measurements made with a glass electrode and a potentiometer (radiometer) of inferior accuracy (0.3 to 0.6 mv.)

In Table II Grunwald's values at low ionic strength have been compared with our values. Here C_i and C_e are the stoichiometric concentrations of acetic acid at the inflection point and equivalent point, respectively. I is the ionic strength of the solution. Our values deviate from each other much less than those of Grunwald, owing partly to the somewhat greater accuracy of the potentiometer used by us. For the thermodynamic constant our values give 1.754×10^{-5} in perfect agreement with the value of Harned and Ehlers[9] 1.753×10^{-5} (20°).

Because this differential method is based on the measurement of small potential differences, great accuracy of the potentiometer is essential. On the other hand the accurate measurement of the small potential jumps is possible because the uncontrolled factors, which often disturb the potentiometric measurements, very largely cancel each other out in a differential method in which the measurements are carried out under constant conditions.

Our measurements given here were made with a potentiometer of the Cambridge Instrument Co., slidewire-type, graduated in 0.2-mv. intervals and with an accuracy of 0.1 mv. We have since used the Vernier potentiometer of the Cambridge Instrument Co., graduated on 0.01-mv. intervals and a potentiometer of Leeds–Northrup graduated on 0.05-mv. intervals and with an accuracy of 0.01 mv. Now the error due to the potential measurement is of the same order of magnitude as the other experimental errors.[8a,e]

Next to the potential jumps, the accuracy in measuring the volume increment of the reagent added is important. With our drop method,[5b,p.126] if a micro-buret is used, an accuracy of 0.001 ml. may easily be reached. An accuracy of 0.0002 ml. may be attained with micrometer pipets. This corresponds to the accuracy obtained with the accurate potentiometers described.

These technical improvements are important in the studies on the dissociation constants in mixtures of electrolytes being made in this Laboratory. Further, we are investigating the dissociation of bases in acetic acid solutions by means of our method described above.

HELSINKI, FINLAND

(9) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652 (1933).

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. VIII. Zirconium(IV) Complexes with 2-Nitroso-1-naphthol[1a]

BY HANS B. JONASSEN AND WINSTON R. DEMONSABERT[1b]

RECEIVED JANUARY 2, 1952

The complexes formed between 2-nitroso-1-naphthol and zirconium(IV) have been investigated in mixtures of water and ethanol and water and dioxane in the absence and presence of $HClO_4$. It has been found that in the absence of $HClO_4$ a one-to-one complex forms, whereas in solutions 3 M or larger in $HClO_4$ and 3×10^{-3} M Zr(IV) a one-to-four complex is formed. The pK instability values have been determined: for the one-to-one complex in ethanol–water it is 3.7 and for the one-to-four complex in 50% dioxane–water it is 11.6.

Introduction

Distribution studies by Connick and McVey[2] show that Zr^{+4} or $(ZrOH)^{+3}$ ions are present in 2 M perchloric acid and low zirconium(IV) ion concentration. Connick and Reas[3] report the formation of zirconium polymers at zirconium ion concentrations of 2×10^{-3} M in 2 M $HClO_4$ and 2×10^{-4} M in 1 M $HClO_4$ solutions.

Thamer and Voigt[4] have investigated zirconium chloranilate complexes in 1 M and 2 M $HClO_4$ solutions and find evidence to support a one-to-one and a one-to-two monomeric complex.

Bellucci and Savoia[5] reported that 1-nitroso-2-naphthol precipitates zirconium(IV) in acid solution forming $ZrO(C_{10}H_6(NO)O)_2$ and that the isomeric 2-nitroso-1-naphthol behaves in a similar manner. The composition and stability of the 2-nitroso-1-naphthol zirconium(IV) complex is only a matter of conjecture.[6] Its study in aqueous, alcoholic and dioxane media in the absence and presence of perchloric acid was initiated in order to determine their possible effects on these zirconium complexes.

Experimental

Zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, obtained from the Fairmount Chemical Company was recrystallized six times from concentrated HCl solutions.

Zirconium tetrachloride, $ZrCl_4$, obtained from the Fairmount Chemical Company, was added directly to the solvent (alcohol, dioxane) and the resulting solution standardized by precipitation of the zirconium with aqueous NH_3 and igniting to ZrO_2.

The sodium nitrate solution was prepared from Baker C.P. grain sodium nitrate.

2-Nitroso-1-naphthol, Eastman Chemical Company, was weighed directly in the preparation of the standard solutions.

The Beckman model DU spectrophotometer equipped with 10-mm. Corex cells was used throughout the deter-

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(1) (a) Presented before the Division of Physical and Inorganic Chemistry at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March 23–27, 1952. (b) Department of Chemistry, Loyola University of the South, New Orleans, Louisiana.

(2) R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

(3) R. E. Connick and W. H. Reas, *ibid.*, **73**, 1171 (1951).

(4) B. J. Thamer and A. F. Voigt, *ibid.*, **73**, 3197 (1951).

(5) I. Bellucci and C. Savoia, *Atti congr. nazl. chim. pura applicata*, 183 (1923).

(6) Fritz Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, p. 253.

minations. The values are reported in optical density units which equal log 1/transmittance.

Discussion and Results

(1) Studies in Absence of $HClO_4$

a. Absorption Studies.—The absorption spectrum of 50% ethanol solutions of 2-nitroso-1-naphthol (2.5×10^{-4} *M*) and of zirconium oxychloride containing the following ratios of 2-nitroso-1-naphthol to $ZrOCl_2$ (1:4, 1:1, 1:$^1/_2$, 1:$^1/_3$, 1:0) were determined from 300 to 600 mμ. Constant ionic strength was maintained at 2.5×10^{-2} *M* with $NaNO_3$. Curves obtained for ratios 1:$^1/_4$, 1:$^1/_5$ and smaller were the same as that of the 1:$^1/_3$ and are therefore not shown.

Figure 1 depicts the absorption spectra of the dye and its zirconium(IV) complex.

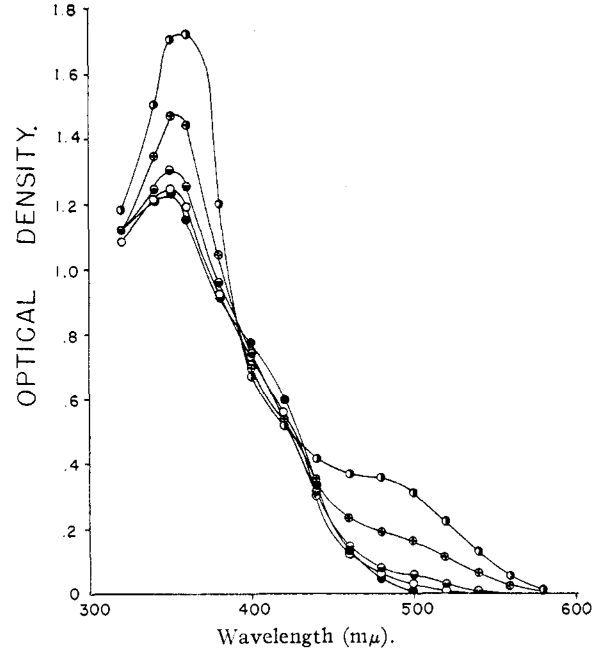

Fig. 1.—Absorption spectra of various mixtures of $ZnOCl_2$ and 2-nitroso-1-naphthol (abbrev. 2-ni-1-na) in 50% ethanol and 2.5×10^{-2} *M* $NaNO_3$: $T = 28°$ (24 hour standing); path length of cell = 1 cm.

2-Ni-1-Na, *M*	$ZnOCl_2$, *M*
◑ 2.5×10^{-4}	10×10^{-4}
⊕ 2.5×10^{-4}	2.5×10^{-4}
◒ 2.5×10^{-4}	1.25×10^{-4}
○ 2.5×10^{-4}	0.833×10^{-4}
● 2.5×10^{-4}	0

Continuous variation studies[7] performed in 8% ethanol, 50% ethanol and 95% ethanol are shown in Fig. 2 for the wave length region of 500–560 mμ. All these curves show an approximate peak at a 1:1 ratio of dye to zirconium(IV), however, only curve I is adjusted to constant *p*H and constant ionic strength. Only under conditions of constant *p*H and constant ionic strength will the curves be symmetrical. The absorption spectrum indicates that the region between 320 and 380 mμ may also give information about complexes by the method of continuous variation. However, only very small optical density differences are obtained in this region due to the high absorption of the dye and no definite conclusions about complexes can be drawn from the wave length region of about 320–380 mμ. The data obtained in the 500–560 mμ region indicate that for solutions containing varying concentrations of water in alcohol a one-to-one complex is present in the absence of perchloric acid.

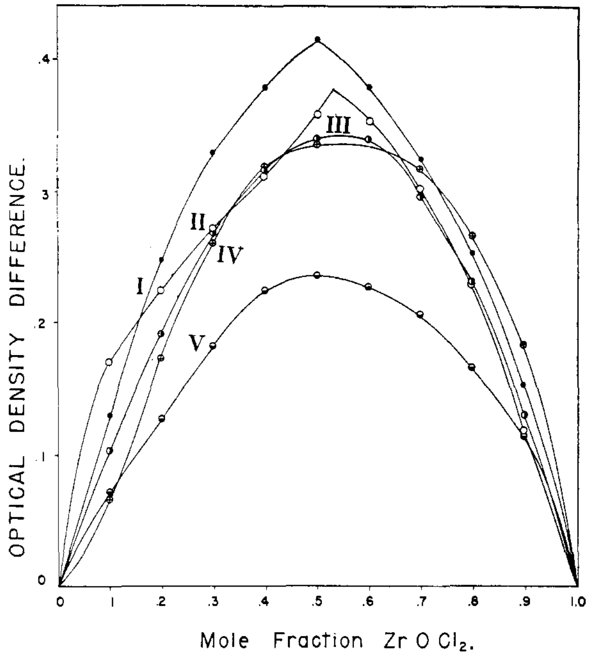

Fig. 2.—Continuous variation studies at 25°: path length of cell = 1 cm.

	% ethanol	Total solute concn.	$NaNO_3$, *M*	*p*H	λ
I ●	50	3×10^{-3}	2×10^{-1}	2.4	540
II ○	50	2.5×10^{-3}	2×10^{-1}	Not adjusted	560
III ⊕	95	1×10^{-3}	0	Not adjusted	500
IV ◒	50	8×10^{-4}	0	Not adjusted	500
V ◑	8	8×10^{-4}	0	Not adjusted	540

b. Determination of Instability Constants.—In order to obtain *pK* values for this complex the solutions were prepared at constant ionic strength and constant *p*H. The solutions were 0.2 *M* in $NaNO_3$, 50% in ethanol, and 0.003 *M* in $ZrOCl_2$ and 2-nitroso-1-naphthol. A *p*H of 2.4, about the normal *p*H of the above zirconium(IV) solution, was maintained by adjustment with 1 *M* HNO_3.

Calculations of *pK* values were performed by the method of Turner and Anderson[8] from curve I Fig. 2.

For a range of concentrations from 3 to 30×10^{-4} *M* for both $ZrOCl_2$ and 2-nitroso-1-naphthol an average *pK* value of 3.7 ± 0.1 was obtained.

c. Saturation Studies.—Since the continuous variation studies at wave lengths of about 350 mμ did not give definite information about complexes, saturation studies[9] were conducted at 355 mμ. Figure 3 shows the results for a 50% ethanol solution, 5×10^{-5} *M* in 2-nitroso-1-naphthol. Constant ionic strength was maintained by 1 ×

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[7] W. C. Vosburgh and G. H. Cooper, THIS JOURNAL, **63**, 437 (1941).

[8] Stanley E. Turner and R. C. Anderson, *ibid.*, **71**, 912 (1949).

[9] O. Ruff, *Z. physik. Chem.*, **76**, 21 (1911).

10^{-2} M $NaNO_3$. A break is shown at a 1:1 ratio of dye to zirconium(IV). This is in accord with the data obtained for the continuous variation at wave lengths of around 500–560 mμ.

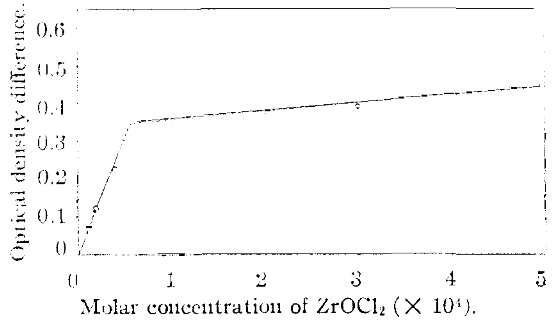

Fig. 3.—Saturation studies in 50% ethanol solutions. The $\beta\alpha$ was kept constant at 5×10^{-5} M and ionic strength adjusted to 1×10^{-2} M with $NaNO_3$: $T = 28°$; path length of cell = 1 cm.

Instability constants were calculated from optical density values where the zirconium(IV) was 500:1 in excess of the dye. It was assumed that the zirconium(IV) was present in the form of the 1:1 complex. The average pK value obtained from these data was 3.8 ± 0.2.

(2) Studies in Presence of $HClO_4$

Experimental

$Zr(ClO_4)_4$ was prepared by heating 10 g. of $ZrOCl_2$ with 70% $HClO_4$.[2] This was then placed in a desiccator and white crystals appeared on standing. The liquid was decanted and the crystals of $Zr(ClO_4)_4$ were dissolved in a solution of 2 M $HClO_4$ and standardized[10] with 8-hydroxyquinoline. Continuous variation and saturation studies were performed with solutions containing 30% ethanol.

$ZrCl_4$ was added directly to dioxane. The solution was then filtered and standardized by precipitation as the hydroxide with NH_3 followed by ignition to the oxide. A 0.006 M $ZrCl_4$ solution was prepared from this standardized solution.

The 2-nitroso-1-naphthol was weighed directly and dissolved in the dioxane to make a 0.006 M solution.

Discussion and Results

Since zirconium(IV) was found to form only a one-to-one complex in the above studies, it was deemed advisable to investigate the possibilities of the formation of a one-to-four complex of zirconium(IV) with dye in $HClO_4$ solutions.[2] When solutions were prepared containing $HClO_4$ in the dye as well as in the zirconium(IV) solution prior to mixing, inconsistent results were obtained. This seems to be due to an equilibrium shift in the dye toward the molecular form as more acid is added, necessitating a larger concentration of dye to furnish sufficient 2-nitroso-1-naphtholate ions for zirconium(IV) complexing.

a. Studies in Ethanol–Water Mixtures.—However, in continuous variation studies using 30% ethanol solutions of 0.003 M zirconium perchlorate and 0.003 M 2-nitroso-1-naphthol, where only the zirconium solution contained $HClO_4$, results followed a definite pattern. Figure 4 indicates the existence of the one-to-four complex in the 3 M and 4 M $HClO_4$ solutions. A decrease in the concentration of $HClO_4$ to 1 molar shows a shift of the maximum to a 2:1 dye to zirconium(IV) ratio. A further change to a 1:1 ratio in the maximum is produced when the pH of the solution approaches that of a solution of $ZrOCl_2$ as shown in Fig. 2.

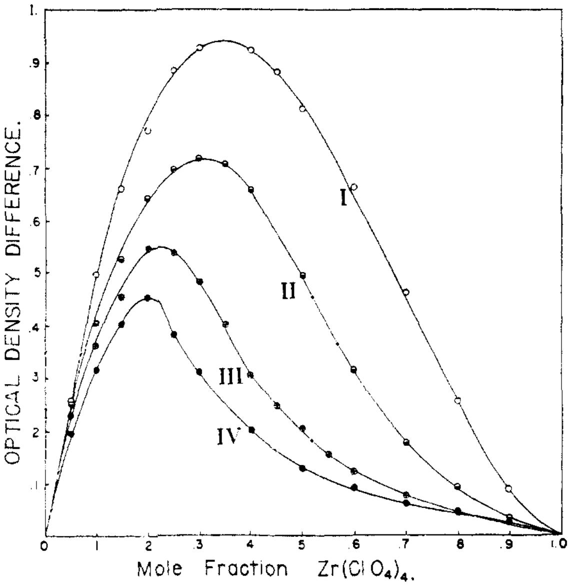

Fig. 4.—Continuous variation studies in varying concentration of $HClO_4$, (total M in $Zn(ClO_4)_4$ and 2-nitroso-1-naphthol = 0.003 M in 30% ethanol) $T = 28°$; path length of cell = 1 cm.; all at $\alpha = 540$: I, ○ 1 M $HClO_4$; II, ◒ 2 M $HClO_4$; III, ⊕ 3 M $HClO_4$; IV, ● 4 M HClO.

b. Studies in Dioxane–Water Mixtures.—Investigations were also conducted in dioxane in an

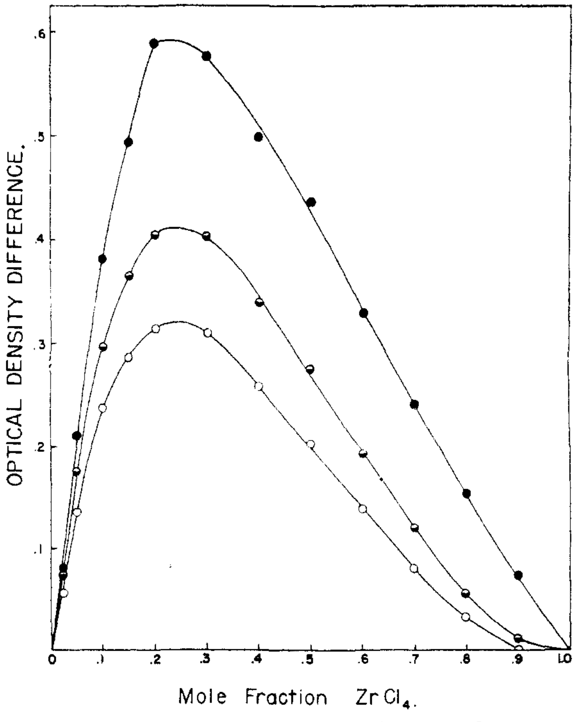

Fig. 5.—Continuous variation studies in 50% dioxane solutions (total M in $ZnCl_4$ and 2-nitroso-1-naphthol = 0.003 M in 1 M $HClO_4$), $T = 28°$; path length of cell = 1 cm.: ●, 500 mμ; ◒, 540 mμ; ○, 560 mμ.

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(10) Gr. Belanescu, *Z. anal. Chem.*, **101**, 101 (1935).

attempt to find a solvent which would preserve the Zr^{+4} species prior to complexing. A series of solutions was prepared with varying amounts of 2-nitroso-1-naphthol and zirconium in each for a continuous variation study. An equal volume of 2 M $HClO_4$ was then added to each to make the total $HClO_4$ concentration 1 M in each solution. Although immediately after preparation the maximum optical density seemed to be in the neighborhood of a one-to-one complex, after 66 hours a shift to a one-to-four ratio occurred as shown in Fig. 5.

A similar investigation was conducted using ethanol in place of the dioxane but the complex remained one-to-one upon the subsequent addition of $HClO_4$.

Since the optical density of the 2-nitroso-1-naphthol at the wave length of 560 mμ was found to be negligible (0.006) instability constants were calculated from a number of points on the 560 mμ curve in Fig. 5 where the dye was present in excess. A modification of Anderson's method[8] was used which gives the equation

$$\frac{(a_1 - x)(b_1 - 4x)^4}{x} = \frac{(a_2 - x)(b_2 - 4x)^4}{x}$$

where x is the concentration of the one-to-four complex, a_1 and b_1 the concentrations of zirconium(IV) and 2-nitroso-1-naphthol in the one-to-four mixture having the same optical density as the sample containing concentrations of a_2 of zirconium(IV) and b_2 of 2-nitroso-1-naphthol. The results of the calculations give an average pK value of 11.7 ± 0.2 for a concentration range of 1.2 to 3.0×10^{-4} M in $ZrCl_4$ and 2.70 to 2.88 M for 2-nitroso-1-naphthol.

The solutions are stable for slightly more than 66 hours but a slow decomposition of the dye sets in after about 85 hours.

NEW ORLEANS 18, LOUISIANA

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Action of Lithium Aluminum Hydride on Nitrate and Nitrite Esters

BY LOUIS M. SOFFER, ELIZABETH W. PARROTTA AND JEWELL DI DOMENICO

RECEIVED JANUARY 29, 1952

A number of organic nitrate and nitrite esters have been shown to react with lithium aluminum hydride in ether solution to give, after hydrolysis, essentially quantitative yields of the parent alcohol. The other products were nitrous oxide, ammonia and hydrogen. Nitrites produced relatively more nitrous oxide and less ammonia than nitrates. Cellulose nitrates of various degrees of nitration were completely denitrated in tetrahydrofuran. Viscosity measurements indicated extensive degradation of the polymer had occurred.

In continuation of this Laboratory's search for a satisfactory method of denitrating nitrocellulose, we have investigated the reactions of lithium aluminum hydride in ether solution with a number of nitrate and nitrite esters. This report will be concerned with the over-all reactions of primary and secondary esters as well as the results obtained with nitrocellulose.

Kuhn[1] has recently reported that *n*-hexyl nitrate and *n*-hexyl nitrite react with hydrazine in the presence of a palladium or platinum catalyst to give nitrous oxide, nitrogen, water and high yields of the parent alcohol. Nitrogen is apparently the product of oxidation of the hydrazine and nitrous oxide the result of reduction of the ester. Thus, the ester produces a single nitrogen-containing material.

For purposes of this discussion the over-all reaction of nitrate and nitrite esters with lithium aluminum hydride will be divided into (1) the reaction step, and (2) the hydrolysis step. We have found the products of the first step to be nitrous oxide and hydrogen. The products of the second step are ammonia, hydrogen and the parent alcohol. Nitrites produce relatively more nitrous oxide and less ammonia than nitrates. The yields of alcohols in all cases are excellent. The results shown in Table I for *n*-hexyl nitrate and 2-octyl nitrite are typical of the various nitrates and nitrites studied, respectively.

TABLE I

REACTIONS OF NITRATES AND NITRITES WITH LITHIUM ALUMINUM HYDRIDE

Reactant	Moles hydride per mole reactant group	Moles gas per mole reactant group (reaction step)	N_2O in gas, % (reaction step)	Original N that forms NH_3, %
n-Hexyl nitrate	3.3	4.0–4.1	1–1.5	84–85
2-Octyl nitrite	1.8	2.6	3–4	56–60

An original aim was to determine the stoichiometric amounts of hydride required per mole of reactant ester. Using the Gilman–Schulze color test[2] data were obtained indicating that two moles of hydride react per mole of nitrate and one mole of hydride reacts per mole of nitrite. However, only modest yields of the alcohols were obtained, with considerable amounts of esters recovered unreacted. From these and other observations it was concluded that these reactions were not stoichiometric and that hydride was being effectively removed from solution. Amundsen and Nelson[3] have recently questioned the suitability of the Gilman–Schulze test for following the course of reduction of nitriles since different results were obtained with two nitriles that react similarly with hydride.

In a series of runs in which the ratio of hydride to reactant ester was varied for a number of nitrates and nitrites the minimum amounts of hydride re-

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[1] L. P. Kuhn, THIS JOURNAL, **73**, 1510 (1951).

[2] R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3740 (1948).

[3] L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 243 (1951).