[A CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Kinetics of the Reaction of Cerium^{IV} and Arsenic^{III} Ions

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The reaction of cerium (IV) sulfate with compounds such as arsenic (III) acid or sodium arsenite has long been known and used in quantitative analysis. It is known that the over-all reaction follows the stoichiometric relation

$$2Ce^{IV} + As^{III} \longrightarrow 2Ce^{III} + As^{V}$$

and that the reaction of the sulfates is quite slow. When used for analysis it is carried out in the presence of a catalyst such as osmium tetroxide or iodine monochloride.

Schaffer has suggested[1] that reactions of the type

$$2Ce^{IV} + Tl^{I} \longrightarrow 2Ce^{III} + Tl^{III}$$

should be slow because of the necessity of a termolecular collision. However, the arsenic^{III} ion does not exist in solution as a simple ion, and experiments on transference[2] and oxidation–reduction potentials[3,4,5] of cerium (IV) salt solutions indicate clearly that some complex ion is formed in cerium (IV) sulfate solution. The existence of such complex ions, as well as a termolecular mechanism, might be an important factor in causing a slow reaction. Accordingly, an investigation of the kinetics of the reaction was undertaken in an attempt to determine the influence of these factors.

After completion of the first part of this investigation,[6] results of similar studies using a different technique and different concentrations were published by Stefanovskii.[7] Upon the basis of rate studies in sulfuric, nitric, and perchloric acids, Stefanovskii concluded the reaction is a "monoelectron" reaction in which the rate-determining step is bimolecular.

The present experiments were then extended to cover also ranges of concentration and reaction comparable to those used by Stefanovskii.

Experimental

Materials.—The cerium (IV) sulfate used in the determination of the reaction velocity constant was prepared from C. P. Cerous Nitrate (Eimer and Amend Co.). This was dissolved in nitric acid, oxidized with potassium bromate, and twice precipitated as basic cerium (IV) nitrate—as described by Kunz.[3] The basic nitrate was reduced and precipitated as cerium (III) oxalate and ignited to cerium (IV) oxide. Analysis of the resulting oxide gave 99% cerium (IV) oxide. The cerium (IV) oxide was then digested with concentrated sulfuric acid and dissolved.

For reasons of economy, the numerous experiments carried out to test comparative effects of various factors upon the rate of reaction were made using cerium (IV) sulfate solutions prepared directly from the best commercial grades of cerium (IV) sulfate or cerium (IV) oxide. Experimental tests showed that rates of reaction observed for these solutions were in agreement with those of the specially purified cerium (IV) sulfate. The traces of other rare earth sulfates, etc., present played no part in the oxidation–reduction reaction and were not sufficient in quantity to change the ionic strength of the solutions appreciably.

The cerium (IV) concentration was determined by standardization against sodium arsenite prepared from primary standard arsenic (III) oxide. The acidity of the solutions was determined by precipitating the cerium with ammonium oxalate and filtering. The filtrate and washings were titrated with standard ammonium hydroxide, using brom thymol blue indicator.

The arsenic (III) solutions were prepared from primary standard arsenic (III) oxide. This was dissolved directly in water or in an equivalent quantity of sodium hydroxide solution. Because of the large excess of sulfuric acid always present in reaction mixtures, the arsenic (III) acid and sodium arsenite gave the same results in rate determinations. The solutions were standardized directly against the cerium (IV) sulfate, using iodine monochloride as catalyst and ferroin as indicator.

Iron (II) sulfate solution was used to determine the cerium (IV) concentration in reaction mixtures at various time intervals. This was prepared by dissolving reagent grade iron (II) ammonium sulfate in very dilute sulfuric acid and standardizing directly against the cerium (IV) sulfate, using ferroin indicator. The solution was stored in the absence of air and restandardized at frequent intervals.

All other reagents and solutions were prepared from C. P., reagent grade materials.

Rate Determinations.—Rate measurements were carried out in an all-glass apparatus designed so that experiments could be made in an atmosphere of nitrogen.

The reaction vessel was a 500-cc. round-bottom flask. This was fitted with inlet and exit tubes and stopcocks such that nitrogen might be bubbled through to sweep out air or to stir the solutions and that the nitrogen pressure might be used when desired to force samples of the reaction mixture into a calibrated pipet. A third inlet tube was connected to an auxiliary vessel so that solutions might be brought to constant temperature in this vessel and then forced into the reaction flask by means of the nitrogen.

The reaction flask and auxiliary were immersed in a thermostat, electrically heated and regulated by a mercury thermoregulator. The bath temperature was held constant to within ±0.03°.

Desired quantities of the reagents were placed in the flasks. After temperature equilibrium was established, they were mixed and stirred thoroughly. One sample was taken as quickly as possible to check the initial concentrations, and other samples were titrated at later times in order to follow the progress of the reaction.

Each sample was allowed to flow from the pipet into chilled water and then titrated quickly with standard ferrous sulfate to determine the cerium (IV) concentration.

The nitrogen used was commercial water-pumped nitrogen. This was bubbled through a purifying and humidifying train containing alkaline pyrogallate, sodium stannite, and a solution of the actual reagents. Blank tests showed that no changes occurred in concentration of the reagent solutions in the presence of this nitrogen within a period of hours.

Some rate measurements were checked by the method used by Stefanovskii—using samples collected in saturated sodium bicarbonate and titrated with iodine to determine the arsenite concentration. Results of the two methods were consistent in general, except that the iodine

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(1) Schaffer, THIS JOURNAL, **55**, 2169 (1933).

(2) Jones and Soper, *J. Chem. Soc.*, 805 (1935).

(3) Kunz, THIS JOURNAL, **53**, 98 (1931).

(4) Noyes and Garner, *ibid.*, **58**, 1265 (1936).

(5) Sherrill, King and Spooner, *ibid.*, **65**, 170 (1943).

(6) J. W. Moore, M.A. Thesis, University of Texas, June, 1942.

(7) Stefanovskii, *J. Gen. Chem.* (U. R. S. S.), **XI**, 970 (1941).

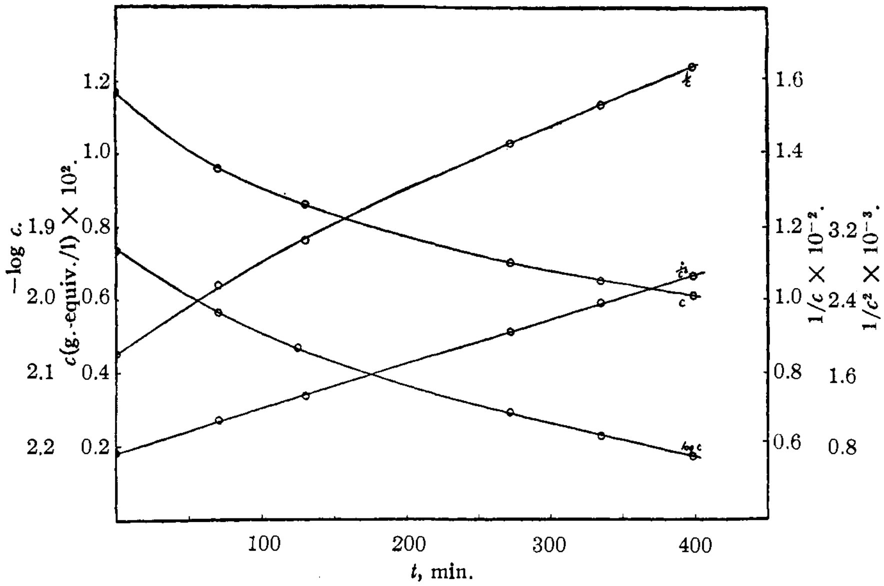

Fig. 1.—Order of reaction.

titration was difficult at any but very low concentrations because the precipitate formed by hydrolysis of the cerium compounds tends to obscure the end-point.

Results

A typical set of data is given in Table I below. In all experiments equivalent quantities of cerium (IV) and arsenic (III) were used. Reproducibility of results varied somewhat according to the speed of reaction, but, in general, titration values could be duplicated within 2% or less. All values for rate constants, etc., are based upon several experiments involving titrations at five to seven varying time intervals for each experiment. Such values, for any given set of conditions of time, concentration, etc., checked within ±5%.

TABLE I

RATE DETERMINATION

Temperature, 30°; H_2SO_4, 0.5 molar

Time, min.	Vol. Fe^{II},[a] ml.	Concn. Ce^{IV}, g. ions/l.	k_2 (2nd order)	k_3 (3rd order)
0	29.55	0.0234		
			0.130	25.3
70	24.45	.0193		
			.112	22.2
130	21.64	.0171		
			.125	24.3
272	17.64	.0139		
			.077	25.9
335	16.45	.0130		
			.079	25.0
399	15.49	.0122	.105	24.5

[a] Concn. Fe^{II} = 0.01978 molar; vol. sample = 25 ml.

Order of Reaction; Rate Constants.—The reaction is clearly complex and cannot be classed by ordinary criteria as to the order. For any particular set of starting conditions and for measurements involving comparatively small concentration changes, the results indicate a third order reaction. In Table I are listed values for the reaction velocity constant k as calculated for a second-order and a third-order reaction. The second-order constants (k_2) were calculated from the equation

$$k_2 = \frac{1}{t}\,\frac{x}{a(a-x)}$$

where a is initial concentration in g. equiv. per liter, and x is equivalents reacted at time t, and the third-order constants (k_3) from

$$k_3 = \frac{1}{2(t_2 - t_1)}\left[\frac{1}{c_2^2} - \frac{1}{c_1^2}\right]$$

where c is concn. of As^{III} = $^1/_2$ concn. Ce^{IV} at time t. It may be noted that the calculated values of k_3 show an average deviation of about 5% from the mean as compared with 20% for k_2. Furthermore, the k_2 values show a general trend toward lower values at longer time intervals.

The order of reaction may also be checked graphically by plotting log c, $1/c$ and $1/c^2$ against time, as shown in Fig. 1. The straight line relationship between $1/c^2$ and time also indicates a third order reaction.

However, the values of k_3 are not constant when experimental conditions are changed. For a typical third-order reaction, a ten-fold decrease in concentration should increase by a factor of 100 the time necessary for any given fraction of the material to react, but in this case such dilution may do little more than double the time of reaction. In general, calculated k_3 values are, therefore, higher for more dilute solutions.

The influence of various changes in concentration, etc., is shown in Table II in the calculated values of k_3 and also in Table III which shows results obtained at different temperatures. It is notable that decreasing the cerium (IV) concentration tends to increase k_3, decreasing the arsenic (III) concentration to decrease k_3.

It may be noted that the products of the reaction have some influence on the rate of reaction, but apparently no more than that of similar electrolytes which take no part in the reaction. Such effects may be expected as a result of changes in ionic strength of the solution, in ionic equilibria, etc.

TABLE II

EFFECT OF CONCENTRATION ON REACTION VELOCITY CONSTANT

Concn. H_2SO_4 is 1 g. mole/l. in all cases

Cerium (IV), g. ions/l.	Arsenic (III), g. ions/l.	Other added substances	k_3
0.05	0.025	None	18.8
.025	.025	None	26.4
.0125	.025	None	30.8
.05	.0125	None	18.0
.025	.0125	None	26.0
.05	.00625	None	6.8
.025	.0125	0.0125 M As^V	24.0
.025	.0125	0.0125 M Al^{III}	22.4
.025	.0125	0.025 M Ce^{III}, 0.0125 M As^V	21.6

Energy of Activation.—In Table III are shown also the results obtained when "energy of activation" values are calculated using the Arrhenius equation. It is apparent that the simple equation is not applicable to this reaction.

Catalytic Effects.—Studies were made of the effect of various added substances on the rate of reaction. In Fig. 2 are shown the results in the presence of hydrochloric, nitric and perchloric acids. In a solution 0.5 molar in sulfuric acid and 1.0 molar in potassium chloride, bromide or iodide, the reaction was too fast to be measured accurately.

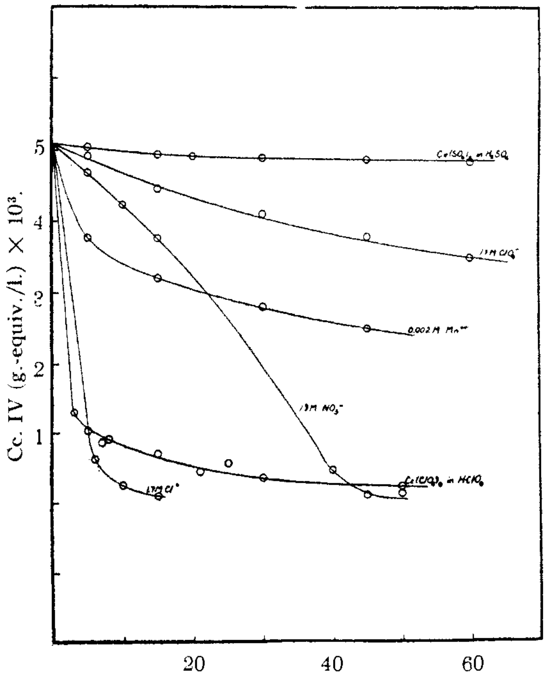

Fig. 2.—Effects of other ions (all solutions contain 2 g.-ions/l. of H^+).

TABLE III

TEMPERATURE EFFECT

Series I, 0.05 M Ce^{IV}, 0.025 M As^{III}, 1.0 M H_2SO_4; Series II, 0.05 M Ce^{IV}, 0.00625 M As^{III}, 2.0 M H_2SO_4

Temp., °C.	Rate constants I	Rate constants II	Calculated values of E I	Calculated values of E II
20	1.4	0.61		
25	2.7	1.0	21,600	19,800
30	4.7	1.6	20,000	14,200

Addition of 0.01 molar quinone was found to double the rate of reaction, and approximately 0.0001 molar manganese (II) sulfate increased the rate seven-fold.

Discussion

The mechanism of reaction must be such as to explain the following facts: (a) within a small range of concentration change the reaction is third order; (b) values of k calculated using the total cerium (IV) concentration vary with dilution of the reaction mixture; (c) the reaction does not follow the Arrhenius equation for the temperature effect; (d) the reaction rate is increased in the presence of perchloric, nitric and hydrochloric acids, manganese (II) salts, quinone.

The first three could be expected if a cerium (IV) and sulfate complex is formed in solution. Steps such as the following should then be involved

$$(1) \qquad Ce(SO_4)_x^{4-2x} \rightleftarrows Ce^{IV} + xSO_4^{''}$$

$$(2) \qquad 2Ce^{IV} + As^{III} \longrightarrow 2Ce^{III} + As^{V}$$

If step (2) were rate-determining, the reaction would be kinetically third-order. The rate of reaction would depend upon the actual Ce^{IV} ion concentration, whereas the analysis used determines only the total of Ce^{IV} and $Ce(SO_4)_2^{4-2x}$. Values of k_3 calculated from the total cerium would therefore not be consistent where conditions such as dilution or temperature change shift the equilibrium in (1).

The exact nature of the ions reacting is not necessarily that shown in these equations.

The work of Sherrill, King and Spooner[5] on ceric perchlorate and that of Garrett, Holmes and Laube[8] on arsenic salts in hydrochloric acid solutions show that it is unlikely that either cerium (IV) or arsenic (III) exists in simple form. The influence of changing arsenic (III) concentration on the rate of reaction suggests that some sort of hydrolytic equilibrium of the As^{III} may also be established in the system. The actual reaction may well be, for example

$$2CeOH^{+++} + AsO^{+} \longrightarrow 2CeOH^{++} + AsO^{+++}$$

but this would cause no change in the results from ordinary kinetic measurements.

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[8] Garrett, Holmes and Laube, THIS JOURNAL, **62**, 2024 (1940).

This concept of the mechanism of reaction is supported by the results in perchloric acid solution. Sherrill, *et al.*,[5] have shown that no complex is formed in cerium (IV) perchlorate. Under such conditions the observed reaction should be essentially the termolecular reaction (2). This would explain why the rate is greater in perchloric acid (Fig. 2), but reaction is still not instantaneous.

The catalytic effect of manganese (II) may be explained by the occurrence of bimolecular reactions, as suggested by Schaffer[1]

$$\begin{aligned} \mathrm{Ce^{IV}} + \mathrm{Mn^{II}} &\longrightarrow \mathrm{Ce^{III}} + \mathrm{Mn^{III}} \\ \mathrm{Ce^{IV}} + \mathrm{Mn^{III}} &\longrightarrow \mathrm{Ce^{III}} + \mathrm{Mn^{IV}} \\ \mathrm{Mn^{IV}} + \mathrm{As^{III}} &\longrightarrow \mathrm{Mn^{II}} + \mathrm{As^{V}} \end{aligned}$$

In the case of quinone, a similar series involving a semiquinone and hydroquinone is possible.

The pronounced effect of halogenides and of nitrate suggests that a series of bimolecular steps may be involved in these cases also, but further studies will be necessary to determine the nature of these effects.

The experimental results seem neither to require nor to support the bimolecular step postulated by Stefanovskii[7]

$$\mathrm{Ce^{++++}} + \mathrm{AsO_2^-} \longrightarrow \mathrm{Ce^{+++}} + \mathrm{AsO_2}$$

The values for the bimolecular rate constant calculated by Stefanovskii show a definite "drift" with time. This, coupled with the rather large uncertainty inherent in such measurements, renders the conclusion that the reaction is second order questionable and seems to offer no justification for postulating a tetravalent state for arsenic. Furthermore, a bimolecular mechanism suggests essentially instantaneous reaction in perchlorate solution and also leaves unexplained the catalytic effects observed.

It is evident, however, that no calculations based on total cerium (IV) values can give conclusive results for a system involving the cerium (IV) sulfate complex. Information is necessary concerning the nature and extent of dissociation of this complex. Spectrophotometric studies are now being carried out in these Laboratories in an attempt to obtain such information.

In conclusion, the authors wish to express their appreciation to the University of Texas Research Institute for a grant made to one of us (R. C. A.) for equipment and materials, and to Dr. A. R. Choppin, Louisiana State University, for his valuable suggestions made at the start of this investigation.

Summary

1. The rates of reaction of cerium (IV) and arsenic (III) ions in sulfuric acid solution and with added perchloric, nitric and hydrochloric acid, halogenides, quinone and manganese (II) sulfate have been observed.

2. The rate-determining step was found to be third-order. The rate of reaction in sulfuric acid is decreased greatly by the formation of a cerium (IV) and sulfate complex, but reaction is not instantaneous in the absence of such complex formation.

3. Substances such as manganese (II) sulfate may catalyze the reaction by making possible a bimolecular mechanism.

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Substituted 2-Sulfonamido-5-aminopyridines. II

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In continuing our studies of substituted 2-sulfonamido-5-aminopyridines,[2] we have synthesized three series of compounds for pharmacological comparison. The compounds of each series contain, respectively, a single atom of halogen or two atoms of the same halogen, or a single cyano radical or its hydration products. We also prepared several compounds, not derivatives of 2-sulfonamido-5-aminopyridine but of sulfanilamide.

Most of the methods given for the preparation of 2-amino-5-iodopyridine[3] (I) were tried, but none gave satisfactory yields. We succeeded however in developing a new procedure by which excellent yields (90%) of the product (I) were obtained.

Iodination of 2-aminopyridine to form a diiodinated product has been tried previously,[3] but, although the corresponding chloro and bromo pyridines have been prepared, 2-amino-3,5-diiodopyridine (II) has not been synthesized before. In agreement with Magidson and Menshikov[3] we found that 2-amino-5-iodopyridine (I) could not be satisfactorily iodinated, although a small quantity of the required compound was isolated after the action of iodine monochloride on 2-amino-5-iodopyridine at 60° in tertiary butanol. Therefore we used an indirect method to obtain (II) as indicated by the following sequence of formulas.

Sodium 2-pyridolate (III) was prepared by the method of Chichibabin and Rjazancev[4] in 95%

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[1] Submitted in partial fulfillment of the requirements for the degree of Master of Arts.

[2] Caldwell and Kornfeld, THIS JOURNAL, **64**, 1695 (1942).

[3] (a) Magidson and Menshikov, *Ber.*, **58**, 113 (1925); (b) Austrian Patent 121,246; (c) German Patents 513,293, 503,920, 473,213, 526,803, 491,681; (d) Swiss Patent 129,173; (e) Chichibabin and Kirsanov. *Ber.*, **60**, 766 (1927).

[4] Chichibabin and Rjazancev, *J. Russ. Phys.-Chem. Soc.*, **47**, 1571 (1915).