color persisted for 30 min. A few drops of 5% sodium bisulfite solution was added to discharge most of the brown color. The reaction mixture was separated and the organic layer was washed with saturated potassium carbonate solution and dried over magnesium sulfate. The acetone solution was concentrated by distillation, followed by the addition of *n*-decane and codistillation of norcamphor on a spinning band column. After *ca.* 50% of the norcamphor had distilled, it was separated from the hydrocarbon by chromatography on Florisil, while additional norcamphor was separated from the pot residue by preparative vpc (20 ft × $^3/_8$ in. FFAP). Both samples of norcamphor were combined and repeatedly sublimed until the melting point was unchanged at 90.5–93.0 (lit.[54] mp 97–98° (racemic)) to yield 7.5 g (16%) of white crystals. The ir and nmr spectra were identical with those of a commercially obtained sample (Aldrich). Analysis by vpc showed no discernible impurity. The material had $[\alpha]^{23}\mathrm{D}$ $-9.74 \pm 0.40°$ (*c* 2.8, chloroform). Comparing this rotation to that obtained by Mislow and Berger,[20] this material is 31.2% optically pure. The ultraviolet absorption spectrum in isooctane solution exhibited λ_{max} 295 mμ (ϵ 23) (lit.[20] 295 (29)). The ORD characteristics in isooctane (*c* 0.3174), corrected to optical purity, were $[\varphi]_{320.5}$ $-896°$, $[\varphi]_{314}$ $+294°$, $[\varphi]_{312.5}$ $+356°$, $[\varphi]_{307}$ 0°, $[\varphi]_{302.5}$ $-922°$, $[\varphi]_{301.5}$ $-895°$, $[\varphi]_{289}$ $-1450°$, $[\varphi]_{255}$ $-704°$, $[\varphi]_{230}$ $-850°$ (lit.[20] $[\phi]_{320}$ $+1480$, $[\phi]_{283}$ -1360). Biot's law was obeyed near 380 mμ. The CD in isooctane (*c* 0.3174), corrected to optical purity, had $[\theta]_{340}$ 0, $[\theta]_{316.5}$ $+1628$, $[\theta]_{313}$ $+1302$, $[\theta]_{305.4}$ $+1986$, $[\theta]_{300}$ $+1387$, $[\theta]_{295}$ $+1202$, $[\theta]_{275}$ 0, $[\theta]_{265}$ -80, $[\theta]_{250}$ -45 (lit.[55] (cyclohexane) $[\theta]_{340}$ 0, $[\theta]_{318}$ -1165, $[\theta]_{313}$ -983, $[\theta]_{306}$ -1463, $[\theta]_{274}$ 0, $[\theta]_{269}$ $+33$). The ORD and CD spectra of this compound are multiplied by -1 and plotted as its enantiomer in Figures 2 and 3.

(−)-2-Phenylnorbornene (5). Phenylmagnesium bromide (20 mmol) was prepared in ether solution, filtered, and slowly added to a solution of 2.20 g (20 mmol) of the (−)-norcamphor described above. Routine work-up afforded an oil which was treated with a tenfold excess of acetyl chloride–pyridine complex in benzene for 17 hr. The crude acetate was pyrolyzed by preparative vpc (20 ft × $^3/_8$ in. FFAP, 250°) to give 0.76 g (22%) of a slightly yellow liquid containing *ca.* 4% of an impurity. Purification was effected by rechromatography on a new FFAP column, column chromatography on Florisil, and kugelrohr distillation to give 0.16 g of clear viscous liquid, homogeneous by vpc. The ir and nmr spectra were identical with those of a commercial sample of racemic 2-phenylnorbornene (Aldrich). The material had $[\alpha]^{24}\mathrm{D}$ $-63.6 \pm 0.6°$ (*c* 1.6, ethanol). Corrected to optical purity, (−)-2-phenylnorbornene had $[\alpha]^{24}\mathrm{D}$ $-204 \pm 22°$.

---

[54] D. C. Kleinfelter and P. von R. Schleyer, *Org. Syn.*, 42, 79 (1962).

[55] P. Witz, H. Herrmann, J.-M. Lehn, and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1101 (1963).

Thermal Decomposition of Tetramethyl-2-tetrazene. Reactivity of the Dimethylamino Radical

C. J. Michejda and W. P. Hoss

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68508. *Received November 5, 1969*

Abstract: The reaction of the dimethylamino radical with toluene and substituted toluenes has been measured and the relative rates are correlated with σ^+ values. The ρ value for the abstraction reaction is -1.08. The deuterium isotope effect was found to be 4.0. The kinetics of the thermal decomposition of tetramethyl-2-tetrazene (TMT) in benzene solution have been measured. A comparison with gas-phase kinetics is made. It was found that at concentrations of TMT greater than 0.2 *M* induced decomposition becomes important.

Tetraalkyl-2-tetrazenes are convenient sources of dialkylamino radicals. The compounds decompose smoothly either thermally or photochemically. It is a little surprising that since the pioneering work of Wieland[1] relatively little work has been published on the chemistry of 2-tetrazenes or the amino radicals derived from them. Rice and Gerlecki[2] showed that when tetramethyltetrazene (TMT) in the gas phase was passed over a hot wire (1300°) the dimethylamino radicals could be trapped at −196°. Several workers studied the thermal decomposition kinetics of TMT in the gas phase. The most complete study was by Gowenlock and his coworkers[3] who examined the decomposition in a flow system over a wide temperature range. The energy of activation was 36.1 ± 1 kcal/mol and the preexponential factor was $10^{14.4 \pm 0.5}$. Watson and Waring[4] examined the decomposition in a static system, over a more limited temperature range, and found $E_a = 31.9 \pm 3$ kcal/mol and $\log A = 11.4 \pm 1.65$. Recently the static system decomposition of TMT was reexamined[5] over a wider temperature range (127–175°); the activation parameter values reported, $E_a = 34.6$ kcal/mol and $\log A = 13.83$, are more in line with Gowenlock's values.

The kinetics of the thermal decomposition of TMT in solution apparently have escaped attention except for the report of a rate constant from a single run at one temperature in cumene solution ($k = 0.56 \times 10^{-4}$ sec^{-1} at 145°).[6]

This paper reports a study of the kinetics of decomposition of TMT in benzene solution, the effect of induced decomposition, the reactivity of the dimethylamino radical toward toluene and substituted toluenes, and the deuterium isotope effect for the abstraction reaction.

Experimental Section

Ultraviolet spectra were obtained with a Cary Model 14 spectrophotometer and the ir spectra were obtained with Perkin-Elmer Model 237 and 621 instruments. The nmr spectra were recorded

---

[1] H. Wieland, "Die Hydrazine," Ferd Enke Verlag, Stuttgart, 1913.

[2] F. O. Rice and C. J. Gerlecki, *J. Amer. Chem. Soc.*, 79, 2679 (1957).

[3] B. G. Gowenlock, P. Pritchard-Jones, and D. R. Snelling, *Can. J. Chem.*, 41, 1911 (1963).

[4] J. S. Watson and A. J. Waring, *ibid.*, 38, 298 (1960).

[5] A. Good and J. C. J. Thynne, *J. Chem. Soc. B*, 684 (1967).

[6] B. L. Erusalimsky, B. A. Dolgoplosk, and A. P. Kavunenko, *J. Gen. Chem. USSR*, 27, 301 (1957).

on a Varian A-60 spectrometer. The glpc analyses were performed on Varian Aerograph Models A90-P3 and 1520 gas chromatographs. Mass spectra were determined on a Perkin-Elmer Hitachi RMU-6D spectrometer.

Materials. **Tetramethyl-2-tetrazene (TMT)** was prepared by the method of Watson[7] and was distilled twice, at reduced pressure, from KOH pellets. **Toluene** (Baker reagent grade) and **benzene** (Mallinckrodt analytical grade) were heated at reflux over sodium and distilled. **Cumene** was washed with concentrated sulfuric acid, 10% sodium bicarbonate, and then water. After drying ($MgSO_4$) it was distilled from calcium hydride and the distillate was stored over sodium. **Dimethylamine** was dried by passage through a tube containing KOH pellets. **Toluene-d_8** (Diaprep, 99% minimum isotopic purity), *m*- and ***p*-xylenes** (Matheson Chromatoquality reagents), **dioxane** (Baker reagent grade), **chlorobenzene**, and other substituted toluenes were reagent grade commercial materials and were used without further purification.

Kinetic Procedures. Solutions which were 0.2 *M* in TMT were prepared by weighing the reagents and an internal standard into volumetric flasks and diluting to volume with benzene. Aliquots of these solutions were sealed in Pyrex tubes and were then placed into a constant temperature oil bath (temperature was regulated to better than 0.1°). At intervals, the ampoules were withdrawn and the reaction was quenched by plunging the tubes into ice-water. In a typical run eight tubes were used, the last tube being withdrawn at approximately 80% completion. The contents were analyzed by glpc.

Analytical Procedures. The contents of the thermolysis tubes were analyzed by glpc. In the kinetic runs the rate of disappearance of TMT was followed. A 7 ft × $^1/_4$ in. Pyrex column packed with 5% Apiezon N on acid-washed Chromosorb W was used. The column was operated at 62° and carrier gas (He) flow rate (exit) of 30 ml/min. Hexane was used as an internal standard in benzene and dioxane was the internal standard in acetonitrile. A working curve of seven known concentrations of TMT and hexane showed that the concentration of TMT could be determined within 3.5% relative standard deviation. The rate constants were determined using the nonlinear least-squares program LSKIN-1.[8]

Relative Rates. The competition method was used to obtain the values of k/k_0 for hydrogen abstraction by the dimethylamino radical from toluene and substituted toluenes. Solutions that were 1 *M* in TMT, 0.5 *M* in toluene, and 0.5 *M* in substituted toluenes in benzene were prepared by weighing the reagents into a volumetric flask and diluting to volume with benzene. Aliquots of these solutions were placed into Pyrex tubes, degassed (three freeze-pump-thaw cycles), and sealed. They were then immersed in a constant temperature bath maintained at 136.0° for 24-36 hr. The contents of the tubes were analyzed by glpc for the relative concentrations of toluene and the respective substituted toluenes. Dimethylamine was identified in all the runs by its retention time and comparison of its ir spectrum with that of an authentic sample. The relative rates were obtained in the following manner. The concentrations of the components were calculated from the equation

$$[\mathrm{Y}] = \frac{[\mathrm{Y}]_{\mathrm{i}}\,(\text{area, }Y)(\text{area, std})_{\mathrm{i}}}{(\text{area, }Y)_{\mathrm{i}}(\text{area, std})}$$

where the subscript i denotes initial conditions and the areas are those of the chromatograph peaks (determined with a Disc integrator), corrected for base line drift. The rate-constants ratio, k/k_0, was then calculated from the equation[9]

$$k/k_0 = \frac{\log\,([\mathrm{X{-}C_6H_4{-}CH_3}]_{\mathrm{i}}/[\mathrm{X{-}C_6H_4{-}CH_3}])}{\log\,([\mathrm{C_6H_5{-}CH_3}]_{\mathrm{i}}/[\mathrm{C_6H_5CH_3}])}$$

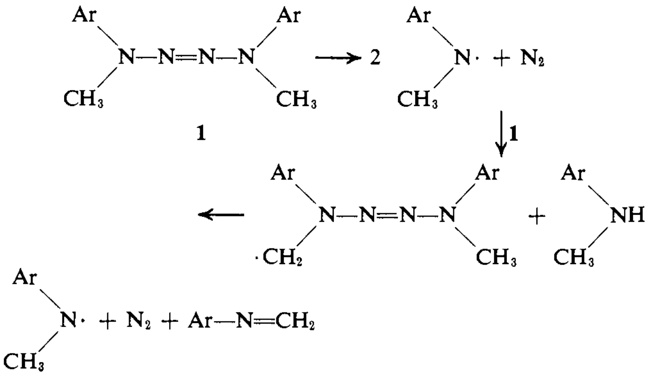
where again subscript i refers to the initial conditions.

Isotope Effect. A competition experiment similar to the toluene *vs.* substituted toluenes runs was used to determine the rate of toluene *vs.* toluene-d_8. The total toluenes were separated from the reaction mixture by glpc. The ratio of [toluene]/[toluene-d_8] was determined with a mass spectrometer by measuring the intensities of the parent ions, *m/e* 92 and 100, respectively. The relative standard deviation in the measurement was 0.7%. The mass spectrum of toluene-d_8 indicated that there was no interfering ion at *m/e* 92. Standard mixtures of toluene-toluene-d_8 were used to calibrate the spectrometer. A discrimination in the ratio of 5.1% in favor of the light toluene was found. A correction for this factor was applied in the calculations. An analogous equation to that used for k/k_0 was used to obtain k_H/k_D.

Thermolysis and Photolysis in Presence of Toluene and Cumene. Photolyses were carried out on degassed and sealed solutions contained in Pyrex tubes. A Hanovia 450-W medium-pressure mercury arc, contained in a quartz water-cooled well, was the light source. The tubes were simply strapped to the well and the whole assembly was immersed in a water bath, cooled by a copper coil with tap water running through it. Thermolyses were carried out in the same way as the kinetic runs. The reactions were analyzed by glpc.

Results and Discussion

There is a remarkable lack of data on the stability and reactivity of neutral amino radicals. The thermal decomposition of 2-tetrazenes has also largely escaped attention. Recently, however, the thermal decomposition of 1,4-diaryl-1,4-dimethyltetrazenes has been reported by Nelsen and Heath.[10] One of the important results of this study was the demonstration of facile induced decomposition of tetrazenes. Erusalimsky and his group[6] have also studied the decomposition of 1,4-diphenyl-1,4-dimethyltetrazene but they failed to mention the importance of induced decomposition. Tetramethyl-2-tetrazene (TMT) was chosen for this study because the dimethylamino radical is the parent radical of the class and data on the gas-phase decomposition were available in the literature.[3-5]



Reactivity of Dimethylamino Radical. It has been noted by Erusalimsky, *et al.*,[6] that TMT is an effective initiator of styrene polymerization and that no dimethylamine was isolated when TMT was decomposed in a large excess of α-methylstyrene. Cowley and Waters[11] found that dimethylamino radicals from TMT failed to add to 1-nonene but addition products were isolated from α-methylstyrene. It was pointed out by Neale, *et al.*,[12] that the products of addition to α-methylstyrene were not characterized and could have been products of allylic abstraction followed by recombination. Our work has also indicated that neutral dimethylamino radicals fail to add to *simple* olefins.[13] These radicals also fail to add to aromatic systems[14] and are not very effective dehydrogenating agents.[15]

---

[7] J. S. Watson, *J. Chem. Soc.*, 3677 (1956).

[8] D. F. DeTar, Ed., "Computer Programs for Chemistry," Vol. 1, W. A. Benjamin, New York, N. Y., 1968, p 126.

[9] E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 394 (1960).

[10] S. F. Nelsen and D. H. Heath, *ibid.*, 91, 6452 (1969). We thank Professor Nelsen for pointing out the possible importance of induced decomposition in our system.

[11] B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1228 (1961).

[12] R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

[13] The results of that study will be submitted for publication shortly.

[14] R. E. Jacobson, K. M. Johnson, and G. H. Williams, *Chem. Ind. (London)*, 157 (1967).

[15] D. Mackay and W. A. Walters, *J. Chem. Soc. C*, 813 (1966).

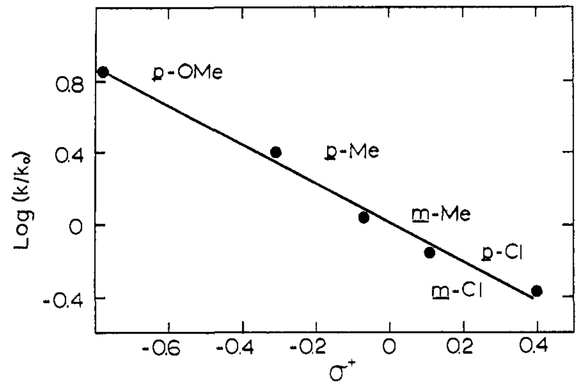


Figure 1. Relative rates of abstraction from toluene and substituted toluenes by the dimethylamino radical plotted against σ^+ constants. The slope of the line (ρ) is -1.08 ± 0.0003.

Table I lists some data on the photolysis and thermolysis of TMT in the presence of cumene and toluene. These data have qualitative meaning only because, as will be seen later, the concentrations of TMT employed were in a range where induced decomposition was not negligible. It is interesting to note that no abstraction from either toluene or cumene occurred when TMT was photolyzed at near room temperature. A moderate amount of abstraction occurred when TMT was thermolyzed at 134°. This suggests that the abstraction reaction may be somewhat endothermic. Indeed, a calculation based on the known bond dissociation energy of toluene[16] (77.5 kcal/mol) and that of dimethylamine (77.9 ± 5 kcal/mol), calculated, in turn, from the heat of formation of the dimethylamino radical,[17] gave a value of -0.4 ± 5 kcal/mol for the heat of reaction between toluene and the dimethylamino radical. The large uncertainty in the value results from the uncertainty in the heat of formation of the dimethylamino radical. The calculated heat of reaction indicates, however, that the reaction may be endothermic.

Table I. Decomposition of TMT in the Presence of Toluene and Cumene[a]

Donor	[Donor]	[TMT]	Reaction condn	% TMT reacted	% abstraction[b]
Toluene	0.41	0.41	$h\nu$, 10 hr	50	0.0
	2.0	0.30	$h\nu$, 55 hr	100	0.0
	0.42	0.76	$h\nu$, 10 hr	73	0.0
	0.43	3.5	$h\nu$, 25 hr	100	0.0
	0.53	1.1	134°, 22 hr	90	3.6
Cumene	0.54	0.87	$h\nu$, 20 hr	100	0.0
	0.54	0.87	134°, 16 hr	81	8.5

[a] All solutions were in benzene and were degassed. [b] Based on moles of dimethylamino radicals formed and moles of donor consumed.

Table II. Relative Rates of Abstraction from Substituted Toluenes by Dimethylamino Radical[a]

Toluene	Log k/k_0[b]	σ^+ value[c]
p-OMe	0.849	−0.78
p-Me	0.405	−0.31
m-Me	0.041	−0.07
p-Cl	−0.170	0.11
m-Cl	−0.373	0.40

[a] All solutions were 1 *M* TMT and 0.5 *M* in both the substituted and unsubstituted toluene. [b] The concentration of TMT was high enough for substantial induced decomposition to take place. This, however, should not have affected the relative rates. [c] Reference 18.

Amino radicals should be electrophilic because of the high electronegativity of the nitrogen atom. To test this hypothesis the relative rates of abstraction from toluene and several *meta*- and *para*-substituted toluenes were measured. The details of the procedure are given in the Experimental Section. The relative rates were correlated with σ^+ constants.[18] The data are presented in Table II. The resulting curve is shown in Figure 1. The ρ value for the reaction was found to be -1.08 ± 0.003. This can be compared[19] with the abstraction from toluene by Br ($\rho = -1.36$)[20] and by trichloromethyl ($\rho = -1.46$).[9] In order to make these data more meaningful the isotope effect for the reaction was measured. The technique for this measurement was similar to the competition runs with substituted toluenes. Dimethylamino radicals from excess TMT were allowed to compete for hydrogen atoms from toluene or deuterium atoms from perdeuteriotoluene. The contributions to the isotope effect from the small secondary isotope effect and the substitution of ring protons by deuteriums were neglected. The value of k_H/k_D was obtained by mass spectroscopic analysis. The value obtained was $k_H/k_D = 4.0$. This can be compared to $k_H/k_D = 4.6$ for the abstraction of hydrogen atoms from toluene by Br·.[21] These data indicate that the dimethylamino radical is indeed electrophilic but, because of the similarity between the isotope effects,[22] it is somewhat less electrophilic than the bromine atom. The transition state for the abstraction reaction thus involves contributions from polar forms.

$$[\mathrm{Ph{-}CH_2{-}{-}{-}H{-}{-}{-}NMe_2}] \longleftarrow [\mathrm{Ph{-}CH_2^+{-}{-}{-}H{-}{-}{-}{}^-NMe_2}]$$

These data are somewhat in variance with the study reported by Johnston, Williams, and Williams.[25] They found that the *m*-Cl and *p*-Cl had only about one-half of the effect found in this study, although in the same direction. The relative reactivities were obtained by

---

(16) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, 22, 151 (1954).

(17) B. G. Gowenlock, P. Pritchard-Jones, and J. R. Majer, *Trans. Faraday Soc.*, 57, 23 (1961).

(18) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, 22, 485 (1957).

(19) A strict comparison of the various ρ values would require the knowledge of the temperature dependence of these various reactions. These data are not available and hence the comparison is largely qualitative. The problem of these "extrathermodynamic" relationships is treated in the monograph: J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

(20) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, 85, 3142 (1963).

(21) K. B. Wiberg and L. H. Slaugh, *ibid.*, 80, 3033 (1958).

(22) The abstraction of hydrogen from toluene by bromine atoms is exothermic by about 10 kcal/mol. Our work indicates that the abstraction by the dimethylamino radical is somewhat endothermic. The transition state for the bromine reaction should involve less C–H bond breaking than the transition state of the dimethylamino radical reaction.[23] The similarity of the isotope effects for both reactions is fortuitous. It is significant, however, that they are a little smaller than would be expected for 50% bond breaking ($k_H/k_D = 6$–10). What this probably means is that both isotope effects bracket the "maximum" value—the bromine atom on the low side of the 50% C–H bond breaking and the dimethylamino radical on the high side.[24]

(23) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).

(24) *Cf.* F. H. Westheimer, *Chem. Rev.*, 61, 265 (1961).

(25) K. M. Johnston, G. H. Williams, and H. J. Williams, *J. Chem. Soc. B*, 1114 (1966).

isolation of the products, formed from the *m*- and *p*-chlorobenzyl radicals, by column chromatography. This technique does not lend itself to quantitative studies of any precision. Our data were obtained at a somewhat lower temperature, which also may have contributed to the difference in values.

Kinetics of Thermal Decomposition in Benzene. The rate of disappearance of TMT was measured by glpc. This technique, although indicated in this case, proved to be imprecise. The areas of the chromatographic peaks could only be calculated to within 3% precision. This error, coupled with the more common kinetic errors meant that the rate constants were somewhat less accurate than usual. The reaction was measured at four different temperatures and the results are summarized in Table III. The rate constants were calculated by a nonlinear least-squares program which was also allowed to find the infinity points. The errors were shown to be random. The Arrhenius plot of the data in Table III gave a value for the enthalpy of activation of 45 kcal/mol (least-squares analysis). This value should be treated with caution in view of the 36 kcal/mol obtained by Gowenlock, *et al.*,[3] in their gas-phase study. There is no *a priori* reason to expect this large increase in going from gas to liquid phase. Our plot probably had too much scatter over the relatively small temperature range (15.6°) and hence a small deviation in either the first or the last point would produce a large error in the slope. The gas-phase Arrhenius plot had at least 50 points and covered a much larger temperature range, even though the precision of the individual points was not much better than the present study.

Table III. First-Order Rate Constants for Thermolysis of TMT in Benzene[a]

Reaction temp, °C	$k \times 10^5$, sec^{-1}
126.6	1.70 ± 0.04[b]
	1.81 ± 0.5
129.6	4.00 ± 0.12
	4.31 ± 0.13
136.3	6.19 ± 0.25
	5.96 ± 0.37
	5.84 ± 0.32
142.2	20.1 ± 0.58
	19.4 ± 0.86

[a] Concentration of TMT was 0.2 *M* in all runs. [b] Standard deviation.

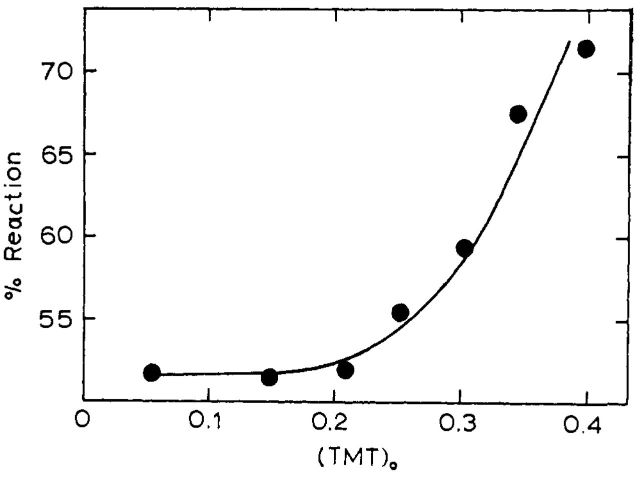


Figure 2. The extent of reaction of TMT as a function of concentration of TMT at constant time. The plot indicates extensive induced decomposition at [TMT] > 0.2 *M*.

The problem of induced decomposition in this system was examined. Figure 2 shows per cent reaction as a function of TMT concentration at constant temperature (136°). It is apparent from Figure 2 that induced decomposition is not very important when [TMT] $\leq$ 0.2 *M*. At concentrations higher than 0.2 *M* there is a rapid increase in rate as the concentration increases. This indicates induced decomposition. This suggests that the rate data summarized in Table III were not greatly influenced by induced decomposition although it may have contributed to the error in the enthalpy of activation.