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Oxidation and Chemiluminescence of Tetrakis(dimethylamino)ethylene

II. Kinetics and Mechanism of the 1-Octanol-Catalyzed Autoxidation

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The rate of oxidation of tetrakis(dimethylamino)ethylene (TMAE) has been measured over a range of concentrations and oxygen pressures at 30° in *n*-decane. The kinetics are first order in TMAE and oxygen and first and fourth order in respect to 1-octanol. A mechanism which explains the kinetics and fits earlier chemical studies is proposed. The catalysis is suggested to be the action of the proton donor upon the TMAE–oxygen donor–acceptor complex permitting ion-pair formation. Both the alcohol monomer and the tetramer, predominant in *n*-decane solutions, catalyze the reaction giving the variable order kinetics. The solvated ion-pair intermediate reacts unimolecularly to give the final products.

INTRODUCTION

Wiberg and Buchler (*1*) have recently published a large number of papers concerning the chemistry of tetrakis(dimethylamino) ethylene (TMAE). Winberg, Downing, and Coffman (*2*) have indicated that there is no significant irreversible reaction of TMAE with air so long as protonic materials are absent. It is the purpose of this paper to show the kinetics of the irreversible reaction of TMAE with oxygen in the presence of a protonic material, 1-octanol, and to postulate a mechanism for the reaction.

Since the major products of the autoxidation of TMAE in organic media are tetramethyloxamide (*1, 2*) (with an equivalent amount of tetramethylhydrazine) (*3*) and tetramethylurea there is, in effect, an addition of the oxygen to the carbon–carbon double bond. The usual product of the reaction of oxygen with a nonconjugated alkene is the formation of a hydroperoxide on the α-carbon through a free-radical chain-propagation step where the peroxide free radical abstracts the α-methylenic hydrogen of the alkene (*4, 5*). These reactions with oxygen are characterized by an induction period and a rate which is independent of the oxygen pressure (above 150 torr or lower). TMAE lacks the α-methylenic hydrogen, adds oxygen to the double bond, and we shall attempt to show that it does not react via a free-radical chain mechanism but rather via a series of ionic reactions.

EXPERIMENTAL

Equipment and materials. Some of the equipment and chemicals are described in a previous paper (*6*). A schematic diagram of the apparatus is given in Fig. 1. The 1-octanol was obtained from Matheson-Coleman and Bell as Lorol 20. It was dried over Molecular Sieve type 4A, filtered, and distilled under argon at atmospheric pressure. A Karl Fischer titration indicated a water content of less than 0.01%.

Procedure. For most of this work, the concentrations of the dissolved oxygen and the 1-octanol were essentially constant throughout the course of a reaction due to the low initial TMAE concentrations. The oxygen partial pressure was controlled between 10 and 1400 torr. Frequent reequilibration between the liquid and the gas phase

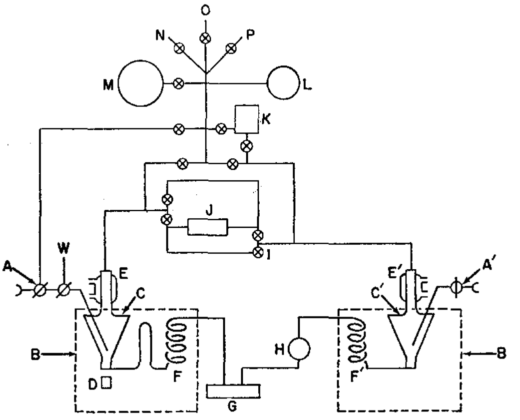

FIG. 1. Apparatus. Tetrakis(dimethylamino)-ethylene (TMAE) is introduced via stopcock A while *n*-decane and 1-octanol solutions are introduced at A′. The solutions are mixed by magnetic stirrer D in 500-ml reservoir flask C which are all contained in bath B. Condensers E–E′ prevent loss of liquid whenever the system is evacuated. For spectrophotometric measurements, the solution is forced through a 25-ft heat-exchanger coil F, through a 1-cm Beckman Spectrophotometer flow cell G, and through a 128-ml light-emission flow cell H. A reciprocating differential pressure maintains liquid at ±0.2° in G by means of programming electrical switches such as I. The pressure differential is supplied by Randolph tubing pump, J, with the oxygen being measured by Beckman E-2 oxygen analyzer K. Total pressure is indicated by Wallace and Tiernan pressure gage L. Vacuum, helium, and oxygen are available from N, O and P, and are premixed in 2000-ml flask M. The mixed gases may be used to force the TMAE solution into the reaction flask. Sample introduction line can be preflushed with TMAE or gas by transferring out waste line W.

was performed whenever there was danger of oxygen depletion. The TMAE was determined spectrophotometrically in the region of 300 to 350 mμ. Weighed solutions of 1-octanol were added to the system and measurements at 1.405 μ were used to evaluate the 1-octanol monomer concentration (7). All transfers were made with negligible contacts between the solutions and the atmosphere.

Many of the reactions were performed in the presence of the reaction products from previous runs. After the effects of variation of oxygen pressure were evaluated at one alcohol concentration, additional alcohol was added the to reaction mixture and the runs were continued at the new alcohol concentration. All runs were performed at 30° ± 0.2° using *n*-decane as the solvent.

RESULTS

The kinetics of reactions performed with and without the presence of reaction products were found to be the same. Reactions were usually performed until 90% to 95% of the initial TMAE had reacted. For TMAE in the concentration range from 10^{-5} to 2×10^{-3} M, a linear relationship between $\ln E$ and the time was found under conditions of constant oxygen and alcohol concentrations,

$$-\frac{d \ln E}{dt} = -\frac{dE}{E dt} = F[(\mathrm{O_2}),A] \qquad (1)$$

where E is the molar concentration of TMAE, t is the time in seconds, and $F[(\mathrm{O_2}),\mathrm{A}]$ is some function of the oxygen pressure in torr, $(\mathrm{O_2})$, and the molar alcohol concentration, A.

$F[(\mathrm{O_2}),A]$ was found to have a linear variation with the oxygen pressure as shown in Fig. 2 so that $F(A)$ was calculated by

$$F(A) = -\frac{d \ln E}{dt} \times \frac{1}{(\mathrm{O_2})} \text{ torr}^{-1} \text{ sec}^{-1} \qquad (2)$$

$F(A)$ was evaluated for varying amounts of 1-octanol added to the system. These results are shown in Fig. 3 where the added 1-octanol concentration, A_o, was varied between 0 and 0.58 M. These results show an apparent third order relationship for the added alcohol between 0.01 and 0.1 M, but this fails rather badly at concentrations above 0.1 M.

If the alcohol monomer concentration, A_m, is plotted rather than A_o, a linear log plot is found for even the highest concentrations of alcohol as shown in Fig. 3. In this case the alcohol monomer concentrations can also be determined using the relationships

$$A_o = A_m + 4A_p \qquad (3)$$

and

$$A_p/A_m^4 = 490 \qquad (4)$$

This relationship was determined through evaluation of the absorbance of the OH

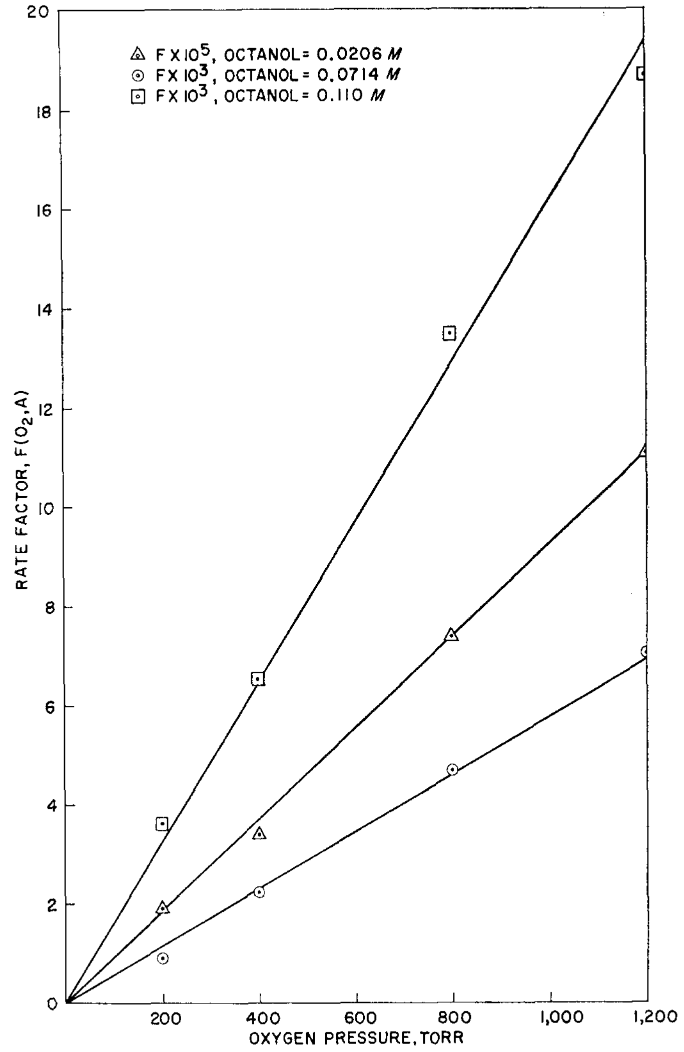

FIG. 2. Effect of oxygen pressure upon the rate of autoxidation of hmettetrakis(diylamino)ethylene.

overtone peak at 1.405 μ using a molar absorbancy index of 1.65 mole^{-1} liter cm^{-1}.[*]

By taking all values of $F(A)_m$ for A_m 0.02 M and higher and dividing by $A_m{}^4$ and averaging, it was found that

$$F(A_m) = 0.75A_m^4 \quad \text{for} \quad A_m > 0.02 \qquad (5)$$

$F(A)$ for the lower concentrations of A_m was evaluated by a linear plot of

$$[F(A_m) - 0.75A_m^4] = a + bA_m \qquad (6)$$

where a and b are constants. Attempts to fit a second order term only resulted in a poorer comparison of measured and calculated results.

Evaluation of the constants leads to

$$F(A_m) = 1 \times 10^{-9} + 4.6A_m \times 10^{-7} + 0.75A_m^4 \qquad (7)$$

Equation 7 is compared to the experimental results in Fig. 3. The average relative difference between calculated and observed for 56 points was found to be 26%, which is roughly twice the average relative difference between an observed rate and the mean value for a specific alcohol concentration.

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[*] This value was obtained at concentrations below 0.01 M where the predominant species is the monomer. It is intended to describe this work in greater detail in a separate paper.

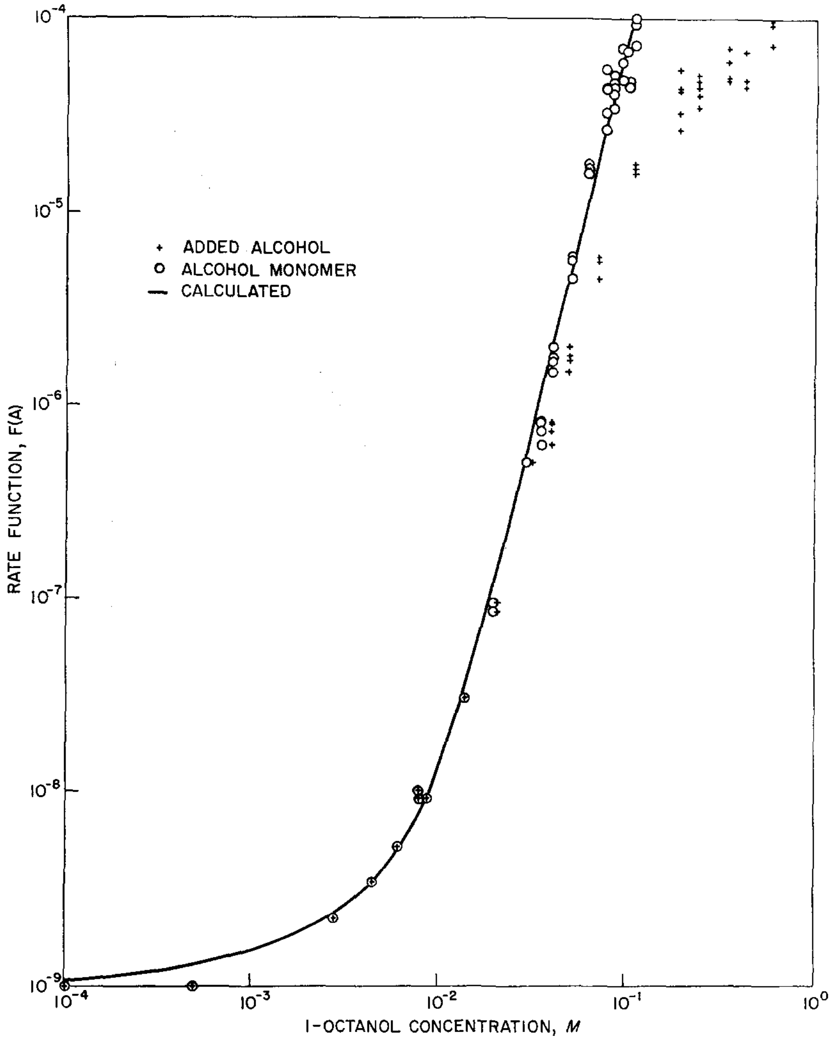


FIG. 3. Effect of the 1-octanol concentration upon the rate of autoxidation of tetrakis(dimethylamino) ethylene. For purposes of illustration on the log plot, the zero alcohol concentration was plotted at a concentration of 10^{-4} *M*.

It has been reported (*2*) that alcohol is consumed in the course of the irreversible oxidation of TMAE. We do not find this to be true where the TMAE concentration is below 10^{-3} *M*. At higher concentrations, however, a decrease in the alcohol absorbance at 1.405 μ is observed. Complete oxidation of 4.3×10^{-2} *M* TMAE caused the alcohol concentration to be reduced from 1.26×10^{-2} down to 0.63×10^{-2} *M*; one molecule of 1-octanol was consumed for seven of TMAE.

In order to evaluate whether the catalysis of autoxidation by protonic agents might be due only to their polarity, the rate of autoxidation in the presence of a few polar nonhydroxylic materials was measured. These results are compared with the rate in pure decane and an octanol solution in Table 1.

DISCUSSION

Reaction Kinetics

The first order dependence of the rate of reaction of TMAE upon the TMAE con-

TABLE 1

EXAMPLES OF REACTION RATE FUNCTIONS, $F(A)$, FOR VARYING CHEMICALS DISSOLVED IN n-DECANE

Chemical	Concentration	$F(A) \times 10^9$
Decane[a]	100%	1.0
Diethylene glycol dimethyl ether[a]	0.35 M	0.94
Dioxane[a]	100%	165.
Valeronitrile[b]	0.057 M	1.5
Valeronitrile[b]	2.16 M	675.
1-Octanol[b]	0.050 M	1800.

[a] Distilled from sodium.

[b] Dried with Molecular Sieve type 4A.

centration and the oxygen pressure is straightforward. The alcohol rate factor, $F(A)$, has been evaluated on the basis of three terms. The constant term in Eq. (7) can be best interpreted through the chemiluminescence of TMAE. Light emission studies, which will be the next paper of this series, gave a strong indication of a wall effect. A 128-ml vessel was drained of a TMAE-decane mixture so that only the liquid on the walls remained. The chemiluminescent light dropped to only 20% of the value observed from the filled vessel. With any appreciable amount of alcohol present, the light from the drained vessel was less than 1% of the value observed from the filled vessel.

Since glass is known to have surface OH groups, and a high affinity to adsorb hydroxylic materials, (*8*), we attributed the rate without added alcohol to be due primarily to a wall catalysis by these OH groups.

The measured values of $F(A)$ for A_0 below 0.01 M show close agreement with each other even though the results were obtained with several different distillations of n-decane. We interpret this to indicate that the effects of impurities were reasonably low. The effect of impurities would be additive to the wall effect in the first constant term of Eq. (7), but any fluctuation in their concentration should be quite evident in the region where the first power of the alcohol concentration yields the predominant term.

The presence of a fourth order term with the absence of any observable second or third order effects is the really interesting feature of Eq. (7). The spectrophotometric results leading to Eqs. (3) and (4) and the rate data both tend to indicate that 1-octanol exists in n-decane primarily as a monomer and a tetramer. If the tetramer concentration, A_p, is substituted in Eq. (7) through use of Eq. (4), then the complete rate expression can be written as

$$-dE/dt = E \times (O_2)[1.0 \times 10^{-9} + 4.6 \times A_m \times 10^{-7} + 1.5A_p \times 10^{-3}] \text{ mole liter}^{-1} \text{ sec}^{-1} \quad (8)$$

Since the rate constant for the tetramer is a thousandfold greater than that for the monomer, it is reasonable to expect that the rate constants for dimers and trimers would be intermediate. The rate of reaction of TMAE serves as a fairly sensitive indicator that the concentrations of dimers and trimers must be quite low compared to that of the monomer.

Reaction Mechanism

Alcohols can be used as inhibitors of free-radical chain reactions (*5*) yet they are found to catalyze the oxidation of TMAE. Urry and Sheeto (*3*) find that even the strong free radical inhibitor (*5*) 2,6-di-*tert*-butyl-4-methylphenol catalyzes the reaction. These facts coupled with the lack of an initiation time and the proportionality of the rate of the reaction upon oxygen pressures up to ten times the maximum value observed for free radical chain reactions, lead us to the conclusion that some other mechanism is required.

Carpenter (*9*) presented evidence that TMAE reacts with polyhalogenated species via an ionic mechanism. Since it has been shown that oxygen can interact directly with TMAE to form a donor–acceptor complex (*6*), it appears reasonable to consider that the polar alcohol might solvate the complex to form an ion pair. This type of interaction has been previously suggested by Mulliken (*10*). The observed kinetics and the mechanism offered below are self-consistent with the concept that the lifetime of the donor–acceptor complex is sufficiently long so that it may be considered as a recognizable kinetic entity (*6*).

Our mechanism for the autoxidation of TMAE is in accord with both the kinetics and the known chemistry of TMAE and oxygen. TMAE can form both a cation radical and a dication (*11*). The cation radical has been shown to exist in *n*-decane-TMAE-oxygen solutions as measured by an absorbance at 405 mμ (*6*) while the dication is the major reaction product for the autoxidation of TMAE over aqueous solutions (*3*). These solutions after oxidation have been shown to also contain large quantities of hydroperoxide (*3*).

The following mechanism is offered as a general outline of the type of reaction intermediates which can explain the kinetics as presently known:

$$E + O_2 = E \cdot O_2 \qquad (9)$$

$$E \cdot O_2 + A \rightarrow E^+O_2^- \text{ (solv.)} \qquad (10)$$

$$E^+O_2^- \text{ (solv.)} \rightarrow E^{2+}O_2^{2-} \text{ (solv.)} \qquad (11)$$

$$E^{2+}O^{2-} \text{ (solv.)} \rightarrow \text{products} + A \qquad (12)$$

Using the steady state assumptions and assuming a rapid equilibrium for reaction (9)

$$-dE/dt = K_9k_{10}(E)(O_2)(A) \qquad (13)$$

where K_9 is the equilibrium constant for reaction (9) and k_{10} is the rate constant for reaction (10). Here A can be the reaction vessel wall, alcohol monomer, or tetramer, each with its own value for k_{10}. This relatively simple mechanism thus fits the observed high-order kinetics.

Reaction 9, forming a donor–acceptor complex, was described in the first paper in this series (*6*) and is too rapid to measure by our techniques. It is reasonable to consider that its equilibrium would not be significantly disturbed by reaction (10).

We indicate reaction (10) as forming an ion pair where the oxygen radical anion is solvated. The enhanced solvolytic effect of hydroxylic groups in the formation of carbonium ion pairs has been explained on the basis of hydrogen bonding to the anion of the pair (*12*). The data given in Table 1 indicate that even very large concentrations of polar nonhydroxylic molecules show very little catalytic effect upon the autoxidation of TMAE. In this instance, we interpret the catalytic effect of the alcohol as being the same as in the formation of a carbonium ion, except that it is now a third species, oxygen, which forms the anion rather than the catalyst or the starting material.

Reaction (11) is not kinetically separate from reaction (10), but a one-electron step has been demonstrated for both TMAE (*11*) and O_2 (*13*). The latter work has also shown that the oxygen molecule can easily go to O_2H^- when protons are available. Perhaps reactions (10) and (11) should be written as

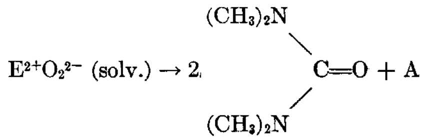
$$E \cdot O_2 + A_n \rightarrow [E^{2+}(HO_2^-)OR^-] \text{ (solv.)} \qquad (10\text{–}11b)$$

where *n* indicates the number of monomer units which have self-associated. Because members of intimate ion pairs have been shown to not be in "mass law" equilibrium with common ions in solution (*14*, *15*), we cannot postulate whether the anion is peroxy or hydroperoxy. If it is hydroperoxy then an additional equilibrium can be written for the exchange of the proton,

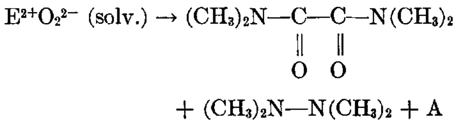
$$[E^{2+}(HO_2^-)OR^-] \text{ (solv.)} = E^{2+}O_2^{2-} \text{ (solv.)} \qquad (11c)$$

This proton transfer, if it occurs, would be expected to be quite rapid and would not affect the mechanism as written.

Reaction (12) can be described as having two reaction paths



$$E^{2+}O_2^{2-} \text{ (solv.)} \rightarrow 2\,((CH_3)_2N)_2C{=}O + A \qquad (12a)$$



$$E^{2+}O_2^{2-} \text{ (solv.)} \rightarrow (CH_3)_2N{-}C({=}O){-}C({=}O){-}N(CH_3)_2 + (CH_3)_2N{-}N(CH_3)_2 + A \qquad (12b)$$

These reactions would seem more reasonable for an ion pair $E^{2+}O_2^{2-}$ (solv.) than for $[E^{2+}(HO_2^-)OR^-]$ (solv.).

The predominance of the dication as the product for reactions of TMAE over water can be explained on the basis that the peroxy anion is protonated and through further solvation is separated from the dication to form solvent-separated ion pairs or completely dissociated ions. Thus we picture a solvated ion pair as a reaction intermediate leading to tetramethylurea or tetramethyloxamide while the dissociated ions dissolve in water as the dication and hydroperoxy anion.

The High Kinetic Order of Alcohol

High-order effects specific to alcohols (*12*) are apparently common in the formation of carbonium ions in nonpolar media. Hudson and Saville find a third-order dependence on the added alcohol concentration in the ethanolysis of triphenylmethyl chloride (*16*). Similarly, they obtain a third order in the ethanolysis of *p*-nitrobenzoyl and acetyl chloride in CCl_4 except for the higher concentrations where the rate approached first order (*17*). This is quite similar to the curve for added alcohol shown in Fig. 3. Thus if they had plotted the alcohol monomer concentration rather than total alcohol, their data probably would have also given a fourth-order relationship.

Hudson and Saville evaluated their high order in alcohol on the basis that the alcohol self-associated and that only the decomposing aggregate served to catalyze the reaction. We agree with their argument with the additional statement that we feel that the lack of effects from other polymeric species is due to their very much lower concentration since we can measure an effect from the monomer alone.

As Hudson and Saville indicate, with a high solvolytic effect due to a polymer, it is not possible to determine whether all of the monomeric species in the polymer serve to catalyze the reaction. Only one of the monomeric units of the tetramer may serve to solvate the peroxy anion.

ACKNOWLEDGMENT

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NOTE ADDED IN PROOF. Our most recent work on the self-association of 1-octanol indicates that both linear and cyclic tetramers are formed. The enhanced catalytic effect of the tetramer compared to the monomer may be due to the greater acidity of the non-hydrogen-bonding proton of the terminal -OH of the linear tetramer. In this case, one would predict that reaction (10–11b) holds and that the linear tetramer would have a very much larger catalytic effect than the cyclic tetramer. Dimers and trimers would also be expected to have an enhanced catalytic effect since they are probably linear (cyclization requires bending the hydrogen bond for polymers smaller than the tetramer). Again since second and third order effects are missing, the dimer and trimer must be in very low concentrations.

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