utilizing the equilibrium relations

$$K_2 = \frac{a_{\mathrm{H}}\, a_{\mathrm{HPO_4}}}{a_{\mathrm{H_2PO_4}}} \qquad (27)$$

$$K_3 = \frac{a_{\mathrm{H}}\, a_{\mathrm{PO_4}}}{a_{\mathrm{HPO_4}}} \qquad (28)$$

and

$$t_{\mathrm{H}} + t_{\mathrm{H_2PO_4}} + t_{\mathrm{HPO_4}} + t_{\mathrm{PO_4}} = 1 \qquad (29)$$

we can obtain

$$\mathrm{d}E_t = (t_{\mathrm{H}} - 2t_{\mathrm{H_2PO_4}} - 0.5t_{\mathrm{HPO_4}} + 0.5)\frac{4RT}{3F}\,\mathrm{d}\ln a_{\pm} \qquad (30)$$

where the mean ionic activity is defined by

$$a_{\pm} = (a^3_{\mathrm{H}}\, a_{\mathrm{PO_4}})^{1/4} \qquad (31)$$

A similar analysis of Cell II leads to

$$\mathrm{d}E = \frac{2RT}{F}\,\mathrm{d}\ln a_{\pm} \qquad (32)$$

so that

$$\frac{\mathrm{d}E_t}{\mathrm{d}E} = \frac{2}{3}\,(t_{\mathrm{H}} - 2t_{\mathrm{H_2PO_4}} - 0.5t_{\mathrm{HPO_4}} + 0.5) \qquad (7)$$

POTSDAM, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.)

The Thermal Decomposition of 2,2'-Azo-bis-isobutyronitrile

BY J. P. VAN HOOK[1] AND A. V. TOBOLSKY

RECEIVED APRIL 30, 1957

The thermal decomposition of 2,2'-azo-bis-isobutyronitrile has been studied at five temperatures between 100 and 37° by applying the ultraviolet absorption technique. The kinetics of the decomposition have also been investigated at 30.5° by a manometric method. A composite Arrhenius plot using all the available data for the decomposition is given. The over-all rate expression for decomposition of the azo compound in solution is: $k_d = 1.58 \times 10^{15} \exp(-30.8 \text{ kcal.}/RT)$.

Introduction

Although the compound 2,2'-azo-bis-isobutyronitrile (Azo I) has been quite extensively studied it was felt that further work at temperatures below 60° was necessary in order to arrive at a more complete and satisfactory expression for the rate of thermal decomposition. This is important for an accurate evaluation of the initiator efficiency. The application of Azo I to polymerization kinetics and particularly to initiator efficiency is discussed in a subsequent paper.

Since the elimination of nitrogen from Azo I is quantitative, several investigators[2-8] have utilized the volumetric technique to establish the over-all rate of decomposition. Roy, *et al.*,[9] have measured the nitrogen evolution manometrically. From these studies it was shown that the rate of decomposition is independent of the nature of the solvent and the reaction has the advantage of not being complicated by induced decomposition. The work of Lewis and Matheson,[1] Ziegler, *et al.*,[5] and Roy, *et al.*,[9] includes rate constants for the azo cleavage obtained both in the presence and absence of radical scavengers such as tetrachloroquinone, chloranil and iodine, respectively. The presence of these strong inhibitors has no apparent effect on the rate of nitrogen evolution. Some investigators have reported a slight induction period in the reaction when the volumetric method is employed but Hyson and Beasley[10] state that this induction period disappears if vigorous agitation is employed.

Another technique which *lends itself particularly applicable* to rate studies on Azo I involves following the change in optical density in the near ultraviolet. Azo I has a symmetrical absorption band in this region with a peak at 345 mμ. This technique eliminates many difficulties associated with the gas evolution method. The results obtained by Talat-Erben and Bywater[11] for the Azo I decomposition from 70 to 105° seem superior to the gas evolution data in many respects, particularly in regard to the minimum of scatter in experimental points. Their results included work over a ten-fold concentration range with no variation in the order of the reaction or specific rate constant, yielding a straight-forward first-order decomposition in agreement with other methods.

The polarographic technique also has been applied to the kinetic study of the Azo I decomposition.[8] The data in methanol solution are quite comparable with the spectrophotometric and gas evolution data but the results when using dioxane as the solvent show a deviation from the composite Arrhenius plot.

2,2-Diphenyl-1-picrylhydrazyl (DPPH) has also been used to study the rate of production of radicals[12-14] and in polymerization inhibition work.[15]

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(1) This paper is based upon a dissertation submitted by James P. Van Hook in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

(2) F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

(3) (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949); (b) L. M. Arnett, *ibid.*, **74**, 2027 (1952).

(4) Hunt, U. S. Patent 2,471,959 (May 31, 1949).

(5) K. Ziegler, W. Deparade and W. Meye, *Ann.*, **567**, 141 (1950).

(6) J. W. Breitenbach and A. Schindler, *Monatsh.*, **83**, 724 (1952).

(7) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(8) J. Ukida, G. Takajama and T. Kominanu, *Chem. High Poly. Japan*, **11**, 233 (1954).

(9) J. C. Roy, R. R. Williams, Jr., J. R. Nash and W. H. Hamill, THIS JOURNAL, **78**, 519 (1956).

(10) A. M. Hyson and J. K. Beasley, Polychemicals Dept., E. I. du Pont de Nemours and Co., Wilmington, Del.; oral presentation at the February 1955 Delaware Chemical Symposium.

(11) M. Talat-Erben and S. Bywater, THIS JOURNAL, **77**, 3712 (1955).

(12) K. E. Russell and A. V. Tobolsky, *ibid.*, **76**, 395 (1954).

(13) A. Chapiro, *J. chim. phys.*, **51**, 165 (1954).

(14) A. Chapiro, *ibid.*, **52**, 645 (1955).

(15) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).

Bawn and Mellish[16] and Matheson[17] have used this method to determine the rate of decomposition of Azo I at various temperatures. However, this procedure has its difficulties as the literature shows. The efficiency of DPPH as a scavenger has not been agreed upon. The work of Bawn and Mellish seems to show that oxygen has no effect on the rate measurements and that the hydrazyl is very nearly 100% efficient in capturing all radicals produced in the system. However, Bevington[18] has decomposed Azo I in benzene solution at 60° in the presence of a high concentration of DPPH and has determined a considerable amount of tetramethylsuccinodinitrile as a product using the isotopic dilution method. He concludes that DPPH reacts with only about 70% of the radicals produced. In a recent publication Hammond, *et al.*,[8] have shown that DPPH is much less than 100% efficient as a scavenger for radicals. Furthermore, Hammond states that oxygen has a decided effect on the system, the results are not reproducible due to the variable stoichiometry of DPPH in apprehending radicals, and hence it should not be recommended as an accurate counter for the production of radicals. Work in this Laboratory supports the view that oxygen plays an important role in the reaction; the stoichiometry is variable and the results obtained depend very much on the experimental procedure. In the light of our work and the previous discussion we tend to agree with Hammond in suggesting that DPPH should not be used as an efficient scavenger.

A very interesting experiment recently was performed by Bevington[19] to determine the value of the specific rate constant for the Azo I decomposition. Tagged (C^{14}) Azo I was used as the initiator for styrene polymerization at 60° and both the polymer and wastage products were subjected to radioassay. He concludes that the efficiency of initiation is well below 100%, consequently if each Azo I decomposition yields two radicals (evidence for which is given in a subsequent paper in this series in which the efficiency of initiation approaches a value of unity at very low rates of initiation), then styrene is approximately 60% efficient in capturing radicals. Bevington furthermore gives strong support for his value of the specific rate constant.

A compilation of all available decomposition data (all methods excluding DPPH measurements) is given along with new data extending the temperature range using the spectrophotometric technique.

Experimental

Materials. 2,2'-Azo-bis-isobutyronitrile.—Porophor N (recrystallized), Westville Laboratories, Monroe, Connecticut, was recrystallized three times from absolute ether and stored under refrigeration until use. It had a melting point of 103.5–104.5° with decomposition.[20]

Solvents, Benzene, Mallinckrodt Analytical Grade, and Toluene, Baker, Reagent Grade, were used without further purification.

Procedure. Ultraviolet Spectrophotometric Experiments.—A Beckmann Model DU spectrophotometer was used throughout this work. The absorption curve for Azo I was determined and the validity of Beer's law was established at 360, 370 and 380 mμ throughout the entire range of Azo concentrations to be studied. The solutions of Azo I were made up in 100-ml. flasks with the appropriate solvent (either toluene or benzene depending on the temperature). Five-ml. portions were then pipetted into 1.5 cm. by 15 cm. Pyrex tubes with an 8 mm. tubing extension sealed on one end. The tubes were then placed on a vacuum manifold and three cycles of freezing (by means of liquid nitrogen traps), degassing and thawing were accomplished before the tubes were sealed off at the neck *in vacuo*. Preliminary thawing was done under cold running water before the tubes were placed in the constant temperature bath regulated to ±0.03°. The tubes were taken out at appropriate time intervals, immediately chilled in cold water, the contents poured into a 1 cm. quartz cell and the optical density determined. The optical density was taken at ten half lives (D_∞) and found to be zero, thus confirming the belief that none of the products of the decomposition absorb at the wave lengths studied. At 50, 43 and 37° D_∞ values were not determined due to the extremely long half-life at these temperatures. Because D_∞ was determined at 60° and found to be zero it was assumed equal to zero at the three lower temperatures. A separate experiment was run to determine the effect of oxygen on the absorption curve. A 100-ml. flask containing the azo solution was placed in the bath at 60° in contact with atmospheric oxygen, samples were withdrawn at various times and the optical density measured.

Manometric Determinations.—A 1.5 cm. by 15 cm. Pyrex tube with a 5 mm. extension tubing sealed on one end and a 0.5 mm. capillary tubing sealed to the side was used in this experiment. The volume of the apparatus was calibrated with mercury. The bulb was charged with a 10-ml. solution of Azo I in toluene and three cycles of freezing, de-

TABLE I

Temp., °C.	k_d (sec.$^{-1}$)
100	1.52×10^{-3}
60	9.15×10^{-6}
50	2.16×10^{-6}
43	7.35×10^{-7}
37	2.83×10^{-7}

TABLE II

Ref.	Method	T, °C.	k_d(sec.$^{-1}$)
2	Volumetric	80	1.533×10^{-4}
2	Volumetric	77	1.21×10^{-4}
3a	Volumetric	69.8	3.80×10^{-5}
3a	Volumetric	80.2	1.60×10^{-4}
6	Volumetric	77	9.50×10^{-5}
6	Volumetric	82	1.45×10^{-4}
10	Volumetric	80.3	1.63×10^{-4}
11	Volumetric	80	1.983×10^{-4}
11	Volumetric	100	2.25×10^{-3}
12	Volumetric	50	2.975×10^{-6}
12	Volumetric	70	4.72×10^{-5}
13	Volumetric	62.5	1.42×10^{-5}
14	Volumetric (MeOH)	60	9.34×10^{-6}
14	Volumetric (Diox)	60	7.68×10^{-6}
14	Volumetric (Diox)	70	3.24×10^{-5}
14	Volumetric (Diox)	80	1.095×10^{-4}
15	Manometric	80	1.50×10^{-4}
20	Ultraviolet	70	4.00×10^{-5}
20	Ultraviolet	80.4	1.55×10^{-4}
20	Ultraviolet	90	4.86×10^{-4}
20	Ultraviolet	100	1.60×10^{-3}
20	Ultraviolet	105	2.61×10^{-3}
28	C^{14}, styrene	60	1.20×10^{-5}
14	Polarographic (MeOH)	60	1.18×10^{-5}
14	Polarographic (Diox)	60	7.00×10^{-6}
14	Polarographic (Diox)	79.5	1.06×10^{-4}

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[16] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

[17] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

[18] J. C. Bevington, *Nature*, **174**, 477 (1955).

[19] J. C. Bevington, *Trans. Faraday Soc.*, **51**, 1392 (1955).

[20] C. G. Overberger and H. Biletch, THIS JOURNAL, **73**, 4880 (1951).

gassing and thawing were completed before the neck was sealed off *in vacuo*. The bulb was then placed in a bath at 30.5° (±0.02°). The entire apparatus was immersed except the thin capillary which was about 800 mm. long and contained a mercury pool at the bottom. Agitation was not provided during the course of the experiment. Pressure readings were taken at appropriate time intervals and corrected for barometric pressure. The pressure at complete decomposition (P_∞) was considered to be that developed by a quantitative elimination of nitrogen.

Results and Discussion

k_d for the Azo I decomposition has been determined spectrophotometrically at 100, 60, 50, 43 and 37°. Beer's law was valid over the entire concentration range and at the wave lengths studied. The absorption curve of Azo I showed a symmetrical band in the near ultraviolet (λ_{max} 347 mu, ϵ_{347} mμ 13.7 in benzene) in agreement with other investigators.[2,3a,11] To show the effect of oxygen on the system the optical density (D_t) is plotted against time in Fig. 2 and for comparison the data in absence of oxygen are shown likewise. Both rate studies were done at 60°. It seems that stable peroxides are formed which absorb in this region of the spectrum, and for this reason oxygen was excluded rigorously from the reaction tubes. A typical first-order plot of log [D_0/D_t] *versus* time ($D_\infty = 0$) is given in Fig. 3 for the decomposition at 37°. The log [D_0/D_t] values did not vary with wave length in any case, hence only the curve obtained at 360 millimicrons is shown. Table I summarizes the results for k_d obtained in this manner.

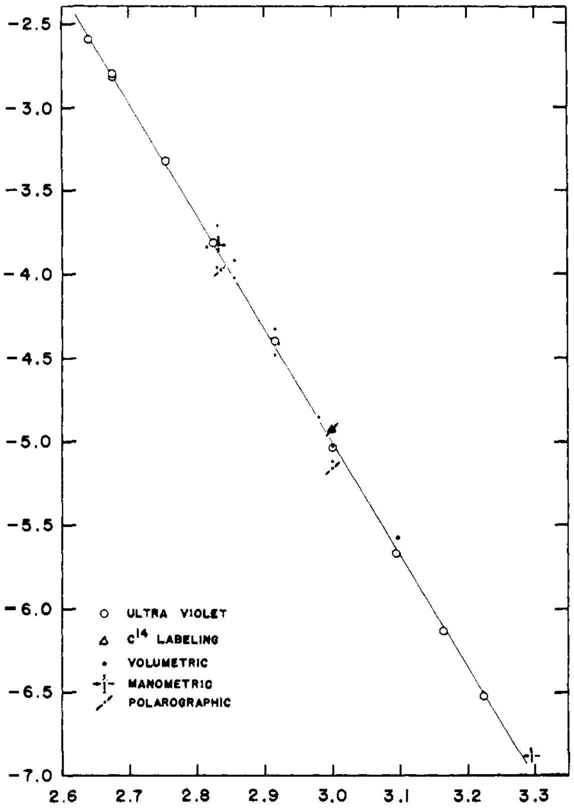

Fig. 1.—Decomposition of Azo I in solution.

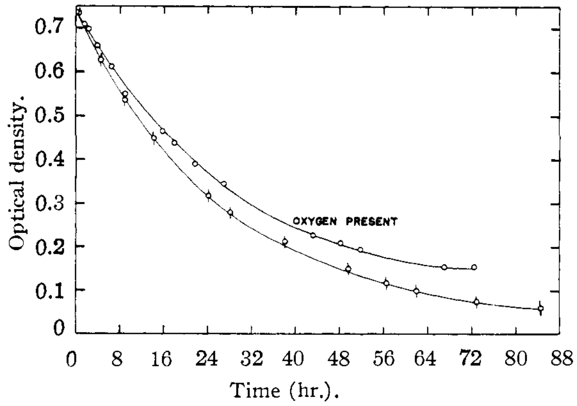

Fig. 2.—Decomposition of Azo I at 60°.

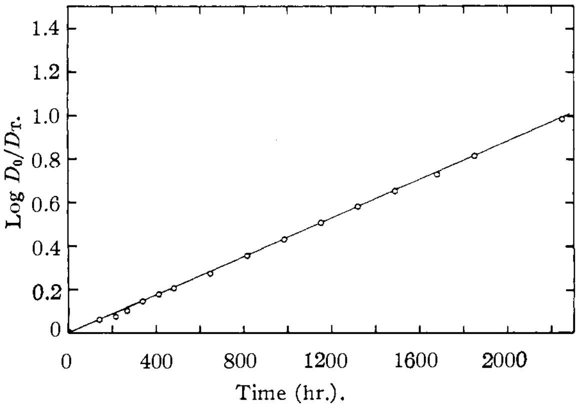

Fig. 3.—Decomposition of Azo I at 37°.

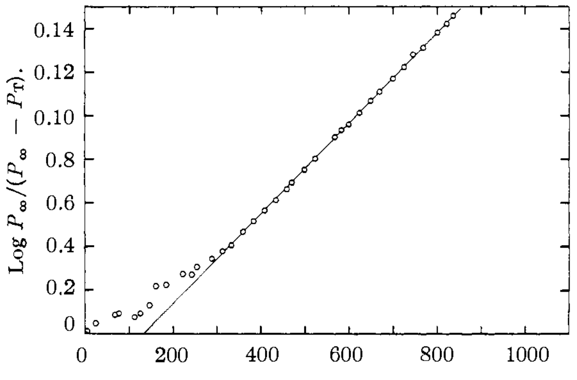

Fig. 4.—Decomposition of Azo I at 30.5°.

Using these values and all the available literature results given in Table II a composite Arrhenius plot is constructed and shown in Fig. 1. We see that our values along with the spectrophotometric results of Talat-Erben and Bywater[11] show little deviation from the straight line. Because this method eliminates many difficulties associated with other methods these points probably best describe the over-all rate of decomposition.

k_d was determined at 30.5° by the manometric technique which seemed to be applicable at this low temperature provided the volume of the apparatus was kept at a minimum. Because pressure change is measured at constant volume (the increase in total volume due to the drop in mercury level in the capillary is negligible) the results might not be too reliable due to the increased solubility of nitrogen with increasing pressure. Figure 4 shows the first-order plot for the process, log $[P_\infty/(P_\infty - P_t)]$ *versus* time yielding a straight line. The induction period and the scatter of points in this region probably can be explained by considering the time required to build up nitrogen saturation in the system and possible thermal equilibration effects. The value of k_d at 30.5° was calculated to be 1.31×10^{-7} and is included in Fig. 1.

Using all the available data for the decomposition of Azo I in solution the equation which best fits the experimental results is: $k_d = 1.58 \times 10^{15}$ exp$(-30.8$ kcal./$RT)$.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BUFFALO]

Kinetics of the Exchange Reaction between Carbon-14-labeled Carbonate and Carbonato-bis-(trimethylenediamine)–Cobalt(III) Complex in Aqueous Solution. Effect of Steric Hindrance in a Ligand Substitution Process

BY JAMES E. BOYLE[1] AND G. M. HARRIS

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The study of carbonate ligand exchange reactions of the carbonato-diamine–cobalt(III) series of complex ions has been extended to the bis-trimethylenediamine (tn_2) analog. The effects of changes in reactant concentration, *p*H and temperature have been determined. Comparisons are made between the behavior of the tn_2 complex and those previously investigated; *viz.*, the pentammine (N_5), tetrammine (N_4) and bis-ethylenediamine (en_2) types. The rates and mechanisms of the reactions which promote carbonate exchange are very similar for N_4 and en_2, but large variations from these are observed for the N_5 and tn_2 forms. The N_5 behavior can be reasonably attributed to hydrogen-bonding factors; for the tn_2, steric hindrance appears to play the predominant role.

Previous publications in this series have reported on the nature of the exchange reaction in aqueous solution between free (uncomplexed) carbonate ion and the corresponding ligand group in a number of carbonato–cobalt(III) complex ions. Included have been the tetrammine (N_4),[2a,b] the pentammine (N_5)[3] and the bis-ethylenediamine (en_2)[4] analogs. The mechanisms of the exchanges conform to a definite pattern of similarity, but some differences do occur both in the relative rates of the reactions and in details of the mechanisms. The present paper reports an extension of these studies to the bis-trimethylenediamine (tn_2) complex, which differs from the en_2 compound only in the insertion of one more CH_2 group in each of the diamine–cobalt chelate rings. Evidence accrues from this study concerning the effect of stereochemical factors on the rate and mechanism of the ligand replacement reaction.

Experimental

Preparation, Purification and Analysis of Materials.—Carbonato-bis-(ethylenediamine)-cobalt(III) chloride was prepared as described previously.[4] The corresponding tn_2 salt was prepared by an extension of the procedure of Bailar and Work.[5,6] $(Cotn_2Cl_2)Cl$ was first obtained, then aquated by allowing it to stand in dilute aqueous solution at room temperature for 45 minutes. Excess of Ag_2CO_3 was dispersed in the solution and kept in suspension by rapid stirring for three hours. The mixture was filtered and the filtrate retreated with silver carbonate for one hour and refiltered. Slight excess of $BaCl_2$ was added to the bright red filtrate containing $(Cotn_2CO_3)_2CO_3$. After standing overnight, the $BaCO_3$ was filtered off, and the filtrate evaporated to dryness in the open air at 70°, causing precipitation of the excess $BaCl_2$ as $BaCO_3$. The cobaltic complex was extracted from the residue with water, recrystallized twice from water, and air-dried at room temperature.

The purified dry solid $(Cotn_2CO_3)Cl{\cdot}H_2O$ remained completely stable at room temperature indefintely. Its complete analysis was carried out as follows: water of crystallization was determined by drying in air at 110°, cobalt by the method of Hillebrand,[7] and by direct ignition of the complex to Co_3O_4 at 700°, carbonate by a modification of the Fresenius vacuum baryta method,[8] chloride by standard gravimetric procedure,[9] and nitrogen by a modified Kjeldahl method.[10]

Anal. Calcd.: H_2O, 5.62; Co, 18.38; CO_3, 18.71; Cl, 11.06; N, 17.47. Found: H_2O, 5.75; Co, 18.26; CO_3, 18.73; Cl, 11.11; N, 17.54.

Carbon-14-labeled sodium carbonate was prepared by reaction of barium carbonate-C-14 with lead chloride and subsequent absorption of the active dioxide in carbonate-free sodium hydroxide.[11]

Apparatus and Technique.—The kinetic runs were made in a manner very similar to that of the previous studies.[2-4] A typical run was commenced by mixing rapidly a weighed portion of the anhydrous complex salt, 15.00 ml. of 0.0834 *M* sodium borate, 1.00 ml. of 0.3153 *M* inactive sodium carbonate, 7.00 ml. of CO_2-free water, and after temperature equilibrium was established, 2.00 ml. of 0.0321 *M* active sodium carbonate. A zero-time sample was removed and the free carbonate precipitated within 90 seconds. Subsequent samples were withdrawn at convenient time intervals, a stream of CO_2-free nitrogen being passed through the reaction flask during sampling. Assay was effected by end-window counting of the uniformly-spread $BaCO_3$ samples in nickel-plated planchets.

Half-times of exchange were obtained from the conventional log $(1 - f)$ *vs.* time plots,[12] using least-squares analy-

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[1] Work done as part of Ph.D. requirement of the University of Buffalo, 1956. Complete report available from University Microfilms, Ann Arbor, Michigan.

[2] (a) G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952); (b) D. R. Stranks, *ibid.*, **48**, 911 (1952).

[3] D. R. Stranks, *ibid.*, **51**, 505 (1955).

[4] J. S. Holden and G. M. Harris, THIS JOURNAL, **77**, 1934 (1955).

[5] J. C. Bailar and J. B. Work, *ibid.*, **68**, 232 (1946).

[6] Experimental quantities of trimethylenediamine were obtained as a gift from the American Cyanamid Company

[7] W. F. Hillebrand, *et al.*, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, New York, N. Y., 1953, p. 418.

[8] W. J. Johnson, *Roy. Aust. Chem. Inst. J. Proc.*, **17**, 327 (1950).

[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, p. 307.

[10] A. Eisner and E. C. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **6**, 473 (1934).

[11] N. Zwiebel, J. Turkevich and W. Miller, THIS JOURNAL, **71**, 376 (1949).

[12] Friedlander and Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 316.