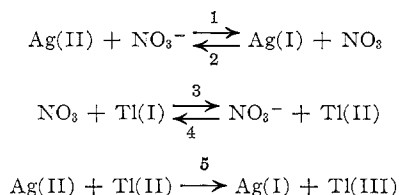


CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND 21218The Kinetics of the Silver(II)-Thallium(I) Reaction in Nitric Acid¹

By ROBERT W. DUNDON AND JOHN W. GRYDER

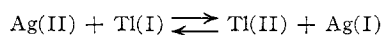
Received November 9, 1965

Kinetic data for the Ag(II)-Tl(I) reaction in 6.18 *F* HNO₃ at 26.2° are interpreted in terms of the mechanism

Values for combinations of rate constants found from a least-square treatment of the data are $k_1 = 0.403$, $k_2/(k_1k_3) = 2.03 \times 10^{-2}$, and $k_3k_4/(k_1k_3k_5) = 1.41 \times 10^{-6}$ where time is in seconds, concentrations are in moles/liter, and rate is expressed as disappearance of Ag(II). These values are consistent with equilibrium and rate constants for related reactions. Unlike other reactions with Ag(II), the oxidation of Tl(I) is independent of HNO₃ concentration over the range 4.66 to 8.82 *F*.

Introduction

This investigation was initiated because of an interest in establishing which oxidation-reduction reactions involving thallium(I) and thallium(III) proceed *via* two equivalent steps and which proceed *via* a kinetically distinguishable Tl(II) intermediate. Several examples of both mechanisms have been reported in the literature.²⁻¹¹ In addition, Stead^{8,9} reports that the step



is of importance in the Ag(I)-catalyzed reaction of Ce(IV) with Tl(I) in perchloric acid. A direct measurement of the forward reaction constant for this step would therefore be of interest.

Experimental Section

Materials and Methods.—Solutions were prepared by mixing water (triply distilled from quartz), reagent grade nitric acid, and measured volumes of standard AgNO₃ solution. Several hundredths of a gram of AgO were added per liter of solution in order to oxidize endogenous reducing agents. This stock was used both for diluting Tl(I) stock and preparing Ag(II) stock solution. The method of solvent purification outlined was found to be superior to purification by ozonization. Ag(II) solutions in solvent prepared by the ozone method were considerably less stable than in the solvent purified with AgO. It is not clear whether impurities came from the ozone-oxygen gas mixture, the apparatus, or from an ozone reaction with some species in solution.

The thallos nitrate in 99.5% purity was purchased from

Varlacoid Chemical Co. and used after recrystallization. AgO was purchased from City Chemical Co. and from K & K Chemical Co. in purified form. The silver content of the AgO as determined by gravimetric chloride analysis was within experimental error of the theoretical silver content. Reagent grade Merck AgNO₃ was used in preparing Ag(I) standard solutions.

The absorption coefficient of Ag(II) was determined at 394 mμ using the method of Kirwin, *et al.*¹² The absorbance of a measured volume of Ag(II) solution is recorded at 394 mμ; a measured volume of Ce(III) solution containing an excess of cerium is added and mixed thoroughly with the Ag(II) solution; and then the resultant solution is analyzed for Ce(IV) at 330 or 355 mμ. The plot of the absorbance of Ag(II) for a series of solutions of varying concentration *vs.* the absorbance of the Ce(IV) produced in each solution is linear. This result indicates that the reaction is stoichiometric and that Ag(II) obeys the Beer-Lambert law. The molar absorption coefficient of Ag(II) at 394 mμ in 6.18 *M* HNO₃ is $2530 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$. In 4.66 *M* HNO₃ the value is the same within experimental error. In 8.82 *M* HNO₃ the absorption coefficient increases to 3400. These values are somewhat larger than one would expect from the data presented graphically by Kirwin, *et al.* Because of the possibility of shifts in the equilibrium among Ag(II), Ag(I), and Ag(III) affecting absorption coefficients, the determination was made at both high and low [Ag(I)]. It was the same in all cases.

Ag(II) solutions undergo reduction at a moderate rate owing to reaction with the solvent. These solutions are made up immediately before use by dissolving AgO in the solvent described above. The Ag(II) concentration at the time of a run was estimated from the absorbance of the stock measured before and after the run, assuming the decay to be linear in inverse absorbance *vs.* time. The Ag(II) concentration was used to compute the Tl(I) concentration, assuming the stoichiometry shown by Noyes.¹³ Tests of stoichiometry under the conditions of our experiments were not good when an excess of Ag(II) was present, and therefore Ag(II) was always the limiting reagent for runs reported here.

Equal volumes of Ag(II) and Tl(I) solutions are mixed and injected into the spectrophotometer cell in the apparatus shown in Figure 1. The apparatus is designed to fit into the sample compartment of a Cary 14 recording spectrophotometer. After

(1) This work was supported in part by the United States Atomic Energy Commission under Contract No. AT(30-1)2918 and is based on the doctoral dissertation of R. W. Dundon, The Johns Hopkins University, 1965.

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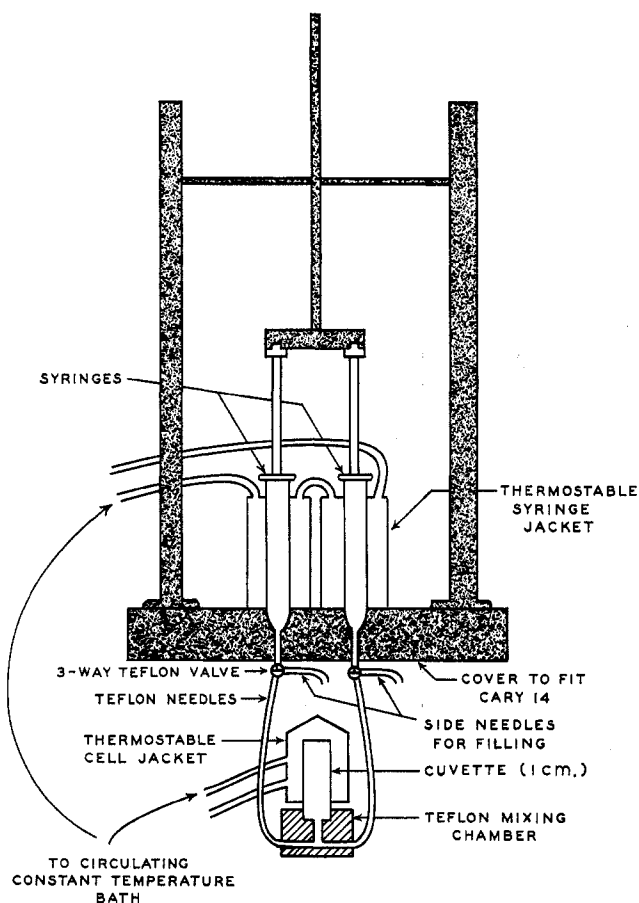


Figure 1.—Mixing assembly.

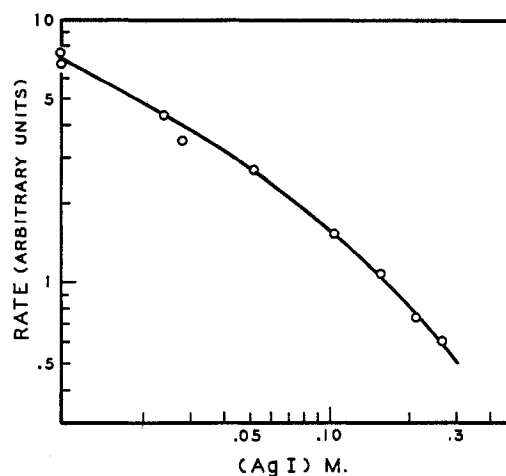
loading the syringes through the three-way valves, these valves are set to discharge through the Teflon needles and into the mixing chamber. The mixing chamber is machined from Teflon so that both the Teflon needles and the round bottom of the cuvette are force-fitted into place. The two inlet tubes (i.d. 0.056 in.) discharge into one tube leading into the open bottom of the cuvette. When the cuvette is filled by the simultaneous discharge of the syringes, the spectrophotometer is turned on and the recorder pen begins to record the absorbance at 394 $m\mu$ vs. time. Thus a continuous record of absorbance vs. time is obtained. The slope of this line at any point gives the rate of consumption of Ag(II), since the recorder is linear in absorbance. The reaction mixture is allowed to remain in the cuvette for several minutes until the absorbance reading has stopped changing.

The adequacy of mixing in this apparatus was tested by taking a solution of approximately 0.01 *M* NaOH colored with phenolphthalein and allowing it to react in the apparatus with a nitric acid solution less than 2% more concentrated. The phenolphthalein was found to be completely discolored within the time taken for injection and pen response, about 1 sec.

The temperature of the water bath was $26.20 \pm 0.01^\circ$. It is possible for the water to be heated by about a tenth of a degree on its way through the pump to the spectrophotometer cell. We may take $26.25 \pm 0.1^\circ$ as the temperature at which the reaction is measured.

Results and Discussion

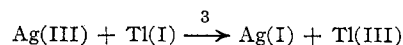
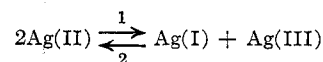
A limiting form for the rate expression was obtained from initial experiments in which all reactants and products except one were in sufficient excess to remain approximately constant during the course of a run. Graphs of log rate vs. log [Tl(I)] and of [Ag(II)]⁻¹ vs. time are linear. Figure 2 shows the variation of log

Figure 2.—Order dependence for [Ag(I)]; [Ag(II)] = 1.186×10^{-5} *M*, [Tl(I)] = 1.82×10^{-3} *M*.

rate with log [Ag(I)]. These results indicate that, under appropriate conditions, the reaction is second order with respect to silver(II), first order with respect to thallium(I), and between zero and inverse first order with respect to silver(I). The rate of the reaction was found to be independent of thallium(III). Hence a limiting form of the rate law is

$$R = k[\text{Ag(II)}]^2[\text{Tl(I)}]/[\text{Ag(I)}] \quad (1)$$

From eq 1 and analogy with other silver(II) reactions,¹²⁻¹⁵ a possible mechanism might be

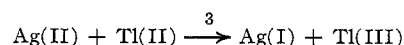
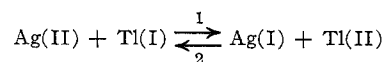


Applying a steady-state approximation to the Ag(III) intermediate, we obtain for the rate expression

$$R = \frac{k_1 k_3 [\text{Ag(II)}]^2 [\text{Tl(I)}]}{k_2 [\text{Ag(I)}] + k_3 [\text{Tl(I)}]} \quad (2)$$

A graph of [Ag(II)]²/R vs. [Ag(I)]/[Tl(I)] should be a straight line with slope of $k_2/(k_1 k_3)$ and intercept of $1/k_1$. The experimental points do not, however, agree with this prediction. The scatter from a straight line is large and there is a systematic variation in [Ag(II)]²/R during the course of many individual runs at almost constant [Ag(I)]/[Tl(I)] in a direction to indicate that the reaction is less than second order in Ag(II). Another reason for rejecting this mechanism is the lack of an appreciable acid dependence for the reaction (see Figure 3). Other reactions involving Ag(III) as an intermediate show large inverse order with respect to hydrogen ion.

Another mechanism in agreement with eq 1 and mechanisms for thallium reactions⁵⁻¹¹ is



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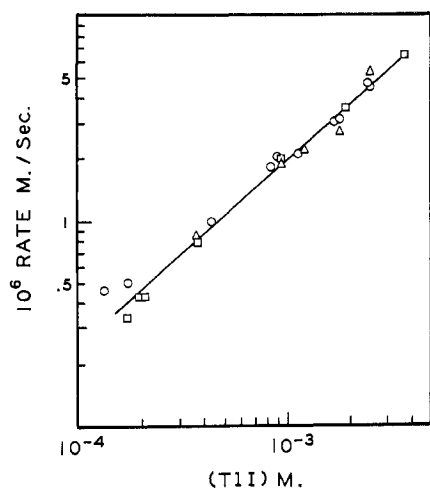


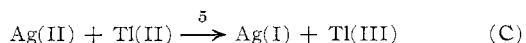
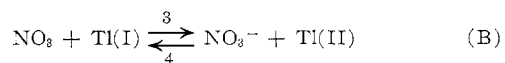
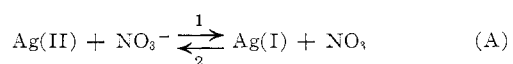
Figure 3.—Acid dependence: $\square$, 8.82 F HNO_3 ; $\circ$, 6.18 F HNO_3 ; Δ , 4.66 F HNO_3 .

which, after a steady-state approximation for Tl(II) is made, yields

$$R = \frac{k_1 k_3 [\text{Ag(II)}]^2 [\text{Tl(I)}]}{k_2 [\text{Ag(I)}] + k_3 [\text{Ag(II)}]} \quad (3)$$

The graph of $[\text{Ag(II)}][\text{Tl(I)}]/R$ vs. $[\text{Ag(I)}]/[\text{Ag(II)}]$ deviates from a straight line as much as does the appropriate graph for the Ag(III) mechanism. In addition, there is systematic variation in $[\text{Ag(II)}][\text{Tl(I)}]/R$ with $[\text{Tl(I)}]$ at constant $[\text{Ag(I)}]$ and $[\text{Ag(II)}]$ in a direction implying that the reaction is less than first order with respect to thallium(I).

The systematic variation from eq 2 and 3 imply that both Ag(II) and Tl(I) must occur in the denominator of this rate expression. A search for a simple mechanism meeting this requirement led to the mechanism



This mechanism is analogous to one of the pathways found for the Ce(IV) oxidation of Tl(I) in the same medium.¹¹ It should be noted that the intermediate free radical could be OH rather than NO_3 . After applying steady-state approximations for NO_3 and Tl(II) , we obtain the rate law

$$R = \frac{k_1 k_3 k_5 [\text{Ag(II)}]^2 [\text{Tl(I)}]}{k_2 k_4 [\text{Ag(I)}] + k_2 k_5 [\text{Ag(II)}] [\text{Ag(I)}] + k_3 k_5 [\text{Ag(II)}] [\text{Tl(I)}]} \quad (4)$$

This rate law predicts that at constant $[\text{Ag(II)}]$ a graph of $[\text{Tl(I)}]/R[\text{Ag(I)}]$ vs. $[\text{Tl(I)}]/[\text{Ag(I)}]$ should be linear. Two such graphs are shown in Figures 4 and 5. The scatter is still large, but qualitative agreement with the mechanism is achieved and systematic trends are not observed. The scatter is probably caused by impurities in the reaction mixtures. A least-squares procedure¹⁶ designed to minimize $\sum [(R_{\text{obsd}}/$

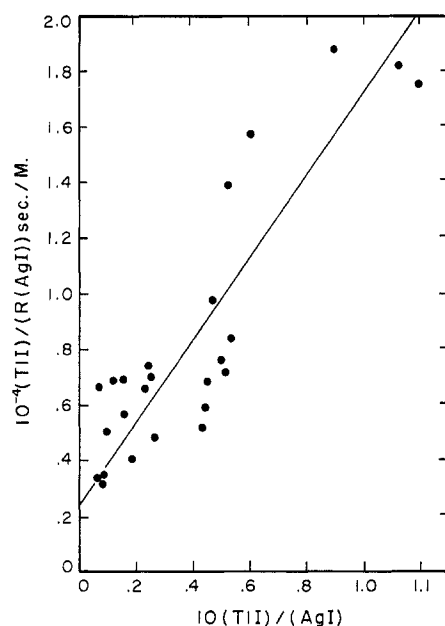


Figure 4.—Test of eq 4; $[\text{Ag(II)}] = 2.37 \times 10^{-4} \text{ M.}$

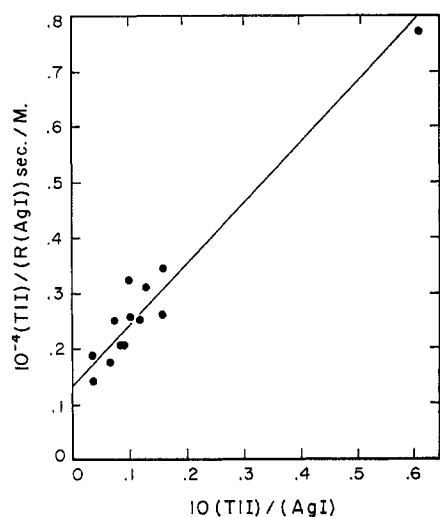
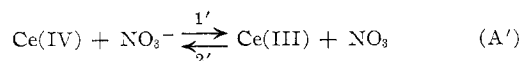


Figure 5.—Test of eq 4; $[\text{Ag(II)}] = 3.56 \times 10^{-4} \text{ M.}$

$R_{\text{calcd}} - 1]^2$, in which R_{obsd} is the observed rate and R_{calcd} is obtained from (4), yielded the following groups of constants: $k_2 k_4 / (k_1 k_3 k_5) = 1.41 \times 10^{-6}$, $k_2 (k_1 k_3) = 2.03 \times 10^{-2}$, and $k_1 = 0.403$. Time is in seconds, concentration in moles/liter, and the temperature is 26.2° . A comparison between observed and calculated values is given in Table I. The rate is in terms of the disappearance of Ag(II) .

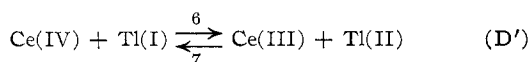
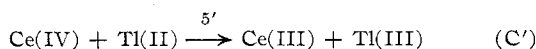
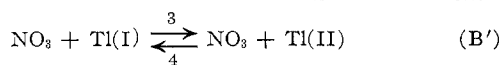
The large scatter and difficulty in proving stoichiometry make these constants somewhat uncertain. They can, however, be shown to be reasonable by comparison with other measurements. Compare the mechanism proposed for this reaction with that for the $\text{Ce(IV)}-\text{Tl(I)}$ reaction.¹¹



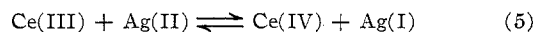
(16) The calculations were performed on an IBM 7094 computer. Details of the program are contained in the thesis of R. W. Dundon, The Johns Hopkins University, 1965, obtainable from University Microfilm, Ann Arbor, Mich.

TABLE I
OBSERVED AND CALCULATED RATES

[Ag(II)]	[Ag(II)]	[Ti(I)]	R _{obs}	R _{cal}	[Ag(II)]	[Ag(II)]	[Ti(I)]	R _{obs}	R _{cal}
x10 ⁵	x10 ²	x10 ⁴	x10 ⁶	x10 ⁶	x10 ⁵	x10 ²	x10 ⁴	x10 ⁶	x10 ⁶
0.593	2.45	8.19	0.55	0.58	1.90	1.65	1.59	1.0	1.6
0.593	2.45	17.3	0.92	0.97	1.94	2.45	17.6	8.6	5.1
0.593	2.45	17.5	0.94	0.97	2.17	1.64	4.12	3.0	3.7
1.07	1.64	4.06	1.1	1.2	2.37	0.146	1.64	5.2	7.4
1.19	0.147	1.58	2.3	3.1	2.37	0.146	1.74	6.8	7.5
1.19	0.147	1.68	2.1	3.2	2.37	0.266	1.59	3.5	6.2
1.19	0.147	3.62	4.4	3.9	2.37	0.433	3.87	4.8	7.0
1.19	0.226	2.13	2.5	3.0	2.37	0.828	1.00	1.7	2.6
1.19	0.267	1.53	1.1	2.4	2.37	0.828	1.55	2.1	3.5
1.19	0.445	1.07	2.4	1.4	2.37	1.57	0.97	1.9	1.5
1.19	0.434	3.81	1.7	2.9	2.37	1.69	1.34	2.5	1.9
1.19	0.829	0.94	0.48	0.80	2.37	1.69	1.39	2.4	2.0
1.19	0.829	1.49	0.97	1.2	2.37	1.73	1.62	1.9	2.2
1.19	0.829	3.47	1.7	2.0	2.37	1.69	1.66	1.9	2.2
1.19	0.829	3.75	1.9	2.1	2.37	1.56	3.49	3.4	2.9
1.19	1.57	0.91	0.55	0.44	2.37	1.69	4.05	3.3	4.1
1.19	1.69	1.28	0.80	0.57	2.37	1.69	4.31	3.6	4.2
1.19	1.69	1.33	0.80	0.59	2.37	1.67	7.79	4.8	5.7
1.19	1.73	1.56	0.47	0.66	2.37	1.62	8.04	5.5	5.8
1.19	1.69	1.60	0.60	0.69	2.37	1.57	8.42	6.4	6.0
1.19	1.75	2.46	1.7	0.96	2.37	1.70	8.75	7.2	5.9
1.19	1.56	3.43	1.0	1.4	2.37	1.69	8.77	3.7	5.9
1.19	1.69	3.99	1.1	1.4	2.37	1.57	17.1	12.0	7.4
1.19	1.69	4.25	0.97	1.5	2.37	2.46	1.71	1.1	1.7
1.19	1.66	7.49	2.3	2.1	2.37	2.45	3.78	2.8	3.1
1.19	1.67	7.73	1.7	2.2	2.37	2.46	3.90	2.3	3.2
1.19	1.63	8.07	4.6	2.2	2.37	2.46	10.6	8.2	5.2
1.19	1.57	8.37	1.7	2.3	2.37	2.46	10.8	7.4	5.5
1.19	1.70	8.69	2.4	2.3	2.37	2.46	11.0	6.6	5.6
1.19	1.57	17.0	2.4	3.2	2.37	3.16	8.31	5.5	4.3
1.19	2.46	1.66	0.50	0.51	2.93	1.69	4.34	5.4	5.7
1.19	2.45	3.72	0.97	1.0	2.85	2.45	8.30	7.1	6.3
1.19	2.46	3.84	0.82	1.0	3.28	1.73	1.67	3.0	3.6
1.19	2.47	10.5	3.0	2.1	3.56	0.265	1.65	8.1	10.3
1.19	2.47	10.8	2.2	2.1	3.56	0.826	1.06	4.1	5.0
1.19	2.46	10.9	2.0	2.1	3.56	1.57	1.03	3.7	3.0
1.19	2.46	17.0	3.0	2.6	3.56	1.69	1.40	4.0	3.7
1.19	2.46	17.4	3.0	2.7	3.56	1.69	1.45	4.1	3.8
1.19	2.45	24.4	4.4	3.1	3.56	1.69	1.72	4.0	4.3
1.19	3.16	0.94	0.28	0.24	3.56	1.73	1.69	3.0	4.1
1.19	3.16	3.37	0.59	0.76	3.56	2.46	1.77	2.9	3.3
1.19	3.16	3.55	0.75	0.80	3.56	2.45	3.83	6.1	5.6
1.19	3.16	8.25	1.3	1.5	3.56	2.46	3.96	4.7	5.7
1.19	3.16	16.9	2.2	2.3	3.56	3.15	1.06	1.8	1.7
1.19	4.66	1.05	0.21	0.13	3.56	3.15	3.67	4.6	4.7
1.19	4.61	35.5	2.5	2.8	3.56	4.66	1.16	1.3	1.3
1.42	2.45	17.5	4.4	3.4	4.27	1.73	1.72	4.4	5.4
1.74	1.73	1.59	1.1	1.3	4.74	2.46	1.83	4.8	5.2
1.62	2.45	8.24	3.0	2.9	5.93	3.15	1.17	3.4	4.1
1.68	2.45	17.4	5.5	4.3	6.32	4.65	1.30	4.4	3.6
					6.44	0.873	1.06	11.0	10.8



From an argument similar to that presented elsewhere,¹⁷ we see that the equilibrium constant in 6 *F* HNO₃ for the reaction



can be obtained from the rate constants for reactions A and A' and is equal to $k_1 k_2' / (k_2 k_1')$. This combination of constants can be obtained from the data presented here and from published values.¹¹ The ratio k_2' / k_2 can be calculated from the ratios of k_2 / k_3 and k_2' / k_3 assuming in the latter case that the ratio is independent of temperature. The value for k_2' / k_2 is 2.6. Preliminary measurements performed by Mr. Eugene Zeltmann to determine k_1' at 35.2° permit us to estimate the value of this constant at 26.2° to be 2.8×10^{-7} . We thus obtain a value for the equilibrium constant for reaction 5 at 26.2° in 6.18 *F* HNO₃ of 3.8×10^6 , which is to be compared with a value of 2.34×10^5 determined by Mr. Zeltmann by emf measurements. Considering the assumption that k_2' / k_3 is temperature independent and the scatter in the present data, the agreement is within probable error.

The mechanisms proposed for the Ce(IV)–Ti(I) and Ag(II)–Ti(I) reactions appear to bear out the proposal made by Uri¹⁸ that reactions involving strongly oxidizing cations would be expected to occur *via* free-radical intermediates. It would be of interest to investigate the Ag(I)-catalyzed reaction of Ce(IV) with Ti(I) in nitric acid to see if the catalysis is perturbed by the reaction of Ag(II) to form NO₃ radical.

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(18) N. Uri, *Chem. Rev.*, **50**, 375 (1952).

CONTRIBUTION FROM THE CARBORUNDUM COMPANY,
NIAGARA FALLS, NEW YORK

A New Route to Boron Nitride

By J. ECONOMY AND R. ANDERSON

Received November 2, 1965

A new synthesis is described for preparation of boron nitride from the reaction of an alkyl polyborate–ammonia complex (RO)₃B₂₅O₃₆·(NH₃)₈ with ammonia in the temperature range of 400–800°. The ammonia complex is obtained *via* a novel disproportionation of a trialkoxyboroxine to the corresponding trialkoxyborane and the ammonia complex. Boron nitride obtained under these conditions possesses a turbostratic structure.

Introduction

A number of preparations for boron nitride have been reported in the literature during the past 120 years.^{1–6}

(1) A. A. Giardini, U. S. Department of the Interior, Bureau of Mines' Information Circular, No. 7664, U. S. Government Printing Office, Washington, D. C., 1953.

(2) P. Popper, Ed., "Special Ceramics," Heywood and Co., London, 1960, Chapter 8.

(3) K. M. Taylor, U. S. Patent 2,808,314 (1957); U. S. Patent 2,855,316 (1958); U. S. Patent 2,888,325 (1959).

(4) T. Renner, *Z. Anorg. Allgem. Chem.*, **298**, 22 (1958).

In most of these reactions ammonia is utilized as a reactant and temperatures of 900–1500° are required for completion of reaction.

The present work describes a new route for preparation of boron nitride by the reaction of an alkyl polyborate–ammonia complex of slightly variable composition (RO)₃B₂₅O₃₄·(NH₃)₈ with ammonia in the temperature

(5) H. Tagawa and O. Itouji, *Bull. Chem. Soc. Japan*, **35**, 1536 (1962).

(6) T. E. O'Connor, *J. Am. Chem. Soc.*, **84**, 1753 (1962).