)^{1/2}\right][\mathrm{TMAE}] \qquad (13)$$

Thus, the rate of decomposition of TMAE is seen to be first order, in agreement with that observed experimentally.

There is support for the fact that methane and dimethylamine are produced predominantly by only one reaction, such as that proposed in steps 7 and 9. If one takes the ratios of the Arrhenius parameters for the formation of CH_4 and DMA, it can be seen from eq 3 and 4

$$\frac{k_{CH_4}}{k_{DMA}} = \frac{4.3 \times 10^{11} e^{-39\,300/RT}\ s^{-1}}{2.5 \times 10^{10} e^{-36\,500/RT}\ s^{-1}} = 17.20 e^{-2800/RT} \qquad (14)$$

that $E_9 - E_7 = 2.8$ kcal/mol. This represents the increase in activation energy required for a $(CH_3)_2\dot{N}$ radical to abstract a hydrogen from TMAE over that required for a $\dot{C}H_3$ radical to remove a similar H atom. If one assumes $E_7 = 7.2$ kcal/mol as an average value for the abstraction of an H atom from amines[11] by a methyl radical, then the activation energy for a similar abstraction by a $(CH_3)_2\dot{N}$ radical, E_9, becomes 10.0 kcal/mol.

Further, if one refers to the data in Table IV at 323 °C, it is seen that the ratio CH_4/DMA = 1.6. At this temperature, the ratio of k_{CH_4}/k_{DMA} is found by eq 14 to be 1.6. This excellent agreement between the observed and calculated values for the CH_4/DMA ratios provides additional support to the argument that these compounds are each the product of a single step reaction.

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COMMUNICATIONS TO THE EDITOR

Evidence for Superficial Reduction of NH_4Y Zeolite Silicon upon Pyridine Adsorption at 150 °C

Sir: A number of studies of zeolites by x-ray photoelectron spectroscopy (XPS) have recently been published,[1–4] but none so far has been concerned with adsorption phenomena of organic bases by zeolites. In particular, this problem constitutes a very interesting field to explore the potentialities of XPS for the characterization of surface acidity, a problem of major interest in catalysis. Some preliminary results[5] have shown that the position of the N_{1s} line of aniline adsorbed at room temperature depends on the activation temperature. It seemed interesting, therefore, to investigate this problem further by using other substances, e.g., pyridine. In infrared spectroscopy studies especially, the adsorption of pyridine has very often been carried out at 150 °C to prevent physisorption of the adsorbing molecule. For the sake of comparison, we have conducted some experiments involving the adsorption of pyridine at 150 °C. We report here the results obtained in this case. An unexpected experimental result brings a new complication in the study of surface acidity by XPS of adsorbed probe molecules.

The procedure includes an outgassing of the NH_4Y zeolite (Union Carbide no. 3606–385, Si/Al molar ratio: 2.2, exchange level: 72%) up to 300 °C at a very slow rate (<100 °C h^{-1}) under 10^{-5} to 10^{-6} Torr; the final temperature is maintained for another 5 h before cooling the sample to 150