complexes the formation of the chelate ring is accompanied by an increase in bond strength. This contrasts sharply with the palladium type Zn^{++} and Cd^{++} ion complexes in which chelate ring formation has no influence on the bond strength.

It is possible (though not yet established with certainty) that transition ions generally form a stronger bond as a result of chelate ring formation and involvement of *d*-orbitals. Calvin and Bailes[7] reported approximate ΔH and ΔS values for the dissociation of $Ni(en)_3^{++}$ and $Ni(NH_3)_6^{++}$ in which increased bond strength due to chelation was indicated for the transition type Ni^{++} ion; however, since their comparison was for the tris-ethylenediamine and hexammine complexes, the data are not strictly comparable to those given above. In addition the previously published data on the cadmium complexes[1] of methylamine and ethylenediamine indicated that data for the simplest species such as MA_2^{++} and Men^{++} are more easily interpreted than data for the higher complexes such as MA_4^{++} and Men_2^{++}. It is still probable, however, that the generalizations reported for $Ni(en)_3^{++}$ and $Ni(NH_3)_6^{++}$ would be qualitatively applicable to a comparison between $Ni\,en^{++}$ and $Ni(NH_3)_2^{++}$.

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[7] M. Calvin and R. N. Bailes, THIS JOURNAL, **68**, 953 (1946).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Spectrophotometric Study of Np(V) Oxalate Complexes[1]

BY D. M. GRUEN AND J. J. KATZ

RECEIVED JANUARY 5, 1953

A spectrophotometric study has shown that the complexes $NpO_2C_2O_4^-$ and $NpO_2(C_2O_4)_2^{=}$ exist in aqueous solution. Their association constants have been estimated in solutions having an ionic strength of 0.5. The heat of formation for the first complex is 0.0 ± 0.3 kcal.

Although the absorption spectrum of NpO_2^+ was extensively studied in aqueous solutions,[2,3] there has been so far no spectrophotometric indication of complex formation. Thus the NpO_2^+ spectrum is the same, in 1 *M* $HClO_4$, 10^{-5} *M* $HClO_4$, 1 *M* HCl, 1 *M* H_2SO_4, 0.5 *M* HNO_3–1.5 *M* H_2O_2 and 1 *M* HNO_3.[2,3] The behavior of NpO_2^+ appears to be radically different from UO_2^{++}, NpO_2^{++} and PuO_2^{++} which complex strongly with a large variety of anions.[4-6] It was therefore of some interest to study in more detail the recent observation that the maximum of the main Np(V) absorption peak, which had always been found at 983 mμ was displaced to 990 mμ in the presence of oxalate ion.[7] The present investigation concerns itself with a quantitative study of this shift as a function of oxalate concentration and of *p*H over the temperature range 10–47°.

Experimental

Procedure.—Preliminary experiments carried out in 0.1 and 1.0 *M* acetate buffers showed that NpO_2^+ forms weak acetate complexes. The 983 mμ band is measurably broader in 1 *M* acetate than in 1 *M* perchlorate for example. A similar broadening effect was observed with citrate and phthalate, the other two common acid buffer substances. All the data presented here were, therefore, obtained in an unbuffered, 0.50 *M* $NaClO_4$ solution.

In a typical experiment, a known volume (≈0.05 cm.^{3}) of Np(V) stock solution was added to a known volume (≈3.00 cm.^{3}) of 0.50 *M* $NaClO_4$ solution in a 1-cm. silica absorption cell to give a fixed Np concentration ≈10^{-3} *M*. A blank cell was filled only with the 0.50 *M* $NaClO_4$ solution. Optical density readings were obtained on a Beckman Model D spectrophotometer in the region 970–1030 mμ at intervals of 2.5 mμ, the maxima of the absorption bands being obtained by slowly rotating the wave length drum and finding the point of maximum deflection of the galvanometer. Small increments (10–100 microliters) of a standardized oxalate solution (10^{-1}–10^{-2} *M* Sörensen oxalate in 0.50 *M* $NaClO_4$ solution) were added by means of a Greiner microburet directly to the absorption cell containing the neptunium solution and optical density readings were obtained after each addition of oxalate. The micro buret had been calibrated with mercury. During these runs water was circulated through the cell compartment from a constant temperature bath. The *p*H's of the solution were determined spectrophotometrically at the same time in the following way. Approximately 10^{-5} mole of a suitable indicator was dissolved in a liter of 0.50 *M* $NaClO_4$ solution and it was this solution to which the neptunium and oxalate were added. Methyl orange was chosen for the *p*H range 3.1–4.4 and methyl red for the range 4.2–6.3. These indicators[8] absorb strongly in the region 400–600 mμ where NpO_2^+ and its complexes have virtually no absorption but they do not absorb at all in the region 970–1030 mμ. The optical densities of the end forms of the indicator solutions were determined at 520 and 400 mμ where the acid and base forms, respectively, absorb strongly. From the known dissociation constants of the indicators and optical density readings at 400 and 520 mμ, it was then possible to calculate the *p*H of the solutions in the transition region of the indicators by well-established methods.[9] Methyl orange and methyl red were chosen because they exhibit very small salt errors[9,10] and their use in *p*H determinations has received intensive study.[8] Before each run, the neptunium and oxalate solutions were brought approximately to the same desired *p*H by the addition of small amounts of $HClO_4$ or NH_4OH. When this was done the *p*H could be maintained constant to within ±0.1 *p*H unit during the entire course of a run.

For the runs in the *p*H range 1–2, no indicators were used. The *p*H was measured directly at the beginning and end of a run by means of a *p*H meter. A standardized oxalic acid solution was used instead of sodium oxalate. The *p*H of this solution had been adjusted to that of the neptunium

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[1] Presented in part at the Fall, 1952, Meeting of the American Chemical Society.

[2] R. Sjoblom and J. C. Hindman, THIS JOURNAL, **73**, 1744 (1951).

[3] J. C. Hindman, L. B. Magnusson, T. J. La Chapelle, Paper 15.2 of Vol. 14B of the NNES, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

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[10] I. M. Klotz, Ph.D. Thesis, University of Chicago, 1940.

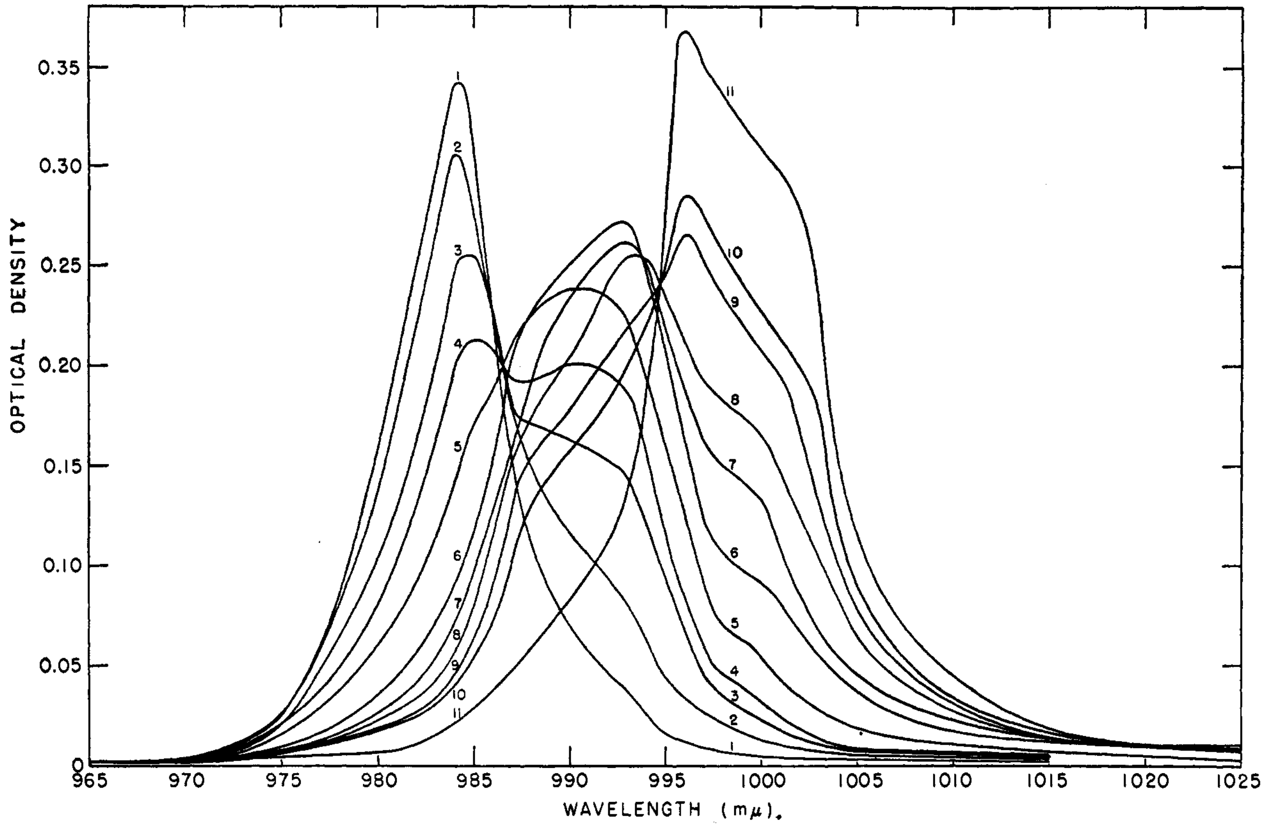

Fig. 1.—Spectral changes in the 983 mμ band of 10^{-3} M NpO_2^+ on addition of oxalate: curve 1, no oxalate; curves 2–5, $10^{-4}-10^{-3}$ M oxalate; curves 6–10, $10^{-3}-10^{-2}$ M oxalate; curve 11, 10^{-1} M oxalate.

solution by means of $HClO_4$ prior to standardization. Water from a constant temperature bath was circulated through the cell compartment. The temperature of the water-bath was regulated by means of a thermoregulator to within ±0.1°. For the low temperature runs, the bath was packed with ice and just enough water was added to provide circulating fluid. The temperature of the absorption cell was measured with calibrated chromel–alumel thermocouples inserted in a sample cell situated adjacent to the cell containing the neptunium solution.

Materials.—The Np(V) stock solution was prepared from a sample of spectroscopically pure Np^{237} dissolved in 0.1 M $HClO_4$. The neptunium was oxidized to the +6 state with Cl_2 and reduced to the +5 state with $NH_2OH{\cdot}HCl$. Then, Np(V) hydroxide was precipitated with NH_4OH, the precipitate centrifuged and washed three times with distilled water, and redissolved in 0.1 M $HClO_4$ to give an approximately 0.08 M Np(V) solution. Neptunium in the +4 state was absent within the limits ($\approx 2\%$) of spectrophotometric analysis.

All other chemicals were of reagent grade. The oxalate solutions were standardized by means of permanganate titrations.

Results and Discussion

Nature and Interpretation of Spectral Changes in the 983 mμ Band.—The molar extinction coefficient, ϵ_M, of the chief NpO_2^+ band at 983 mμ is dependent both on the slit width and the concentration presumably because the spectral band width isolated by the slits is not sufficiently narrow with respect to the band width at the peaks of the absorption bands.[4] However, we have found that for neptunium concentrations in the range 10^{-4} to 10^{-3} M, Beer's law is obeyed at a fixed slit width (0.0175 mm. in our measurements).

The nature of the spectral changes in the 983 mμ band are graphically illustrated in Fig. 1. The various curves were obtained in a typical experiment, keeping the neptunium concentration constant at 10^{-3} M while varying the oxalate concentration. Curve 1 was obtained in the absence of oxalate, and represents the absorption curve of free NpO_2^+; curve 11 in the presence of approximately 10^{-1} M oxalate. The other curves were obtained at intermediate oxalate concentrations. The general pattern of spectral shifts is reminiscent of those observed in the hydrolytic behavior[5] of PuO_2^{++} as well as in rare-earth complexes with ethylenediaminetetraacetic acid.[11]

If one assumes that these shifts are due to complex formation between NpO_2^+ and $C_2O_4^=$, it appears from Fig. 1 that there are at least two stages in this process: the first complex predominating at low oxalate concentrations with an absorption maximum in the neighborhood of 989 mμ, the second complex predominating at high oxalate concentrations with an absorption maximum in the neighborhood of 997 mμ. This assumption is supported by the appearance of two isosbestic points (Fig. 1) at low and high oxalate concentrations where the principal absorbing species would be the pairs free NpO_2^+–first complex and first complex–second complex, respectively.

For each run, curves similar to those of Fig. 1 were constructed from the experimentally determined optical densities at the various oxalate concentrations. Graphs were then drawn of optical densities at three selected wave lengths, 983, 989 and 999 mμ as a function of oxalate concentration

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[11] R. C. Vickery, *J. Chem. Soc.*, 421 (1952).

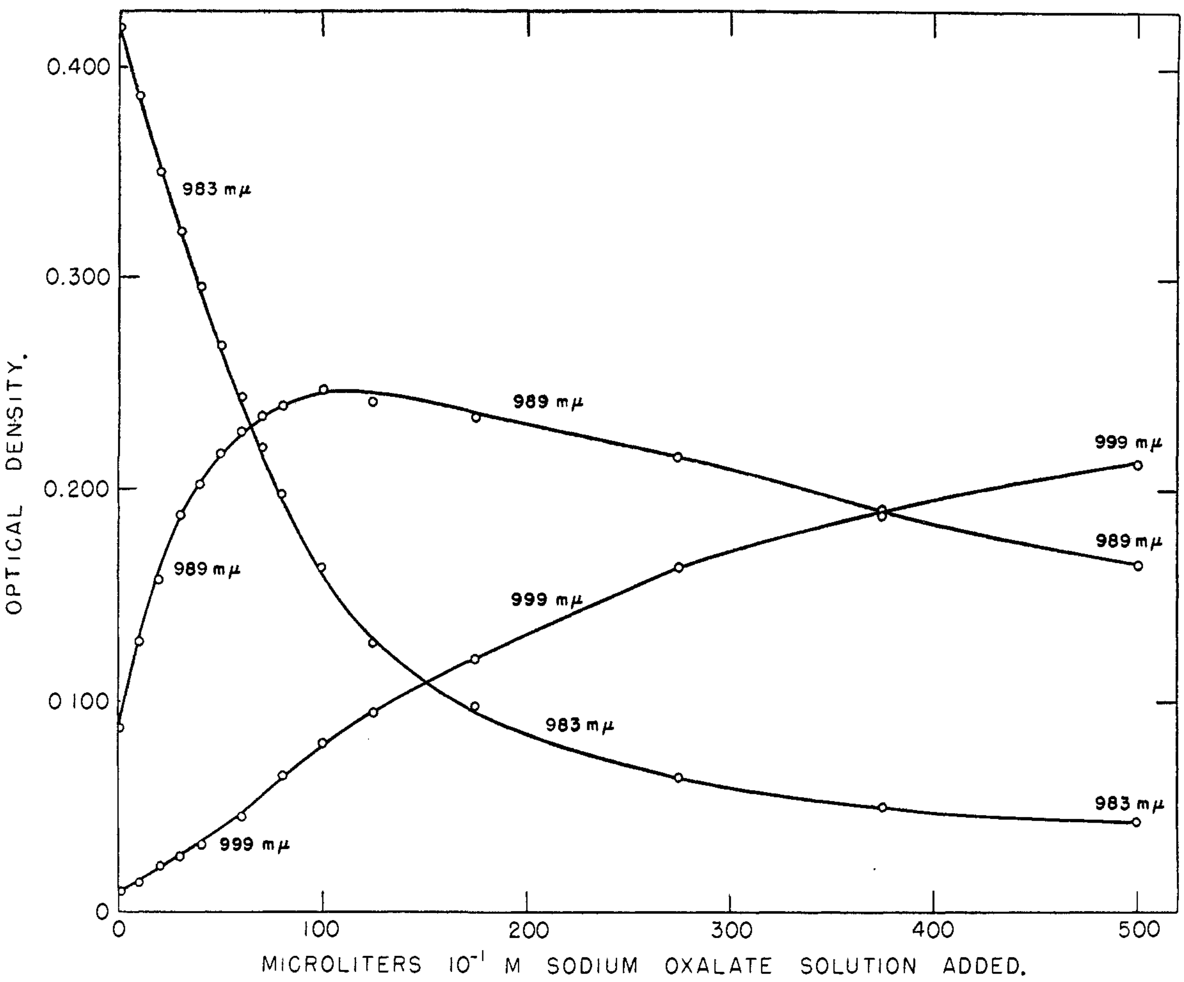

Fig. 2.—Optical densities at 983, 989, 999 mμ as a function of microliters of 10^{-1} *M* sodium oxalate solution added.

(microliters of oxalate solution added). A typical graph of this sort is shown in Fig. 2 which is for the room temperature run at *p*H 3.20. If one could assign values of molar extinction coefficients at these three wave lengths to the three absorbing species, one could calculate the concentration of each species for any oxalate concentration. Molar extinction coefficients can be assigned unambiguously only to the free NpO_2^+ because of the overlapping absorptions of the other species. However, it is possible to make reasonable guesses and to test these against the very stringent requirement that the total neptunium concentration calculated with this set of extinction coefficients for any oxalate concentration be equal to the known neptunium concentration. This requirement is met to within ±5% with the set of extinction coefficients given in Table I.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF Np(V) OXALATE COMPLEXES

Species	Wave length, mμ 983	 989	 999
NpO_2^+	364	53	19
$NpOx^-$ (first complex)	75	366	34
$Np(Ox)_2^=$ (second complex)	9	37	363

The concentrations of the various species were calculated by solving three simultaneous linear equations according to the method of Crout.[12]

Calculation of Association Constants.—In the present case it was found to be impossible to obtain agreement with the experimental data on the assumption that polynuclear complexes were formed. All attempts to interpret the data on the basis of formation of complexes involving the binoxalate ion likewise failed. The following discussion will therefore confine itself to mononuclear species with oxalate ion as the ligand. It is based on a method which has been discussed for example by Leden[13] and by Sullivan and Hindman.[14] The fundamental assumption made here is that the experimental conditions ($\mu = 0.5$) are such that the activity coefficients of the system do not change and that therefore significant values for the concentration association constants of the system can be obtained.

With Sullivan and Hindman[14] we define the function $F([A]) = F([C_2O_4^=]) = \dfrac{C_{Np} - [Np]}{[Np]\,[C_2O_4^=]}$. From a plot of $F([C_2O_4^=])$ against $[C_2O_4^=]$, the various association constants may be evaluated.

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[12] P. D. Crout, *Am. Inst. Electrical Engrs. Trans.* (*Suppl.*), **60**, 1235 (1941).

[13] I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

[14] J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **74**, 6091 (1952).

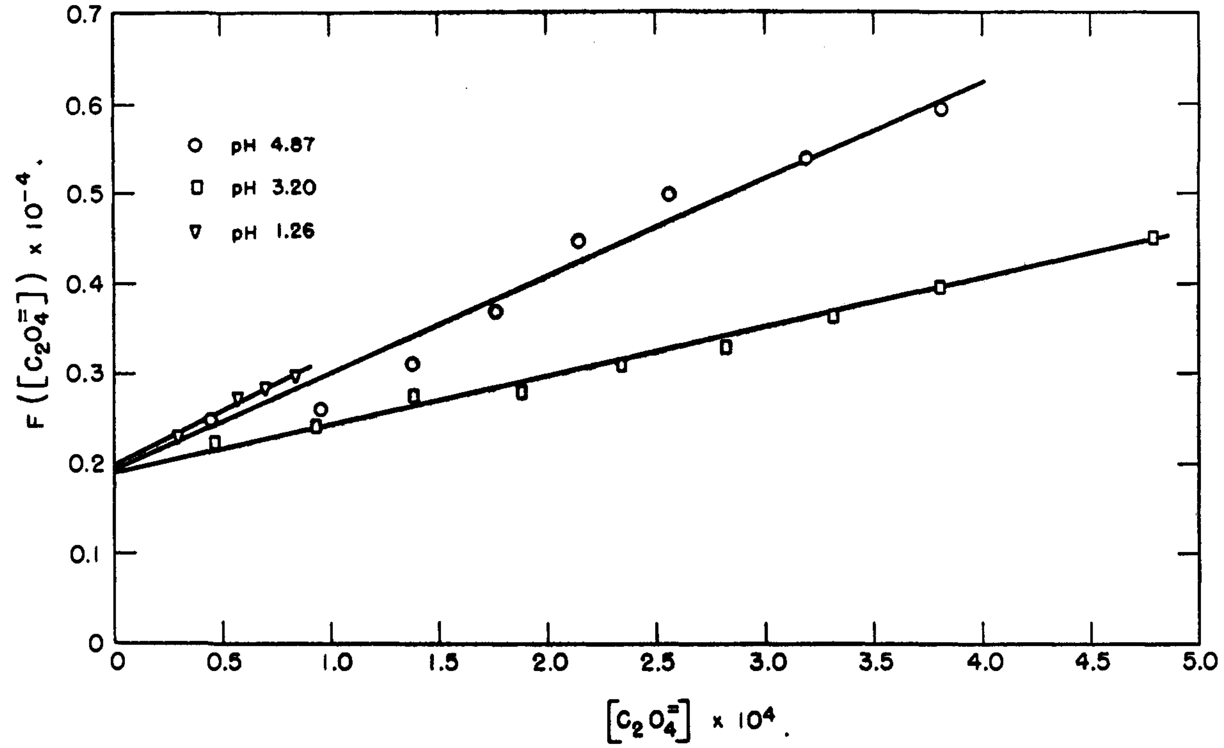

Fig. 3.—Plot of $F([C_2O_4^=]) \times 10^{-4}$ vs. $[C_2O_4^=] \times 10^4$ at various values of pH.

The quantities C_{Np} and [Np], the total and free neptunium concentrations, respectively, were calculated from the spectrophotometric data. All that remains in order to evaluate $F([C_2O_4^=])$ is to obtain $[C_2O_4^=]$, the concentration of free $C_2O_4^=$. From the known total concentration of oxalate present and the calculated concentrations of the complex species one obtains the total concentration of uncomplexed oxalate present as $H_2C_2O_4$, $C_2O_4H^-$ and $C_2O_4^=$. One must know the a_{H^+} of the solution in order to calculate $[C_2O_4^=]$. The pH was determined, as discussed in the experimental section by means of indicators in the case of the solutions near pH 3 and 5 and by means of a pH meter for the solutions near pH 1. The $[C_2O_4^=]$ was then calculated making use of the relation

$$[C_2O_4^=] = \frac{K_1K_2M}{\gamma_1 a_{H^+}^2 + (\gamma_1/\gamma_2)a_H + K_1 + K_1K_2}$$

where

$$K_1 = 5.38 \times 10^{-2} \text{ at } 25°^{15}$$
$$K_2 = 5.42 \times 10^{-5} \text{ at } 25°^{16}$$
$$M = \text{total oxalate concn.}$$
$$\gamma_1 = \gamma_{C_2O_4^=} = 0.22 \text{ at } \mu = 0.5^{17}$$
$$\gamma_2 = \gamma_{C_2O_4^-} = 0.70 \text{ at } \mu = 0.5^{17}$$

The graphs of $F([C_2O_4^=])$ against $[C_2O_4^=]$ for the various runs are given in Fig. 3. It is seen that they are straight lines. The assumption that there are only two complex species in the concentration range investigated appears to be justified.

The constants for the formation of the individual complexes are given by

$$k_1 = \frac{[NpO_2C_2O_4^-]}{[NpO_2^+][C_2O_4^=]}$$
$$k_2 = \frac{[NpO_2(C_2O_4)_2]^=}{[NpO_2C_2O_4^-][C_2O_4^=]}$$

The values of k_1 and k_2 for the various runs were obtained graphically from Fig. 3 and are listed in Table II.

TABLE II

VALUES OF k_1 AND k_2 AT VARIOUS pH'S

pH	$k_1 \times 10^{-3}$	$k_2 \times 10^{-3}$
1.26	1.95	5.54
3.20	1.92	5.92
4.87	2.00	6.10

It should be pointed out that the disproportionation reaction $2Np(V) \rightleftarrows Np(IV) + Np(VI)$ which does not become appreciable in $HClO_4$ solutions until an acid concentration of 5 M is reached,[2] was already pronounced in 10^{-1} M oxalic acid solutions. This accounts for the lack of data at high $C_2O_4^=$ concentrations for the run at pH 1.26.

Effect of Temperature on Association Constants.—A series of experiments at pH 3.2 were performed for temperatures of 10, 29 and 47°. Within the limits of reproducibility of the density readings, (±2%) there was no change in the absorption of free NpO_2^+ in the temperature range investigated. On addition of oxalate, however, marked changes were observed. Increasing the temperature increases the absorption at 983 mμ but decreases it at 989 mμ. This reversal is expected on the assumption that the absorption at 983 mμ is due primarily to NpO_2^+, and that at 989 mμ to $NpO_2C_2O_4^-$.

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The calculations are essentially analogous to those made for the room temperature experiment. It is to be noted, however, that K_2, the second dissociation constant of oxalic acid, depends on the temperature in the following way[16]

$$-\log K_2 = (1423.8/T) - 6.5007 + 0.020095T$$

and it is this temperature variation which is responsible for the observed spectrophotometric changes. The heat of formation of the first complex, $NpO_2C_2O_4^-$, was calculated to be 0.0 ± 0.3 kcal.

Direct Evidence for Formation of Anionic Oxalate Complex.—To confirm the spectrophotometric evidence for the existence of anionic oxalate complexes of NpO_2^+, the technique of paper electromigration was employed. The general experimental technique has been described in the literature.[18] In one case an acetate buffer at *p*H 4.5 was used as the supporting electrolyte, in the other case an oxalate buffer, also at *p*H 4.5, was used. Essentially, the technique consists of placing a drop of the test solution, in this experiment, a drop of NpO_2^+ stock solution containing approximately 0.3 mg. of neptunium on the wet filter paper and to observe the migration of the radioactive species in an electric field. A radioautograph made of the paper after allowing migration to proceed for five hours, showed that, in acetate solution, the neptunium moved toward the cathode while in oxalate solution it moved toward the anode proving that in the former medium Np(V) behaves like a cation, while in the latter, Np(V) is bound in an anionic complex.

Other Np(V) Complexes.—Spectrophotometric studies of NpO_2^+ in the presence of other ions are currently under way. Preliminary work shows that spectral changes of the type described here occur in the presence of salicylate and thiocyanate ions. However, the association constants for these ions are smaller by a factor of 10^3 compared with oxalate ion.

Acknowledgments.—It is a pleasure to acknowledge the coöperation of Dr. Harold Strain and Mr. Herbert Diamond in the electromigration experiment and to thank Dr. J. C. Hindman and Mr. J. C. Sullivan of Argonne and Dr. Donald Long of Universal Oil Products for stimulating discussions.

LEMONT, ILL.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Interaction of Dienophiles with Aromatic Substances

BY L. J. ANDREWS AND R. M. KEEFER

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It has been demonstrated through spectrophotometric studies that benzene and other aromatic substances interact with maleic anhydride, chloromaleic anhydride and benzoquinone in chloroform solution to form 1:1 complexes which have characteristic absorption spectra in the ultraviolet or visible region of the spectrum. Methods of previous investigations have been used to evaluate equilibrium constants for formation of the complexes. The stabilities of the complexes are enhanced slightly by the presence on the aromatic ring of substituents which increase its electron density. Structures are proposed for the complexes in which the aromatic nucleus functions as an electron donor in coördinating with the dienophile.

Among a large group of polarizable substances which function as electron acceptors in forming addition complexes with aromatic and other unsaturated substances should be included compounds such as maleic anhydride and benzoquinone which serve as dienophiles in the Diels–Alder reaction. As evidence for such interaction may be cited the observation that intense coloration is observed when maleic anhydride[1] or quinones[2] are fused with highly methylated benzenes, diphenylpolyenes and related substances. It should also be recalled that the transient color formation frequently observed to occur during the diene synthesis is ascribed to a diene–dienophile complex which is regarded as an intermediate in the formation of the colorless addition product.[3]

Little attention has been paid to the extent of such interactions in solution, although Michaelis and Granick[4] have demonstrated by spectrophotometric studies that chloranil and benzoquinone interact with phenolic compounds in solution to form 1:1 complexes with characteristic absorption spectra. However no quantitative estimate of the extent of such interactions in solutions has been made, nor has it been demonstrated that dienophiles will undergo coördination with simpler aromatic substances, such as benzene itself, which lack substituents that strongly enhance the electron density of the aromatic nucleus.

Using spectrophotometric procedures similar to those employed previously in studying aromatic addition complexes[5] equilibrium constants for the interaction of benzene with maleic anhydride, chloromaleic anhydride and benzoquinone have now been determined. Additional studies have been made to determine the extent to which the tendency for such interaction is influenced by substituents in the aromatic nucleus. Equilibrium constants for complex formation of anthracene and

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[1] (a) P. Pfeiffer and T. Böttler, *Ber.*, **51**, 1819 (1918); (b) R. Kuhn and T. Wagner-Jauregg, *ibid.*, **63**, 2662 (1930);

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[5] (a) H. A. Benesi and J. H. Hildebrand, *ibid.*, **71**, 2703 (1949); (b) L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 5400 (1952) and preceding papers.