

Communications to the Editor

Metal Ion Catalyzed Decomposition of Tetramethyl-1,2-dioxetane in Methanol

Sir:

We have previously shown¹ that the greatly increased rates of decomposition of tetramethyl-1,2-dioxetane (TMD) in methanol and ethanol² were due to trace amounts of catalytic impurities in those solvents. We have since found that many transition metal ions catalyze the decomposition of TMD.

The catalytic effects of the following series of transition metal ions (as the dichlorides) were investigated: Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Mn²⁺, and Cd²⁺. Treatment of TMD in CD₃OD with 1 equiv of each salt at room temperature resulted in the quantitative formation of acetone. The rate of decay of chemiluminescence³ of TMD in treated methanol⁴ with 9,10-dibromoanthracene as fluorescer was measured at 57° before and after the addition of known amounts of transition metal chlorides (in treated methanol). The second-order rate constants for the catalyzed decomposition, k_2 , were calculated by the following expression

$$k_2 = \frac{k_{\text{obsd}} - k_u}{[\text{metal salt}]} = \frac{k_{\text{cat}}}{[\text{metal salt}]}$$

where k_u is the rate constant for the uncatalyzed decomposition and k_{obsd} is the observed rate constant for the catalyzed decomposition. Although the rates of decomposition of TMD in the presence of metal ions were much greater than the uncatalyzed rates, the initial intensity of chemiluminescence immediately after the addition of metal ions was never greater than that before addition of the catalysts, in accord with previous evidence that the catalyzed decomposition was nonchemiluminescent.¹

Cupric ion was found to be the most effective of these metal ions in catalyzing the decomposition of TMD. The cupric ion-catalyzed decomposition was of first order with respect to both TMD and metal ion.⁵ A counterion effect⁶ was observed for the cupric ion catalysis (Table I). The data in Table I indicate that the greater the complexation of the metal ion, the less effective the catalysis and that the uncomplexed metal ion was necessary for most efficient catalysis.

Addition of equal molar CuCl₂·2H₂O to solutions of TMD in acetonitrile-*d*₃ produced a yellow-green solution in contrast to the pale blue solution produced

upon adding CuCl₂·2H₂O to methanol-*d*₄. The nmr spectrum of the acetonitrile-*d*₃ solution showed slow decomposition of TMD to acetone (approximately 20% acetone after 60 min) whereas the reaction was found to be essentially instantaneous in methanol-*d*₄. Cupric chloride does not readily dissociate in acetonitrile but forms a complex [CuCl_{*n*}(CH₃CN)]_{4-*n*}^{(*n*-2)-}, *n* = 0-4.⁷ In methanol, CuCl₂ dissociates to the solvated ion Cu²⁺-(MeOH)_{*z*}. Two necessary conditions for catalysis are dissociation of the metal salt and rapid exchange of ligands around the metal ion.

Table I. Cupric Ion^a Catalyzed Decomposition of TMD^b in Treated Methanol

Anion or salt	[Anion]/[Cu ²⁺]	k_{cat} , sec ⁻¹ (at 57°)
None		8.6×10^{-2}
NaO ₂ CCH ₃	2.1	2.6×10^{-2}
Troponoxy ^c	2.0	1.4×10^{-3}
Na citrate	2.0	4.0×10^{-4}
Na ₂ EDTA	1.2	0

^a [CuCl₂] approximately 6.6×10^{-5} M; [DBA] = 7.8×10^{-4} M. ^b [TMD] ≈ 10^{-3} M. ^c No Na⁺ or Cl⁻ present.

The second-order rate constants, k_2 , for the catalyzed decompositions and experimental conditions have been summarized in Table II. A linear free energy correla-

Table II. Catalyzed Decomposition of TMD^a by Metal Ions in Treated Methanol at 57°

Salt ^b	[Metal ion], ^c M	k_2 , M ⁻¹ sec ⁻¹	Log k_2	-Log K_{MAL} ^d
CuCl ₂ ·2H ₂ O	$67-3.2 \times 10^{-6}$	1,300	3.114	+5.553
NiCl ₂ ·6H ₂ O	$16-1.5 \times 10^{-5}$	9.6	0.982	+4.004
CoCl ₂ ·6H ₂ O	$6.4-1.6 \times 10^{-4}$	2.3	0.362	+3.721
ZnCl ₂	$4.6-2.3 \times 10^{-4}$	1.3	0.114	+3.65 ^e
MnCl ₂ ·4H ₂ O	$16-8.0 \times 10^{-5}$	0.6	-0.222	+3.293
CdCl ₂	$12-6.2 \times 10^{-4}$	0.2	-0.698	+3.252

^a [TMD] was approximately 10^{-3} M; [DBA] was 7.8×10^{-4} M for all salts except NiCl₂·2H₂O (for which [DBA] was 1.5×10^{-5} M); the solvent system consisted of 50 μl of benzene and 550 μl of treated methanol (this amount of benzene had no effect upon the catalysis). ^b Added in treated methanol. ^c The catalytic constants, k_2 , for the less effective metal ions decreased at higher concentrations of the metal ion. ^d See ref 8b. ^e Taken from ref 8a.

tion was found between the logarithms of these catalytic rate constants and the Lewis acidities of the metal ions, as measured by the negative logarithms of the dissociation constants (K_{MAL}) of the metal malonates.⁸ A plot of log k_2 vs. -log K_{MAL} afforded a straight line (Figure 1).

(7) A. G. Massey, "Comprehensive Inorganic Chemistry," Vol. 3, A. F. Trotman-Dickenson, Ed., Pergamon Press, Elmsford, N. Y., 1973, Chapter 27, p 62.

(8) (a) M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins," Wiley, New York, N. Y., 1971, p 218; (b) J. E. Prue, *J. Chem. Soc.*, 2337 (1952).

(1) T. Wilson, M. E. Landis, A. L. Baumstark, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **95**, 4765 (1973).

(2) (a) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **95**, 264 (1973); (b) *Pure Appl. Chem.*, **33**, 363 (1973).

(3) The instrumentation was identical with that previously described: T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).

(4) Methanol was freed of most catalytic impurities by stirring with Chelex 100 for at least 4 days followed by a low temperature molecular distillation. Typical rate constants for thermolysis of TMD in this treated methanol were in the range $5-15 \times 10^{-5}$ sec⁻¹ at 57°.

(5) The pseudo-first-order rate constant was constant through at least three half lives. A 20-fold variation in cupric ion concentration resulted in a 20-fold variation in the pseudo-first-order rate constant.

(6) Such effects of counterions on rates of catalysis by metal ions (acting as Lewis acids) have been observed before. See, for example, R. Steinberger and F. H. Westheimer, *J. Amer. Chem. Soc.*, **73**, 429 (1951).

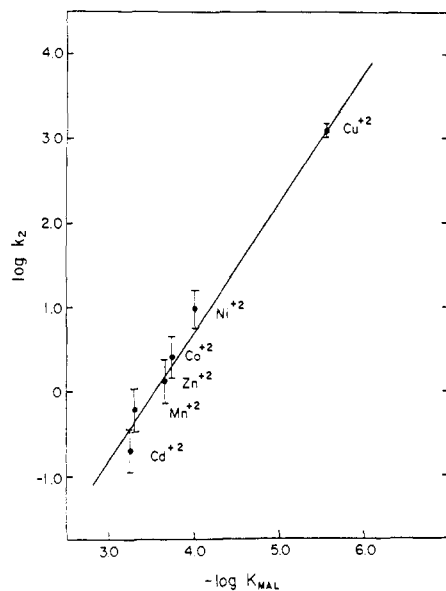
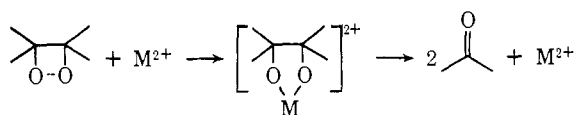
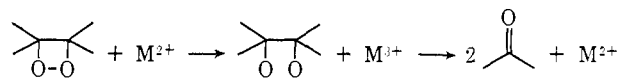


Figure 1. Linear free energy relationship for the metal ion catalyzed decomposition of TMD.

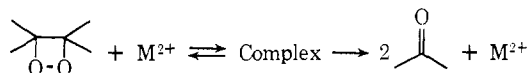
Three mechanistic possibilities can be considered for the observed catalysis: (a) insertion



(b) electron transfer



(c) coordination or Lewis acid



An insertion mechanism requires a formal two-electron oxidation of the metal ion while an electron transfer mechanism involves a one-electron oxidation. Both of these mechanisms seem unlikely because the logarithms of the second-order rate constants (k_2) do not correlate with either the third or the sum of the third and fourth ionization potentials⁹ of the neutral metals.

A coordination mechanism, involving the metal ion as a Lewis acid, is completely consistent with the counterion effect and the linear free energy relationship. Complexation of TMD by a metal ion might facilitate decomposition by removing orbital symmetry restrictions¹⁰ or by lending positive character to one or both oxygen atoms, thereby destabilizing the peroxy bond and allowing for a more facile ring cleavage.

Currently, research is in progress to determine whether the complexation involves one or both oxygen atoms of TMD. We shall report shortly on the rearrangements of TMD by strong Lewis acids.

Acknowledgments. This work was supported by grants from the National Science Foundation and the

(9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley, New York, N. Y., 1972, p 801.

(10) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

National Institutes of Health. We thank Dr. T. Wilson for the use of her chemiluminescence-monitoring system.

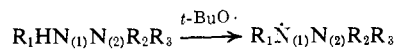
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Electron Paramagnetic Resonance Spectra of Alkylhydrazyl Radicals in Solution¹

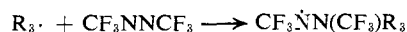
Sir:

The solution epr spectra of a great many trisubstituted hydrazyls containing aryl substituents and other electron withdrawing substituents have been known for many years.² Only recently has interest turned toward trialkylhydrazyls with Nelson and Landis' discovery³ that two bicyclic hydrazyls, $[(\text{CH}_2)_n\text{CHNN}[\text{C}(\text{CH}_3)_3]\text{CH}(\text{CH}_2)_2]$ ($n = 1$ and 2), were remarkably long lived. In this communication, we report epr spectral parameters for the first acyclic and monocyclic trialkylhydrazyls⁴ and for the first 1,2-dialkylhydrazyl to be observed in solution.

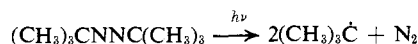
The majority of the radicals were generated by the technique we have used previously to produce 2,2-dialkylhydrazyls⁵ and 1-alkylhydrazyls,⁶ viz., photolysis of solutions of the parent hydrazines in di-*tert*-butyl peroxide directly in the cavity of an epr spectrometer.



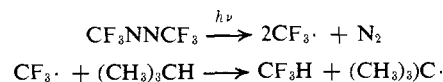
1,2-Di(trifluoromethyl)-2-alkylhydrazyls ($\text{R}_1 = \text{R}_2 = \text{CF}_3$) were prepared by alkyl radical addition to azo-trifluoromethane.



For $\text{R}_3 = t$ -butyl, the CF_3NNCF_3 was photolyzed either with azoisobutane in the absence of solvent



or in isobutane



The same spectrum was obtained in $(\text{CD}_3)_3\text{CD}$ and a closely analogous spectrum was produced in isopentane^{7,8} but not in cyclopentane (presumably be-

(1) Issued as N.R.C.C. No. 14204.

(2) For a leading review see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968. For more recent work see, e.g., A. T. Balaban and R. Istratiou, *Tetrahedron Lett.*, 1879 (1973); V. Malatesta and K. U. Ingold, *ibid.*, 3311 (1973).

(3) S. F. Nelson and R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 6454 (1973).

(4) Two tris(trialkylsilyl)hydrazyls, $(\text{R}_3\text{Si})\text{NN}(\text{SiR}_3)_2$, have been described very recently: R. W. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **95**, 7897 (1973).

(5) V. Malatesta and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6110 (1973).

(6) V. Malatesta, D. Lindsay, E. C. Horswill, and K. U. Ingold, *Can. J. Chem.*, **52**, 864 (1974).

(7) Unless oxygen and hydroperoxides are carefully eliminated the corresponding hydrazoxyl radical is formed,⁹ $\text{CF}_3\text{N}(\dot{\text{O}})\text{N}(\text{CF}_3)\text{R}_3$; $g = 2.0062$; $a^{\text{N}} = 1.3$ and 11.9 ; $a^{\text{F}}(3\text{F}) = 2.4, 7.4$ G. This radical is stable indefinitely at room temperature. At low concentrations it disappears temporarily during photolysis.