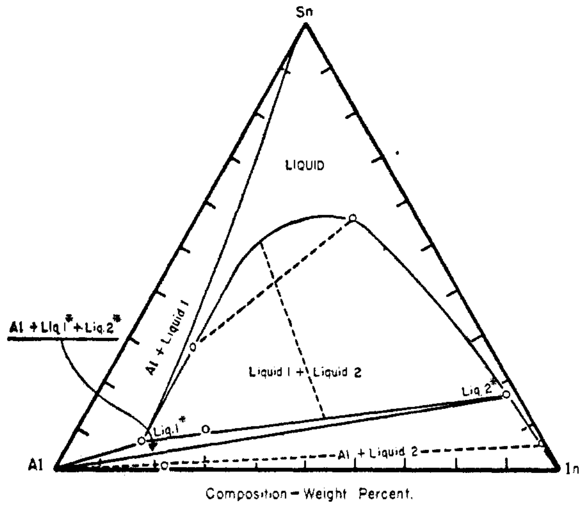

Fig. 4.

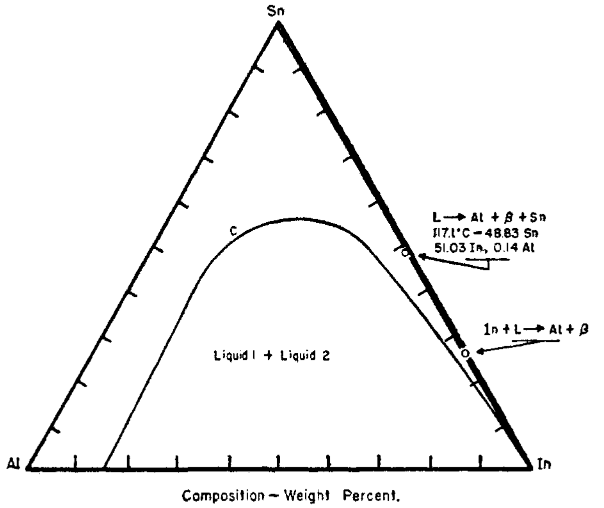

Fig. 5.

Figure 5 is a liquidus projection, showing the ternary eutectic and peritectic transition.

The X-ray data have shown that aluminum does not enter into the In–Sn solid solutions to an extent greater than 5%, and probably not at all, since the lines of the pure phases were not shifted to any observable extent. Sufficient aluminum lines were observed to indicate the presence of aluminum as a solid phase.

Acknowledgment.—Three of us (L. B. B., J. M. K. and R. H. T.) have held Fellowships granted by the Consolidated Mining and Smelting Company of Canada, Ltd. We are indebted to the same Company for a fund which has defrayed most of the expense of this research.

WINNIPEG, CANADA RECEIVED SEPTEMBER 27, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Spectra of Cerium(IV) in Perchloric Acid. Evidence for Polymeric Species[1,2]

BY EDWARD L. KING AND MARY L. PANDOW

The spectra of cerium(IV) perchlorate in perchloric acid–sodium perchlorate solutions have been studied. It has been found that Beer's law is not obeyed in the wave length region of 440–530 mμ over the cerium(IV) concentration range of 4×10^{-4} to 10^{-1} molar at hydrogen ion concentrations of 0.85 and 2.57 molar. The spectral data are consistent with the existence in the solutions of equilibria between monomeric and polymeric species. The extinction coefficient of cerium(IV) in solutions which are relatively concentrated in perchlorate ion (>6 *M*) is much greater than in dilute solution. This is observed for both perchloric acid and perchloric acid–sodium perchlorate solutions. The system cerium(III)–(IV) does not exhibit "interaction-absorption" under the concentration conditions studied.

Several experimental studies have been made which are relevant to the question of what species of cerium(IV) exist in perchloric acid solutions. The study of the cerium(III)–cerium(IV) potential in perchloric acid by Sherrill, King and Spooner[3] indicates that the hydrated but unhydrolyzed Ce^{+4} does not exist to a predominant extent even in 2.4 *M* $HClO_4$. They propose the value 0.6 for the concentration equilibrium quotient for the reaction

$$CeOH^{+++} + H_2O \rightleftarrows Ce(OH)_2^{++} + H^+ \quad (1)$$

in which only monomeric species of cerium(IV) are present. Heidt and Smith[4] have studied the photochemical oxidation of water by cerium(IV) in perchloric acid solution and have concluded from the dependence of the quantum yield on the cerium(IV) concentration that cerium(IV) forms a dimeric species in 1 *M* $HClO_4$. These authors have also shown that the existence of such species would remove the anomalies in certain of the data of Sherrill, King and Spooner. Evans and Uri[5] have presented a mechanism for this photochemical reaction which does not necessitate the postulation of dimeric species of cerium(IV). This does not rule out the possibility of the existence of such dimeric species, however, as conclusions regarding equilibria drawn from kinetic studies are not always valid.

In solutions of constant hydrogen ion concentration, the relative concentrations of any number of soluble species involving cerium(IV) and hydroxide will be independent of the cerium(IV) concentration if all of these species contain the same number of cerium(IV) atoms. If species containing different

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(1) Presented before the Division of Physical and Inorganic Chemistry, 119th Meeting, American Chemical Society, Cleveland, Ohio, April 8-12, 1951.

(2) This work was supported in part by a grant from the U. S. Atomic Energy Commission.

(3) M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

(4) L. J. Heidt and M. E. Smith, *ibid.*, **70**, 2476 (1948).

(5) M. G. Evans and N. Uri, *Nature*, **166**, 602 (1950).

numbers of cerium(IV) atoms are present, their relative concentrations are dependent upon the cerium(IV) concentration. A consequence of this is that Beer's law will be obeyed by solutions of constant acidity at all wave lengths if only monomeric cerium(IV) hydroxide species exist. If species involving different numbers of cerium(IV) atoms exist in the solutions studied, Beer's law will not be obeyed at wave lengths at which the several species have different extinction coefficients (based on cerium(IV) concentrations expressed in gram atoms per liter). Spectral studies have been carried out in this work in order to learn more regarding polymeric species of cerium(IV).[6]

Polymeric Species.—The spectra of two series of solutions were determined. In one of these the compositions of the solutions were 2.57 molar H^+, approximately 0.43 molar Na^+, 3.00 molar ClO_4^- and 4×10^{-4} to 4×10^{-2} molar cerium (IV); in the other series the compositions were 0.85 molar H^+, approximately 2.15 molar Na^+, 3.00 molar ClO_4^- and 4×10^{-3} to 4×10^{-2} molar cerium(IV). In the wave length region 440 to 530 mμ, Beer's law is definitely not obeyed. In Fig. 1 ϵ is plotted against the logarithm of the cerium(IV) concentration ($\bar{\epsilon} = (\log I_0/I)/l(\mathrm{Ce^{IV}})_t$, l is cell length in cm. and $(\mathrm{Ce^{IV}})_t$ is the total concentration of cerium(IV)).

The data obtained from solutions of constant acidity provide no information regarding the extent of hydrolysis. Information regarding the number of cerium(IV) atoms per polymer unit may be derived from these data, however. Calculations have been carried out under two sets of assumptions: only monomeric and dimeric species exist, and only monomeric and trimeric species exist. Under each of these assumptions a single equilibrium quotient can determined at each acidity. In addition, two average extinction coefficients must be determined for each wave length being considered. Equations relating these quantities to the measured quantities $\bar{\epsilon}$ and $(\mathrm{Ce^{IV}})_t$ are

$$k_n = C_n/C_1^n \tag{2}$$

and

$$\bar{\epsilon}_\lambda\, (\mathrm{Ce^{IV}})_t = \sum_n \epsilon_{n\lambda} C_n \tag{3}$$

where

$$C_n = \sum_m \mathrm{Ce}_n\,(\mathrm{OH})_m^{+4n-m}$$

The calculations have been made by first assuming a value of k_2 or k_3; it is then possible to determine the values of C_1 and C_2 or C_1 and C_3 corresponding to the various concentrations of cerium(IV) which were studied. Using these concentrations in equation 3 leads to a set of equations in ϵ_1 and ϵ_2 or ϵ_3 for each wave length; for each concentration of cerium(IV) there is one equation. The values of ϵ_1, ϵ_2 and ϵ_3 have been calculated by the method of averages.[7] This was done for a number of assumed values of k_2 and k_3; the averages of the percentage differences between the calculated and observed values of $\bar{\epsilon}$ were taken as a measure of how closely the particular assumed value of k_2 and k_3 approximated the true equilibrium quotient.

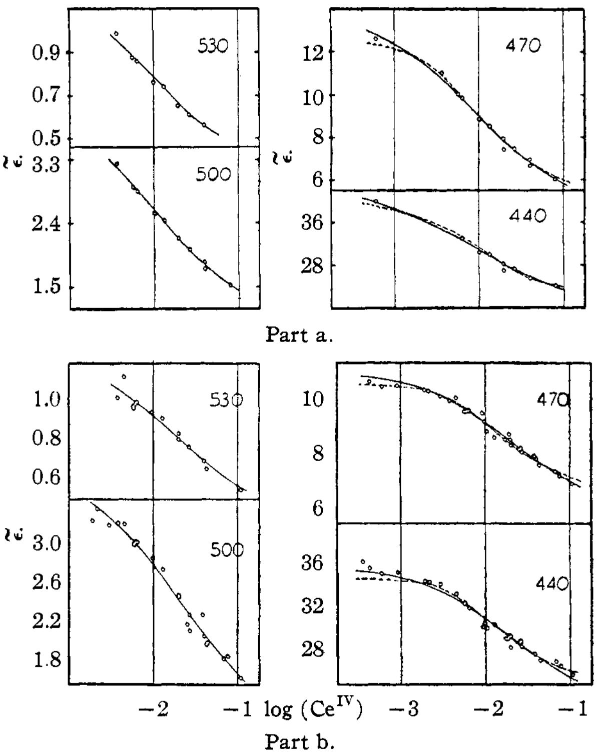

Fig. 1.—$\bar{\epsilon}$ as a function of $\mathrm{Ce^{IV}}$ concentration: a, experiments at 0.85 M H^+. Solid lines calculated using $k_2 = 75$ and dashed lines calculated using $k_3 = 9000$; b, experiments at 2.57 M H^+. Solid lines calculated using $k_2 = 36$ and dashed lines calculated using $k_3 = 4000$.

Good agreement was obtained using values of k_2 of 75 and 36 at 0.85 and 2.57 molar hydrogen ion, respectively. The values of k_3 which give good agreement between observed and calculated values of $\bar{\epsilon}$ are 9000 and 4000 at 0.85 and 2.57 molar hydrogen ion. The curves plotted in Fig. 1 have been calculated using these constants (calculations involving k_3 have been carried out at 440 and 470 mμ only). It was observed that the same value of the equilibrium quotient did not give the best fit at all wave lengths. This is attributed, in part, to the scattering of some of the experimental points. It may also indicate that the underlying assumption that only monomers and dimers or only monomers and trimers are present is not completely valid.

The agreement between the observed and calculated values of $\bar{\epsilon}$ based on the assumption that only monomeric and trimeric species exist is almost as good as was achieved under the assumption that only monomeric and dimeric species exist. The calculations do indicate that the existence of polymeric species involving more than two cerium(IV) atoms per ion-molecule at higher concentrations of cerium(IV) cannot be ruled out. *This spectrophotometric study, while ideal for demonstrating that polymeric species do exist, is not necessarily well suited for completely elucidating the equilibria if several polymeric species exist.*

No attempt has been made to correlate the data

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[6] T. J. Hardwicke and E. Robertson (in press, *Can. J. Research*) have carried out a study rather similar to the one being reported here. These authors have also found that Beer's law is not obeyed.

[7] F. Daniels, J. H. Mathews and J. W. Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 369.

with the existence of monomers, dimers and trimers although this is probably a more correct picture than one in which only monomers and dimers or monomers and trimers are assumed. A large number of combinations of k_2 and k_3 would undoubtedly give good fit. Certain conclusions seem reasonable from trends observed in the calculations which have been made. The "best" k_2 and k_3 values decrease with increasing acidity. This indicates that the average positive charge per cerium(IV) is larger in the monomer than in the polymers in the hydrogen ion concentration range studied here. A similar conclusion was drawn by Connick and Reas[8] in their work on zirconium(IV) polymerization.

The spectra of solutions of compositions 3.00 molar ClO_4^-, 4×10^{-4} and 6×10^{-4} molar cerium(IV), and 0.33 to 3.00 molar H^+ were studied. Over the wave length range 470 to 390 mμ, the values of ϵ decrease about 20% in going from 0.33 to 3.00 molar H^+. The decrease in $\tilde{\epsilon}$ is more pronounced at the higher hydrogen ion concentrations, and ϵ does not appear to be approaching constancy with increasing hydrogen ion concentration at the highest concentration studied. These observations are consistent with the value of the quotient $(Ce(OH)_2^{++})(H^+)/(Ce(OH)^{+++}) = 0.6$ only if the values of the extinction coefficients of $Ce(OH)_2^{++}$ and $CeOH^{+++}$ are rather similar at the wave lengths studied. In addition the relatively large change in $\tilde{\epsilon}$ with acidity at the higher hydrogen ion concentrations indicates the rate of change of the ratio of the concentrations of two different species with hydrogen ion concentration is going through a maximum at a hydrogen ion concentration of about 3 molar or greater. It would appear, then, that the value of the quotient $(CeOH^{+++})(H^+)/(Ce^{++++})$ is 3 or greater.[9]

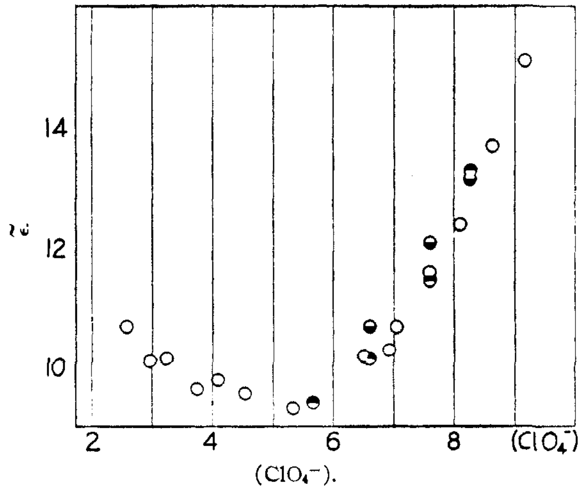

Fig. 2.—$\tilde{\epsilon}$ as a function of ClO_4^- concentration: ○, perchloric acid only; $\sim 3 \times 10^{-3}$ *M* Ce^{IV}; ◓, perchloric acid only; $\sim 10^{-3}$ *M* Ce^{IV}; ◒, perchloric acid and sodium perchlorate (5.7 *M* $HClO_4$); $\sim 10^{-3}$ *M* Ce^{IV}.

Spectra Studies at High Concentrations of Perchloric Acid.—The interpretations of spectral measurements made on relatively concentrated acid or salt solutions may be rather uncertain. With changing concentration of salt or acid, an appreciable change in the activity of water occurs as well as changes falling into the category of ill-defined "medium effects." It seemed worthwhile, nevertheless, to study the spectra of solutions of cerium(IV) perchlorate in relatively concentrated perchloric acid–sodium perchlorate solutions. The results of such experiments are presented in Fig. 2. It is seen that after first decreasing with increasing acidity, the value of the average extinction coefficient of cerium(IV) at 470 mμ increases at high concentrations of perchloric acid. This is not due predominantly to the increase in the activity of hydrogen ion because the ϵ values are comparable for solutions of the same perchlorate ion concentration containing some sodium perchlorate. The effect then is due to the increasing activity of perchlorate ion, decreasing activity of water or both. Both of these changes would favor the formation of some sort of cerium(IV)–perchlorate ion pair. It cannot be stated with certainty that such species are present for with the decreasing activity of water the hydration of the ion may change in a manner which does not involve replacement of water molecules by perchlorate ions in the primary coördination sphere. If, on the other hand, the changes of the spectrum are caused by the formation of cerium(IV)–perchlorate ion pairs, the existence of such species in this sort of medium does not invalidate the usual assumption that metal ion–perchlorate ion pairs (or complexes) do not form in dilute aqueous solution.

The Effect of Cerium(III) on the Spectrum of Cerium(IV) in Perchloric Acid.—The phenomenon of "interaction absorption" by aqueous systems containing an element in two different oxidation states has been observed in some cases where halide complex ions of the metal in one or both valence states are known to exist.[10–12] In perchlorate solutions there is a possibility of hydroxyl bridging which would lead to "interaction absorption" although it has not been observed in studies on iron(II) and (III)[12] and thallium(I) and (III).[13] Since all of the cerium(IV) solutions contain some cerium(III) formed in a reduction reaction by water, it was desirable to check on the possibility of "interaction absorption" occurring in the system cerium(III) and (IV). Solutions of the compositions 2.57 molar H^+, 3.0 molar ClO_4^-, 0.025 molar Ce^{IV} and 0.01 to 0.04 molar Ce^{III} were studied. The optical densities of these solutions were within several per cent. of those of a similar solution containing a very much smaller amount of cerium(III). Any "optical interaction" is slight under the conditions of these experiments; perhaps it might be detectable at lower concentrations of hydrogen ion and higher concentrations of cerium(III) and cerium(IV).

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[8] R. E. Connick and W. H. Reas, THIS JOURNAL, **73**, 1171 (1951).

[9] T. J. Hardwicke and E. Robertson[6] have reported the value of this quotient as 5.2 at 25°.

[10] J. Whitney and N. Davidson, THIS JOURNAL, **69**, 2076 (1947), **71**, 3809 (1949).

[11] H. McConnell and N. Davidson, *ibid.*, **72**, 3168 (1950).

[12] H. McConnell and N. Davidson, *ibid.*, **72**, 5557 (1950).

[13] J. Whitney, *et al.*, "Isotopic Exchange Reactions and Chemical Kinetics," Brookhaven National Laboratory Report C-8, Dec., 1948, p. 197.

Experimental

Reagents.—All solutions were prepared using doubly distilled water. The second distillation was from an alkaline permanganate solution in a Barnstead still. The perchloric acid used was Reagent Grade (Merck, G. F. Smith or Baker). The sodium perchlorate was from two sources: some was prepared from Reagent-grade sodium carbonate and perchloric acid while other batches were prepared by recrystallizing G. F. Smith sodium perchlorate. Most of the experiments were performed using G. F. Smith Reagent Grade "Perchloratoceric Acid" in perchloric acid. Some were performed, however, using a solution prepared by electrolytic oxidation of a cerium(III) perchlorate solution. This cerium(III) perchlorate was prepared by conversion of cerium(III) chloride which had been recrystallized from concentrated hydrochloric acid. The spectra of solutions prepared using this cerium(IV) perchlorate were the same as those of similar concentrations using the other source of cerium(IV) perchlorate. Stock solutions of perchloric acid were analyzed by conventional volumetric procedures. The primary standard upon which the concentrations were based was mercuric oxide. The stock solutions of sodium perchlorate were analyzed by evaporating measured volumes of the solution, drying the solid salt at 120° and weighing.[14] The cerium(IV) concentration in each solution used in a spectral study was determined at the time of the spectrum determination by titration with a solution of iron(II) sulfate in sulfuric acid. The iron(II) sulfate solution was standardized at the same time by a similar titration with a standard cerium(IV) solution in sulfuric acid. Ferrous orthophenanthroline was used as the indicator. The acidity of those solutions which were relatively concentrated in perchloric acid was reduced by adding sodium sulfate before the cerium(IV) determinations were carried out.

Spectrophotometric Studies.—The spectra were determined using a Model DU Beckman spectrophotometer. Measurements were made using both one cm. and ten cm. cells. Light path lengths of 0.302 and 0.102 cm. were also realized by using quartz inserts for the one cm. cells; these were obtained from the Pyrocell Manufacturing Co. In the case of the ten cm. cells, a special thermostatic compartment, which was constructed in the shop of this Chemistry Department, was used. The temperature of the one cm. cells was controlled by use of the "Thermospacer" arrangement manufactured by the National Technical Laboratories. Temperature control was within several tenths of a degree of 25.4°. The blank cell in each case contained a solution of perchloric acid and sodium perchlorate. The optical density of each solution was determined at least twice.

Discussion

Cerium(IV), in forming polymeric species in acidic solution, is not exhibiting a unique behavior. Studies on bismuth(III) by Graner and Sillén,[15] on zirconium(IV) by Connick and Reas,[8] and on uranium(VI) by Sutton,[16] have demonstrated the existence of polymeric species of these metal ions in acidic solution. It is generally believed that the binding of the metal ions in these polymeric species is by oxide or hydroxide bridging. The species existing in cerium(IV) solutions are probably similarly constituted. A comparison of the fraction of the metal ion present in monomeric forms in the case of cerium(IV) and zirconium(IV)[8] indicates a greater tendency on the part of zirconium(IV) toward polymerization. This is particularly interesting since existing data indicate that the equilibrium quotient $(MOH^{+++})(H^+)/(M^{+4})$ is greater in the case of cerium(IV) than in the case of zirconium (IV).[8] It would appear that the factors which determine the tendency for simple hydrolysis are not identical with those which determine the tendency for polymer formation.

The value of the dimerization equilibrium quotient calculated by Heidt and Smith[4] ($k_2 = 50$ at 1.00 molar perchloric acid) is in agreement with those derived from this research This is support for the mechanism of the photochemical oxidation of water by cerium(IV) proposed by these authors as opposed to that proposed by Evans and Uri.[5]

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[14] Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 73.

[15] F. Graner and L. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947).

[16] J. Sutton, *J. Chem. Soc.*, suppl. issue No. 2, S 275 (1949).

MADISON, WISCONSIN

RECEIVED JULY 23, 1951

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Catalytic Hydrogenation of the Oxides of Carbon to Higher Hydrocarbons[1]

BY ROBERT N. R. MULFORD AND W. WALKER RUSSELL

The effects of carbonate, chloride, sulfate, thiosulfate and sulfide, added singly as potassium or sodium salts prior to catalyst precipitation, upon ceria promoted, copper containing cobalt catalysts in the syntheses of hydrocarbons from the oxides of carbon at atmospheric pressure have been studied. All of these cobalt catalysts produced oil when the initial carbon dioxide–hydrogen mixture was first passed over a supported iron, water gas catalyst, but with no water gas catalyst present only the cobalt catalysts containing potassium carbonate or sulfate produced oil. In general the effects of certain of these catalyst additives were to alter the distribution between liquid and gaseous synthesis products, to increase oil yields, and to shift the temperature range of maximum oil yields. The effects of the additives are attributed to selective activation and/or beneficial poisoning of the cobalt catalysts.

Introduction

The problem of producing higher hydrocarbons from the oxides of carbon may be considered one of controlled or partial reduction followed by polymerization. The complete reduction of either oxide produces methane when polymerization does not intrude. More specifically the problem becomes that of stopping the reduction process short of methane when polymerizable intermediates are present. A previous study[2] indicated that by the proper selective activation and/or poisoning of cobalt catalysts some control over the reduction and polymerization processes occurring on the catalyst surface could be obtained. In the present work the effects of certain additives upon the catalytic behavior of cobalt in producing oil from the reduction of the oxides of carbon have been studied. These additives included substances containing sulfur or chlorine which are usually considered

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[1] This paper is based on a portion of a thesis presented by R. N. R. Mulford in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, October 1950.

[2] W. W. Russell and G. H. Miller, THIS JOURNAL, **72**, 2446 (1950).