which is generally considered to be characterized by a coördination number of four, gives rise to an EDTA chelate which apparently has the same gross structure as the other MEDTA chelates studied (with the exception of PbEDTA). This might suggest that all the MEDTA ions, with the possible exception of PbEDTA, have four EDTA groups (presumably the two nitrogens and two carboxyl groups) bonded to the metal. Recent evidence,[21] however, favors a structure for the CuEDTA ion in which all six of the groups from the EDTA, ion are bonded to the metal. This evidence, together with Fig. 1, would seem to favor a hexa-coördinated structure for all the MEDTA ions studied here (again with the possible exception of PbEDTA).

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PITTSBURGH 35, PA.

(21) S. Kirschner, THIS JOURNAL, **78**, 2372 (1955).

[CONTRIBUTION NO. 1356 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Kinetics of the Iodide-catalyzed Reaction between Cerium(IV) and Arsenic(III)[1]

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The rates at 25° of reactions in sulfuric acid solutions between ceric sulfate and arsenious acid catalyzed by iodide have been measured for a variety of concentrations of reactants and catalyst. A mechanism for the reaction is proposed. Except at low cerium/arsenic ratio, a steady-state equation derived from the mechanism adequately describes the results. Possible limitations of the treatment are discussed.

It is well known that compounds of iodine at quite low concentration are catalysts for the reaction between Ce(IV) and As(III). Micro-determinations of iodine have been based on the effect,[3-5] but the kinetics of the processes involved have not been extensively studied. Stefanovskii[6] and Moore and Anderson[7] have reported studies on the apparently uncatalyzed reaction. The effect of catalysts has been the explicit concern of Anderson, Lasater and Lippman.[8] The present work was undertaken in the hope of finding a reasonable explanation for the somewhat singular behavior of the catalyst in this reaction.

The salient qualitative features of the reaction between ceric sulfate and arsenious acid in sulfuric acid solution are simple and striking. If the solutions are mixed in the absence of added catalysts, the reaction is slow, and reproducible rate determinations are difficult to obtain. In one such experiment of ours, with concentrations about 0.02 N in the reactants and 2 M in sulfuric acid, two hours were required for 50% reaction. If potassium iodide, in amount sufficient to give a concentration of 1.6×10^{-7} M in the reaction mixture, is initially mixed with the *arsenite* solution, the reaction proceeds smoothly and is some 60% complete in ten minutes. If, on the other hand, the iodide is added to the ceric solution 15 minutes or so before this is mixed with the arsenite solution, no catalytic effect is observed—even 20 minutes after mixing no certainly detectable reaction has taken place.

We have measured the kinetic behavior of the catalyzed reaction at 25° and suggest a mechanism which gives an adequate interpretation of all of our experimental results.

Experimental

The experiments were designed so as to permit the independent variation of the initial concentrations of the reactants, the catalyst and of the sulfuric acid. Each of these substances in the form of standardized solutions was introduced volumetrically into the legs of a Λ-shaped reaction vessel. After at least 15 minutes in a water thermostat at 25 ± 0.02°, the solutions were mixed and the reaction allowed to proceed for a measured time interval, when the reaction was quenched by the rapid admixture of a measured excess of standard ferrous sulfate solution. The extent of the reaction was then determined by titrating the excess ferrous ion.

It was shown that ferrous sulfate does not react with any substance in the solution (*e.g.*, arsenate) in such a way as to affect the results of the determinations. To this end the reactions were carried out with a small excess of arsenite and the solutions allowed to stand at elevated temperatures for several hours after the ceric color disappeared. Ferrous sulfate was added and the solution again allowed to stand for periods up to 100 minutes. Titration with ceric sulfate showed that no ferrous ion had been oxidized.

The ceric sulfate used in the rate determinations was prepared *via* hydrous ceric oxide precipitated from reagent grade ammonium hexanitratocerate. A solution of the washed precipitate in a weighed amount of sulfuric acid was standardized against National Bureau of Standards arsenious oxide. The arsenious acid solution used was prepared from Bureau of Standards arsenious oxide and analyzed by titration with ceric sulfate. Solutions of sulfuric acid, prepared by diluting J. T. Baker Analyzed reagent, were standardized through a precipitation of barium sulfate. The catalyst was a very dilute solution of potassium iodide (9.81×10^{-7} M) prepared by successive dilutions of a solution of a weighed amount of reagent grade salt. Ferrous sulfate solution for quenching purposes was kept under hydrogen and standardized each day it was used.

The distribution of the reagents in the legs of the reaction vessels was arranged so as to keep the sulfuric acid concentration nearly the same in both in order to minimize temperature changes on mixing.

The reactions were started by vigorous shaking of the vessels, and times were noted from an electric clock to the

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(1) The experimental part of this paper has been taken from the dissertation presented in 1944 by John Stanley Yates to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Dr. Yates died in 1945 as the result of a tragic accident in his home. The publication of Dr. Yates' excellent experimental work has been so long delayed because of lack of adequate interpretation.

(3) E. B. Sandell and I. M. Kolthoff, *Microchim. Acta*, **1**, 9 (1937).

(4) H. Yoto and E. Sudo, *J. Chem. Soc. Japan*, **63**, 1324 (1942).

(5) A. Lein and N. Schwartz, *Anal. Chem.*, **23**, 1507 (1951).

(6) V. F. Stefanovskii, *J. Gen. Chem. U. R. S. S.*, **XI**, 970 (1941).

(7) J. W. Moore and R. C. Anderson, THIS JOURNAL, **66**, 1476 (1944).

(8) R. C. Anderson, J. A. Lasater and D. Lippman, *ibid.*, **71**, 2577 (1949).

nearest second. Before a tube was replaced in the thermostat, it was momentarily inverted in such a way as to drain virtually all of its contents into one leg. Thirty seconds before a reaction was due to be quenched, the standard ferrous sulfate solution was pipetted into the empty leg of the tube. The reaction was stopped by violently shaking the tube. The reaction between ferrous ion and Ce(IV) appears to be nearly instantaneous, so the time taken to quench the reactions was no longer than that required for mixing the solutions. The excess ferrous sulfate was titrated with ceric sulfate using ferrous *o*-phenanthroline as indicator.

The over-all analytical uncertainties are estimated to be 0.3%. Their effect on the final results is discussed below.

The final volume of the reacting solution was calculated assuming additivity of the volumes of its components except in the case of sulfuric acid, where a correction of about 0.5% was necessary. The uncertainty in the values of the final volumes is no more than 0.15%.

Results and Discussion

About two hundred and thirty rate determinations were carried out; it is possible to present here only a portion of these results. All concentrations are taken to be in equivalents per liter and are denoted as follows: *a*, initial arsenious acid; *c*, initial ceric sulfate; *j*, initial potassium iodide (moles/l.); *s*, equivalents reacted at time *t* (minutes).

The qualitative and, for the most part, the quantitative features of the reaction can be accounted for on the basis of the following considerations. We suppose: (1) that the principal reaction of iodide is with a dimer of cerium (IV), the concentration of which is, with sufficient accuracy, in constant ratio to the square of the total cerium (IV) content of the solution; (2) that the only reaction of arsenic (III) is with hypoiodous acid; (3) that the cerium dimer can form a hypoiodite complex (analogous to a chloride complex) *which does not react with* As(III); and (4), of course, that at sufficiently high iodide concentrations, iodide and hypoiodous acid react to liberate free iodine. Point (3) is an *ad hoc* assumption; but it is reasonable in itself, and without it or some equivalent assumption it appears to be impossible to account either for the catalysis by small iodide concentrations or the failure of the catalytic effect when the iodide is initially exposed to the cerium. Thus in the presence of arsenic, HIO is regenerated by reactions (3) and (4) of the scheme below; in the absence of arsenic all iodine finds its way into the non-reactive complex.

(1) $I^- + (Ce(IV))_2 \cdot A + H_2O \xrightarrow{k_1} HIO + 2Ce(III) + H^+$

(2) $HIO + (Ce(IV))_2 \cdot A \xrightarrow{k_2} (Ce(IV))_2 \cdot IO + H^+ + A$

(3) $HIO + HAsO_2 \xrightarrow{k_3} HAsO_3 + H^+ + I^-$

(4) $I^- + (Ce(IV))_2 \cdot IO + H_2O \xrightarrow{k_4} 2HIO + 2Ce(III)$

and, significant only at higher iodide concentrations than used in the present work

(5) $I^- + HIO + H^+ \xrightarrow{k_5} I_2 + H_2O$

The non-committal formula $(Ce(IV))_2 \cdot A$ is used to denote some anionic complex of dimerized cerium. The regeneration of iodide ion through the action of the arsenious acid will lead to a steady concentration of HIO. We find at once for the rate of this steady-state reaction

$$-\frac{d}{dt}[As(III)] = \frac{k_1 k_3}{k_2}[I^-][As(III)] \frac{1 + \dfrac{2k_4}{Kk_1}\dfrac{[Ce_2IO]}{[Ce(IV)]^2}}{1 + \dfrac{k_3}{Kk_2}\dfrac{[As(III)]}{[Ce(IV)]^2}} \tag{1}$$

writing K for $[(Ce(IV))_2 \cdot A]/[Ce(IV)]^2$. The constant k_4 will not be greatly different from k_1; both refer to reactions of iodide ion with similar complexed cerium dimers. We may certainly suppose that the concentration of the hypoiodite complex of cerium is small compared to that of the sulfate complex. The second term in the numerator of the above expression is therefore negligible. For the steady-state reaction, the expression for the ambient iodide concentration, $[I^-] = j - [HIO] - [(Ce(IV))_2 \cdot IO]$, is solvable explicitly for this concentration, which is thus seen to be a slowly varying function of the composition of the solution and proportional to the concentration of added iodide. We shall write $[I^-] = \kappa j$. The factor κ can be seen to be more nearly constant for high cerium concentrations, as is qualitatively evident from the mechanism above. We find finally the following approximate rate equation for the steady-state reaction

$$\frac{ds}{dt} = kj \frac{a - s}{1 + \dfrac{k'}{2}\dfrac{a - s}{(c - s)^2}} \tag{2}$$

with $k = k_1 k_3 \kappa / k_2$ and $k' = k_3/Kk_2$.

Rate equation 2 at once accounts for the often observed linear dependence of the rate on the concentration of added iodide. The equation is readily integrated and gives

$$\ln \frac{a}{a - s} + k' \frac{s}{2c(c - s)} = kjt \tag{3}$$

The agreement between duplicate experiments in terms of the functions in equation 3 is generally about what would be expected from the estimated uncertainties in the measurements. Thus in one case the estimated uncertainty in $\ln(a/(a - s))$ is 0.011; the difference between the duplicates is 0.023. For $s/2c(c - s)$ the estimate gives 1.1; the difference between duplicates is 1.3. These remarks apply only to the smoothly running reaction in the presence of added iodide.

Plots against the time have been made for each of the functions on the left of (3). The curves so obtained individually show quite long regions of linearity (but see below); several of these are given in Fig. 1a and 1b. The initial slopes of these curves divided by the appropriate values of *j* (six pairs in all) served to determine first approximations to *k* and *k'*. To get a somewhat more accurate set of values for the constants, the data for a series of determinations in which the value of *j* was increased a hundred-fold, from 0.033×10^{-7} to 3.28×10^{-7}, were also treated according to (3). Using the approximate value of *k'*, 0.0456, the function on the left of (3) divided by the time was plotted against *j*. This plot is given in Fig. 2, with *j* as the ordinate. It is seen that a straight line results, with, as might be expected, a negative intercept. This intercept is taken as a measure of the concentration of catalytic halide-like impurity which must be assumed in order that the above mechanism be quite in accord with the data. This interpretation is supported by

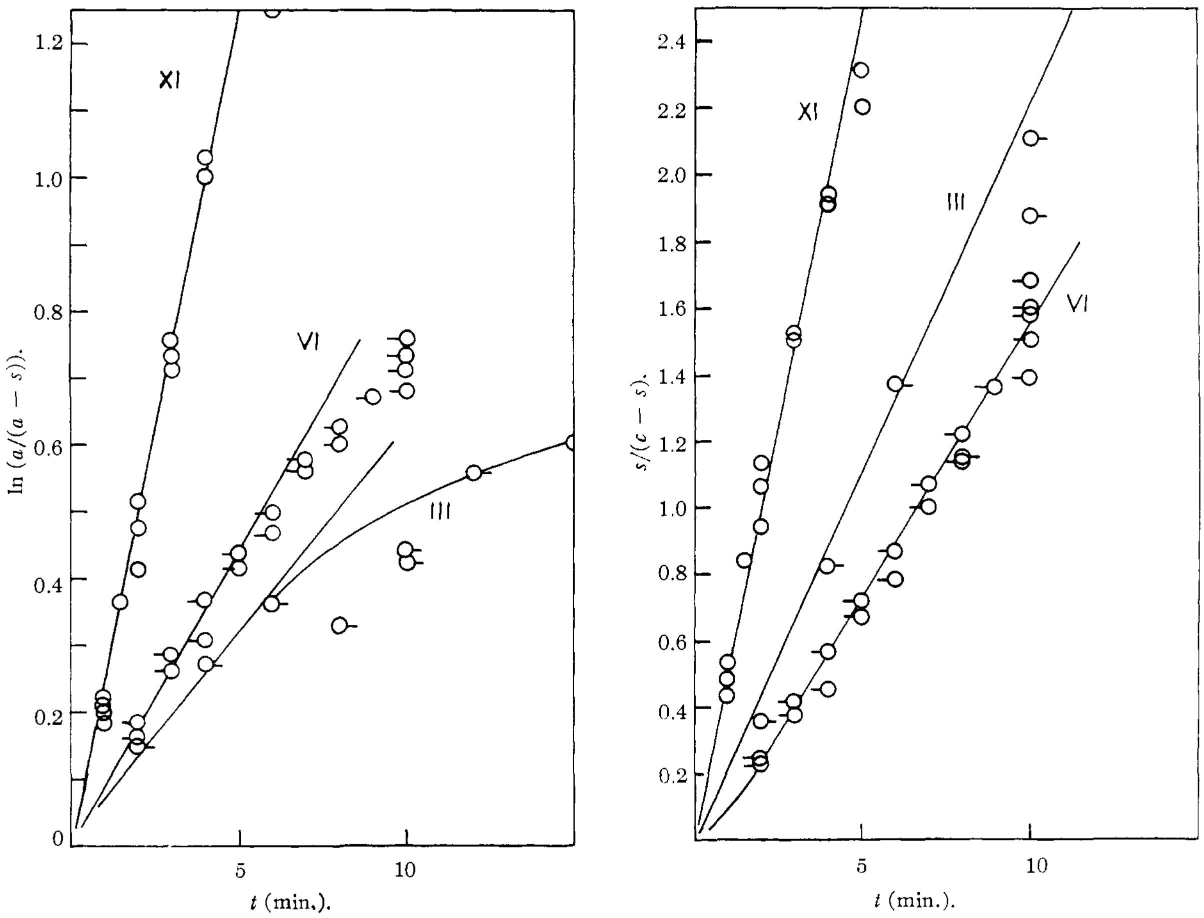

Fig. 1a, b.—Typical series of kinetic measurements calculated according to equation 3. Initial conditions are given in Table I. In Fig. 1b for Series XI divide the ordinate given by ten.

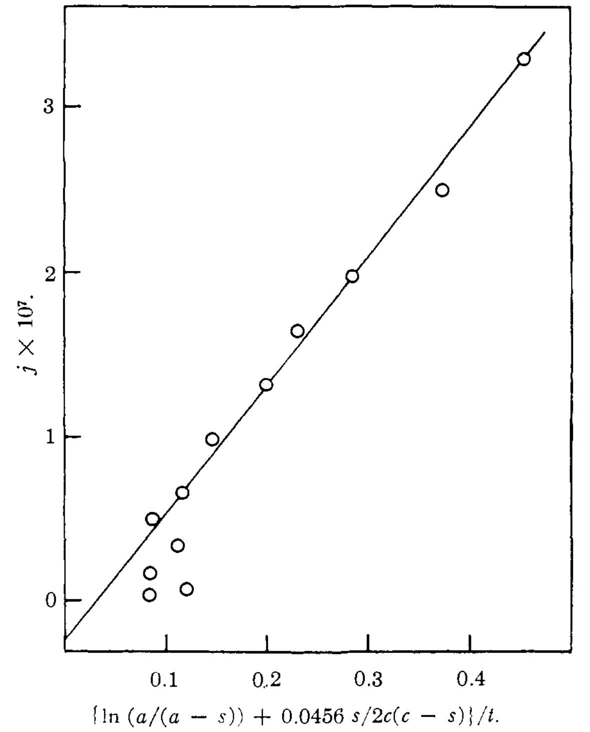

Fig. 2.—Integrated rate law (3) as a function of added iodide.

the experimental fact that the addition of mercuric ion to the reactants greatly represses the rate of the reaction. Thus with a concentration of 3.7×10^{-5} *M* Hg(II) the reaction was only 4% complete after two hours. In the absence of mercury, other conditions being the same, the extent of the reaction reached 50% in the same time. The straight line of Fig. 2 implies a catalytic impurity at concentration 0.24×10^{-7} *M*. Since all of the experiments were carried out with reagents from the same stock, it is supposed that this catalyst concentration is applicable in all cases. The slope of the line of Fig. 2 is $k = 1.3 \times 10^{6}$. Second approximations to k and k' have been obtained by using as j the value of added iodide increased by 0.24 ×

TABLE I

STEADY-STATE SLOPES

$$A = \ln(a/(a - s))/(j + 0.24) \times 10^7 t$$
$$B = (s/2c(c - s))/(j + 0.24) \times 10^7 t$$

Series	[H⁺]	[SO₄⁼]	$a \times 10^2$	$c \times 10^2$	$j \times 10^7$	$A \times 10^{-6}$	$B \times 10^{-7}$
II	3.74	1.92	2.300	2.416	1.649	0.519	1.545
III	3.73	1.91	4.573	2.407	1.643	.334	2.470
V	3.98	2.01	2.292	1.066	1.644	.254	1.558
VI	3.94	2.01	2.291	1.940	1.643	.478	2.174
VII	3.90	2.01	2.290	2.817	1.643	.686	1.332
VIII	3.87	2.01	2.289	3.637	1.642	.931	0.888
XI	3.83	2.01	1.142	4.510	1.641	1.346	0.297
XVI	3.28	1.66	2.291	0.965	1.643	0.209	4.003

10^{-7}. (In most cases this amounts to a correction in j of 15%.) The values of the corresponding slopes of $\ln(a/(a - s))$ and $s/2c(c - s)$ divided by the corrected j values are given in Table I, together with the initial conditions of the reactions and the formal concentrations of hydrogen and sulfate ion. The linear relation between A and B, the slopes of the functions in (3), predicted by the mechanism is borne out by the data, except possibly for Series V and XVI. In these latter cases the low values of c cause a large multiplication of the errors. The discrepancies in these two cases we do not consider to be particularly significant, but we shall return to the point. Largely disregarding Series V and XVI, we select the values

$$k = 1.4 \times 10^6 \text{ l./mole min.}$$
$$k' = 0.047 \text{ mole/l.}$$

The value 0.047 for k' is used in the computation of Table II, which presents the results of an independent series of experiments done at increasing iodide concentration and at approximately the same extents of reaction. The mechanism is here tested by computing values for k. We obtain for this series the value $k = 1.1 \times 10^6$, in sufficiently good agreement with the summary value given above.

TABLE II

TEST OF MECHANISM

Series XIII: $a = 0.03390$, $c = 0.02407$, k' taken to be 0.047.

t (min.)	$(j + 0.24) \times 10^7$	$s \times 10^2$	$k \times 10^{-6}$
100	0.568	2.022	1.28
50	.897	1.822	1.03
25	1.553	1.782	1.10
20	1.883	1.744	1.06
16.7	2.210	1.749	1.10
10	3.523	1.725	1.10

The agreement of the approximate rate equation with the experimental data is less satisfactory in the region of initially low cerium concentration. While, certainly, analytical errors are badly multiplied in this region, it is probable that the difficulty is more fundamental. The effect is seen in Table III, which gives the results of a series of measurements at constant added iodide concentration and in which the ratio of initial arsenic to initial cerium is varied twenty-four-fold. Assuming $k' = 0.047$ as before, we compute the corresponding values of k. While in the main the results are satisfactory below $a/c = 2.4$, the large values of k for low c together with the slight drift throughout the series (and this combined with other similar results) makes it apparent that the reaction is actually faster at low cerium concentration than can be accounted for by our equation.

TABLE III

EFFECT OF INITIAL CERIUM CONCENTRATION

Series X, $a = 0.04578$ to 0.04570, $j = 1.644 \times 10^{-7}$.

$c \times 10^2$	t (min.)	s	$k \times 10^{-6}$	Av. $k \times 10^{-6}$
0.188	5	0.104	16.4	
0.188	10	.150	32.8	25
1.066	5	.592	3.1	
1.066	10	.836	4.4	3.8
1.940	5	1.065	1.8	
1.940	10	1.499	2.4	2.1
2.817	5	1.521	1.5	
2.817	10	2.108	1.6	1.6
3.637	5	1.949	1.4	
3.637	10	2.813	1.7	
3.637	10	2.726	1.5	1.6
4.510	5	2.331	1.3	1.3

We can give no satisfactory quantitative discussion of this point. Qualitatively one would expect a higher ambient iodide ion concentration in the steady state for low cerium and hence a higher rate than given by equation 2 with constants determined for high cerium concentrations. But it may well be entirely illusory to apply the steady-state equation to our data for low cerium concentrations. The mechanism demands a slower approach to steady state for low cerium. Indeed, in the plots of $\ln(a/(a - s))$ and $s/2c(c - s)$ the individual curves are linear over a longer period of time if cerium is present in excess of arsenic, a fact at least consistent with the idea of early onset of steady state for high cerium. Finally, there always exists the possibility of another mechanism of importance at low cerium concentrations. The following scheme gives a lower dependence on cerium concentration, and thus for the purpose at hand has some merit

$$I^- + Ce(IV) \longrightarrow I^0 + Ce(III)$$
$$2I^0 + As(III) \longrightarrow As(V) + 2I^-$$

Here, however, the catalyst must presumably be destroyed by an exothermic combination of iodine atoms to form elementary iodine. Such a set of reactions applied to the data can be shown to demand far too much iodine to explain the catalysis at the low concentrations which are actually effective.

The results of the present work are consistent with the implicit assumption that reaction (2) is of more importance than reaction (5) at low iodide concentration. Disregarding differences in the medium, we use the value $k_3 = 0.23 \times 60 = 14$ for the reaction between arsenite and hypoiodous acid and $k_5 = 2800$ for the oxidation of iodide by HIO.[9] Combined with our value $k_3/Kk_2 = 0.047$, these give $Kk_2 = 292$ and

$$\text{rate (2)/rate (5)} = 0.026\ [Ce(IV)]^2/[H^+][I^-]$$

Thus in the solutions with which we are concerned ($[Ce(IV)] = 0.02$, $[H^+] = 4$) the ratio is $2.6 \times 10^{-6}/[I^-]$. Even if the ambient iodide concentration were no smaller than 10^{-7} M as added, the rate of (2) is already much greater than that of (5). For the much smaller iodide concentrations which must actually be present, reaction (5) is of no significance, at least in the presence of arsenic.

There is some evidence in the present results that the rate of the reaction assumes a maximum value with respect to the sulfuric acid concentration at about 2 M. The data are considered to be of insufficient accuracy to warrant a discussion of this point.

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(9) The data for these estimates are to be found in "Tables of Chemical Kinetics," U. S. Department of Commerce, National Bureau of Standards, Circular 510 (1951), pp. 660, 694, 695.