ments of sulfur dioxide were added and the equilibrium pressure was determined. Table I presents the results of one such experiment done at 25°. Although the results are admittedly somewhat rough, it is clear that a minimum in the vapor pressure occurs near a mole ratio corresponding to the 1:1 addition compound.

TABLE I

VAPOR PRESSURES OF $SO_2$–$Et_3N$ MIXTURES, $T = 25°$

| Mole ratio $Et_3N/SO_2$ | Pressure, mm. |
|---|---|
| 3.65 | 41 |
| 2.08 | 33 |
| 1.46 | 19 |
| 1.12 | 9 |
| 0.912 | 10 |
| .849 | 11 |
| .663 | 27 |

In further observations, it was found that the quantitative mixing of equimolar quantities of triethylamine and sulfur dioxide led always to the formation of a yellow-orange viscous oil, which solidified only at low temperatures, in conformity with the observations of Bateman, *et al.*,[3] and others,[7] and in no case did we observe a crystalline material of the type described by Wickert and Jander.[2] Only in the presence of water (see below) was such a substance formed.

In order to test its rate of exchange with solvent sulfur dioxide, a small amount of $S^{35}$-labeled addition compound was prepared by distilling together into a reaction tube equimolar quantities of reactants. After permitting reaction to occur, a tenfold excess of inactive sulfur dioxide was distilled in at liquid air temperature. Zero exchange time corresponded to the liquefaction of the mixture, which was accomplished by replacing the liquid air with a Dry Ice–acetone-bath. After about four minutes a volatile fraction was distilled off and radioassayed as barium sulfate; similarly another volatile fraction was taken at about 20 minutes. Finally, after distilling off the remaining excess solvent, the addition compound itself was radioassayed. The specific activities of these three fractions were, respectively, 33.6, 32.7, and 35.0 counts/min./mg. Exchange is thus complete in less than four minutes at −70 to −80°.

**The Addition Compound Hydrate and its Exchange with Sulfur Dioxide.**—In agreement with the observations of Bateman, *et al.*,[3] we have found the addition compound to form a crystalline hydrate when exposed to moisture. Several grams of this hydrate was prepared by a procedure similar to that used by others with related compounds.[8] Anhydrous sulfur dioxide was passed into a solution of the amine in dry ether. Evaporation of this solution yielded the anhydrous liquid addition compound. However, if a little water was first added, evaporation then yielded a white crystalline mass. Since this method was difficult in application, variable yields being obtained, and difficulty being experienced in drying the highly hygroscopic material, our analytical results were somewhat disappointing. However, the agreement with Bateman, *et al.*,[3] is probably reasonably satisfactory.

*Anal.* Calcd. for $Et_3NSO_2{\cdot}H_2O$: S, 17.5. Found: S, 14.3 (three determinations). M.p. expected 74–75°[3,9]; found 73–75, 71, 67–68°.

In order to determine its exchange rate with liquid sulfur dioxide, a small quantity of labeled hydrate was prepared in the vacuum system. To a portion of the anhydrous addition compound, prepared as before, an equimolar quantity of water was added by means of a micro pipet built into the vacuum line. After completion of reaction, an approximate fourfold excess of sulfur dioxide was distilled in and the same exchange procedure (at Dry Ice–acetone temperature) followed as with the anhydrous addition compound. The specific activities of four-, ten- and twenty-minute volatile fractions and of the addition compound hydrate itself were, respectively, 23.9, 25.2, 25.5 and 24.6 counts/min./mg. Again exchange is complete in less than four minutes at −70 to −80°.

## Discussion

Our observations, qualitative and quantitative, on the addition compound and its hydrate appear to agree completely with those of Bateman, *et al.*,[3] and we must conclude that the anhydrous compound is not a crystalline material, melting at 70–80° as reported by Wickert and Jander,[2] and again in Jander's book,[5] but rather that this crystalline substance is the monohydrate.

Our original interest in an exchange with the anhydrous compound was related to Jander's formula (I), the thought being to find whether the cation had sufficient stability to inhibit the exchange of the thionyl sulfur. When it became evident that (I) did not in fact represent the constitution of the material, it seemed of some interest to find whether the monomeric addition compound was of sufficient stability to retard the exchange. Our results, however, indicate a ready dissociability, even at Dry Ice temperature.

The exchange experiments with the hydrate seemed originally to be of greater interest. These were started at a time when our experiments[7b] semed to suggest that the exchange between solvent sulfur dioxide and dissolved sulfites might be measurably slow. In view of the formulation by Bateman, *et al.*,[3] of the hydrate as a bisulfite, it seemed of interest to measure its exchange rate. Again our results show a rapid and complete exchange even at Dry Ice temperature. This observation is in harmony with the earlier results involving tetramethylammonium pyrosulfite.[6b] However, whether the exchange is to be related to a ready mobility of oxide ions in liquid sulfur dioxide, as suggested in the earlier work,[7a,b] or whether it may proceed *via* a reversible dissociation such as

$$2HSO_3^- = H_2O + SO_2 + SO_3^=$$

is not clear at this point. Certainly, though, there is no evidence here for slowness in the sulfite–sulfur dioxide exchange.

**Acknowledgment.**—This research has been carried out under Contract AT(45-1)-244 between the U. S. Atomic Energy Commission and Oregon State College. The authors are indebted to Professor J. L. Huston for much helpful discussion.

CHEMISTRY DEPARTMENT
OREGON STATE COLLEGE
CORVALLIS, OREGON

---

[7] (a) J. R. Bright and J. J. Jasper, THIS JOURNAL, **65**, 1262 (1943); (b) J. A. Moede and C. Curran, *ibid.*, **71**, 852 (1949)

[8] A. Michaelis, *Ann.*, **274**, 173 (1893).

[9] On exposure to dry air, Bateman, *et al.*,[3] report the melting point to drop overnight to 55–60° and subsequently to rise slowly to 117–120°.

---

# Absorption Spectra of Uranium(IV) Fluorides

BY DIETER M. GRUEN AND MARK FRED[1]

RECEIVED FEBRUARY 6, 1954

Progress has been made in recent years toward the elucidation of the electronic structures of the heaviest elements, but detailed correlations of theory with magnetic susceptibility and spectroscopic data for example, have not yet been possible.[2]

---

[1] Presented at the Fall, 1953, Meeting of the American Chemical Society.

[2] G. T. Seaborg, "The Actinide Elements," McGraw-Hill Book Co., Inc., New York, N. Y., 1954, Chap. 17.

The situation in the actinides is complicated by many factors which must as far as possible be investigated separately.

Uranium +4 with two unpaired electrons possesses sharp absorption bands in many of its compounds,[3] resembling in this way compounds of the rare earth elements. However, the uranium spectra as well as the spectra of other actinides vary a good deal from compound to compound, indicating that the surroundings about the metal ions influence the electronic energy states much more profoundly here than in the rare earths. To obtain a better understanding of this interaction, the absorption spectra of $UF_4$, $NaUF_5$, $KUF_5$, $\delta$-$Na_2UF_6$ and $\gamma$-$Na_2UF_6$ were studied. The reasons for choosing this series of compounds are twofold. First, if one assumes that the crystalline field around each uranium ion is determined to a first approximation by its fluoride ion nearest neighbors, changes in the field from compound to compound would arise from changes in the number, distance and symmetry of the fluoride ions about each uranium, and since a great deal of crystallographic information is available on these compounds[4] it is tempting to correlate spectral changes with known changes in the crystalline environment. Second, it was hoped that the aforementioned changes would be small compared with the changes to be found in going from U(IV) sulfate to U(IV) oxalate for example, thus enabling one to trace a particular electronic transition from one fluoride to another in this series and to study the fine structure of the transition due to the crystalline Stark effect.

### Experimental

The spectra were obtained using the technique of pressed potassium bromide disks.[5,6] The fluorides were ground for several hours with potassium bromide to give intimate mixtures containing approximately 10% by weight of fluoride. After sifting through a 174-mesh nylon screen and drying for 24 hours at 110°, 200-mg. portions of the samples were weighed out and pressed into disks in a specially constructed mold using a Carver laboratory press. The disks were held in a copper block which formed part of a stainless steel metal double Dewar. Spectra were taken at room temperature and at the temperatures of liquid nitrogen and liquid helium in the region 4000–7000 Å. A Cary spectrophotometer was employed for a rapid survey. The spectra were photographed at high resolution using a 3.4 meter stigmatic grating spectrograph. The samples of $NaUF_5$, $\gamma$-$N_2UF_6$ and $\delta$-$Na_2UF_6$ were kindly furnished by Professor Zachariasen. They were part of the original materials prepared by him for use in the crystallographic investigations. A sample of 99.9% $UF_4$ was given to us by Dr. Harold Lohr. $KUF_5$ was prepared from solution and its identity established by X-ray analysis.

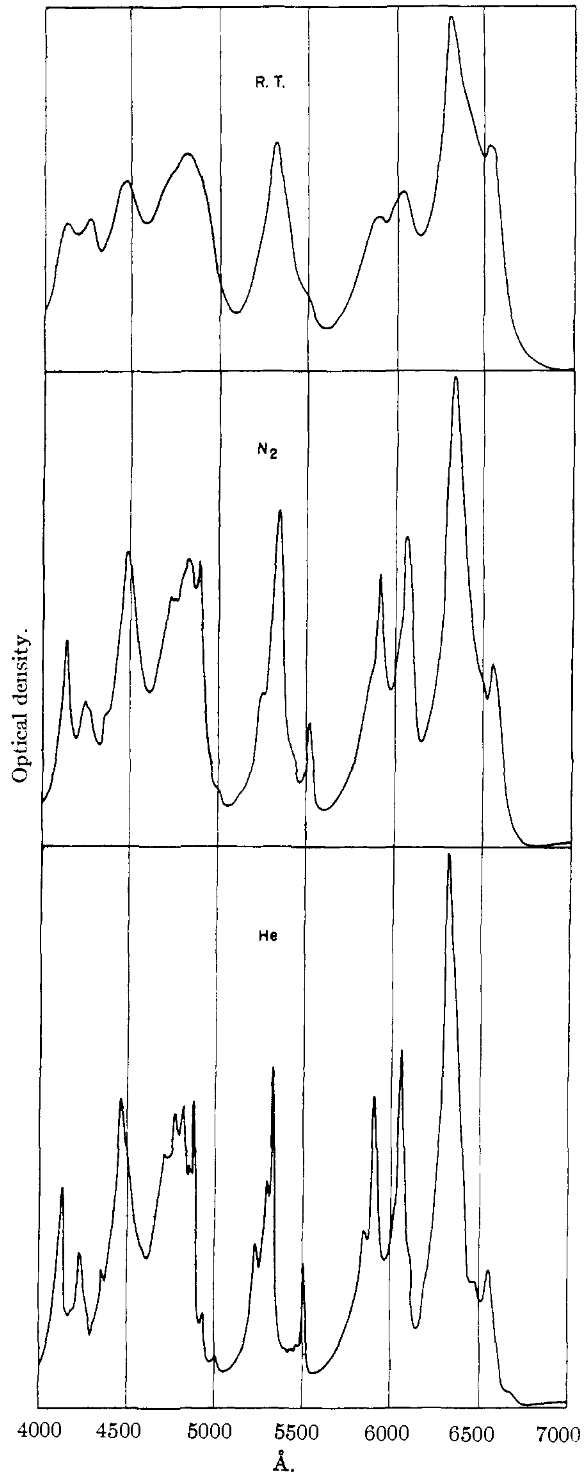

Fig. 1.—Absorption spectra of $\delta$-$Na_2UF_6$ at various temperatures.

### Results and Discussion

At room temperature, the spectra in the region 4000–7000 Å. of the five fluorides are characterized by a series of absorption bands falling in roughly the same spectral regions. At liquid nitrogen temperature, the bands are resolved into several components, the resolution increasing still further at helium temperatures. This behavior is reminiscent of the absorption spectra of rare earth salts and is illustrated with $\delta$-$Na_2UF_6$ in Fig. 1. In Table I are listed the absorption maxima of the various compounds at helium temperature, and their spectra taken on the Cary spectrophotometer are reproduced in Fig. 2. The most intense absorption band on the photographic plates is that which lies between 6530 and 6620 Å. Microphotometer tracings of this band photographed at helium temperature

[3] F. Ephraim and M. Mezener, *Helv. Chim. Acta*, **16**, 1257 (1933).

[4] W. H. Zachariasen, THIS JOURNAL, **70**, 2147 (1948).

[5] M. M. Stimson, *ibid.*, **74**, 1805 (1952).

[6] U. Schiedt, *Z. Naturf.*, **7b**, No. 5, 270 (1952).

TABLE I

ABSORPTION MAXIMA IN URANIUM FLUORIDES AT He TEMPERATURE, mμ

| $UF_4$ | $NaUF_5$ | $\delta$-$Na_2UF_6$ | $\gamma$-$Na_2UF_6$ |
|---|---|---|---|
| 413 | 410 | 413 | 427 |
| 424 | 428 | 424 | 445 |
| 426 | 437 | 427 | 448 |
| 434 | 443 | 437 | 480 |
| 447 | 475 | 448 | 489 |
| 480 | 485 | 473 | 508 |
| 489 | 489 | 478 | 548 |
| 527 | 522 | 482 | 597 |
| 531 | 529 | 483 | 618 |
| 540 | 535 | 487 | 629 |
| 542 | 538 | 489 | 637 |
| 575 | 540 | 493 | 653 |
| 578 | 566 | 500 | 656 |
| 618 | 568 | 524 | |
| 622 | 597 | 530 | |
| 627 | 614 | 533 | |
| 635 | 618 | 552 | |
| 640 | 628 | 585 | |
| 643 | 631 | 592 | |
| 647 | 633 | 606 | |
| 660 | 635 | 611 | |
| 662 | 645 | 633 | |
| 663 | 656 | 639 | |
| | 657 | 648 | |
| | 661 | 659 | |
| | 662 | | |

are reproduced in Fig. 3. The complexity of the band varies from compound to compound. Thus in $\delta$-$Na_2UF_6$, there is only a single component (the long wave length shoulder of this band seen in Figs. 1 and 2 does not appear in the microphotometer traces); in $\gamma$-$Na_2UF_6$, the single band has a shoulder on the long wave length side; the $NaUF_5$ absorption has four distinct components, while there are three peaks in $UF_4$. If one assumes that the bands in Fig. 3 arise from the same electronic transition, changes in the number of components may be associated with changes in the symmetry of the electric field. This problem has been discussed theoretically by Bethe.[7] In general, with decreasing symmetry of the electric field, the number of Stark components into which a band is split increases. In $UF_4$, each $U^{+4}$ is surrounded by eight $F^-$. The $UF_8^{-4}$ configuration is geometrically similar to the arrangement in the $Mo(CN)_8^{-4}$ ion[8] which approximates to the symmetry of the point group $D_{2d}$-$\bar{4}2m$ in the tetragonal system.[9] In $\gamma$-$Na_2UF_6$ each $U^{+4}$ is bonded to eight equidistant $F^-$ in an almost cubic arrangement.[10] Although the uranium positions in $NaUF_5$ and $\delta$-$Na_2UF_6$ are known,[4] there is apparently no information on the disposition of the fluorines. Since the number of components in the 6600 Å. region of the $NaUF_5$ spectrum is larger than in $UF_4$, it may be argued that the symmetry of the electric field in the former

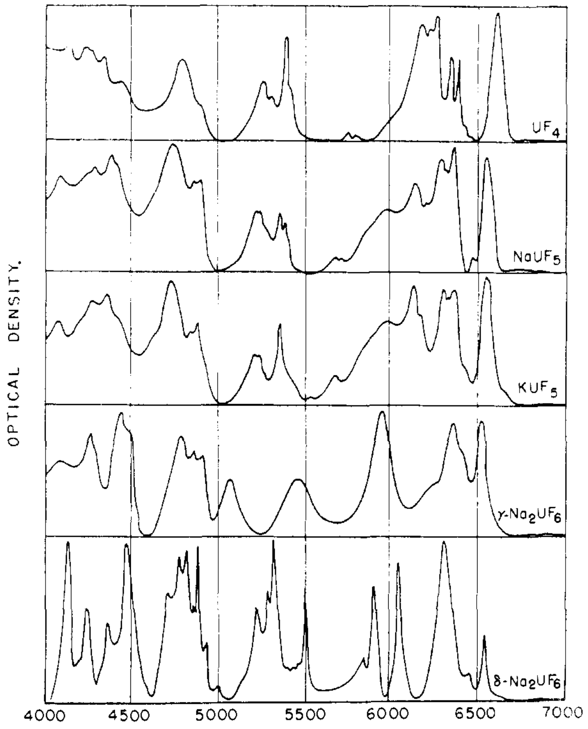

Fig. 2.—Absorption spectra of uranium(VI) fluorides at the temperature of liquid helium.

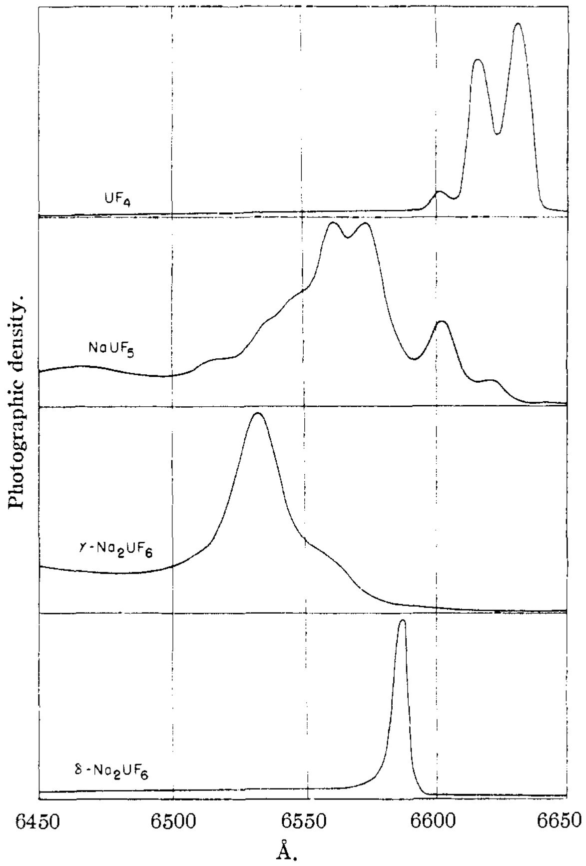

Fig. 3.—Microphotometer tracings of uranium(IV) fluoride absorption spectra at high resolution at temperature of liquid helium.

---

[7] H. Bethe, *Ann. Physik*, **3**, 133 (1929).

[8] R. D. Burbank, AECD-3216, June 6, 1951.

[9] J. L. Hoard and H. H. Nordsieck, THIS JOURNAL, **61**, 2853 (1939).

[10] W. H. Zachariasen, private communication.

is less than tetragonal. In δ-$Na_2UF_6$, by a similar argument, the symmetry of the electric field should be close to that found in γ-$Na_2UF_6$. Unfortunately the absorption bands at shorter wave lengths cannot be traced with the same degree of assurance from compound to compound, thus severely limiting the interpretation of the results.

It can be seen from Fig. 2 and Table I that the spectra of $KUF_5$ and $NaUF_5$ are identical. Since these two salts are isomorphous,[4] the result is not surprising but is merely an illustration of the fact that it is the fluoride ions which influence the electronic configuration of the $U^{+4}$ ions, the particular cation, whether $Na^+$ or $K^+$, having no observable effect.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

---

## The Acidity Function of Perchloric Acid in Aqueous Acetic Acid

BY FREDERICK J. LUDWIG[1] AND KENNETH H. ADAMS

RECEIVED FEBRUARY 17, 1954

In the course of investigations of the kinetics of of the rearrangement of benzopinacol[2] and of the dehydration of 1,1,2-triphenylethanol[3] it became necessary to have available acidity function,[4] $H_0$, values for solutions of perchloric acid in acetic acid–water mixtures. $H_0$ values for perchloric acid in this solvent previously have been reported only for anhydrous acetic acid[5a] and for acetic acid containing 0.12 wt. % of water.[5b] Our measurements cover the water concentration range of 0 to 5 wt. % and perchloric acid concentration range of $10^{-2}$ to $10^{-5}$ $M$.

### Experimental

Materials.—Acetic acid (Mallinckrodt, A. R. Bichromate Test Grade) was distilled from chromic acid[6] and dried by azeotropic distillation with benzene and fractionation[7]; m.p. 16.60–16.64°. Titration with Karl Fischer reagent[8] indicated a water content of less than 0.004%. Acetic acid–water mixtures were prepared by the addition of water from a weight buret to a weighed portion of the anhydrous acetic acid. Stock solutions of perchloric acid were prepared by the addition of 1.00 ml. of the 70–72% reagent grade commercial product to approximately 250 ml. of anhydrous acetic acid which contained the stoichiometric amount of redistilled acetic anhydride required to react with the water of the aqueous perchloric acid. The solution was standardized by titration with a standard solution of sodium acetate in glacial acetic acid with brom phenol blue as indicator.[9] 4-Chloro-2-nitroaniline (I) (Eastman Kodak Company, practical grade) was crystallized twice from ethanol–water solution; m.p. 116.0–116.5° (cor.). *o*-Nitroaniline (II) was purified in a similar manner; m.p. 71.0–71.6°. 2,4-Dinitro-N,N-diethylaniline (III) was prepared by heating 2,4-dinitrochlorobenzene in a large excess of diethylamine at reflux temperature for 1 hour. The product was precipitated with water and crystallized twice from ethanol; m.p. 79.6–79.9°.

**Procedure.**—The molar extinction coefficient, $E_N$, of each of the indicator bases, B, was measured at the wave length of maximum absorption in anhydrous acetic acid with a Beckman DU spectrophotometer and 1.00-cm. cells. For indicator I, $E_N$ = 4730 l./mole-cm. at 4060 Å.; for II, $E_N$ = 4800 l./mole-cm. at 3950 Å.; for III, $E_N$ = 15,950 l./mole-cm. at 3720 Å. These values of $E_N$ were not changed by the addition of a small quantity of potassium acetate to the solution, and were the same for 95% acetic acid and for the anhydrous solvent. Values of $E_B$, the molar extinction coefficient of the conjugate acid of the indicator $BH^+$, measured at these wave lengths, were zero for I and II and 150 l./mole-cm. for III. The indicator ratio was calculated from the relationship[10]

$$(B)/(BH^+) = (E_A - E_B)/(E_N - E_A)$$

in which $E_A$ is the molar extinction coefficient of a given acid solution. The value of $H_0$ for each such solution was then calculated from the equation[9]

$$H_0 = \log \frac{(B)}{(BH^+)} + pK_a \qquad (1)$$

Values of $pK_a$ used in these calculations were −0.91[5] for I, −0.17[4] for II and 0.30[6] for III.

### Results

In the anhydrous solvent and in water–acetic acid mixtures containing up to 2% of water $H_0$ varies linearly with log $[HClO_4]$, as reported by Smith and Elliott[5b] for approximately anhydrous solutions in which the indicator concentration is small relative to that of the acid. The lines shown in Fig. 1 have slopes varying between −1.02 and −1.09 with an average value of −1.05. This establishes the relationship

$$\frac{H_0 - H_0'}{\log [HClO_4] - \log [HClO_4]'} = -1.05 \qquad (2)$$

which is valid if the solvent composition is constant. A linear variation of $H_0$ with log molarity of sulfuric acid in glacial acetic acid has been reported.[11]

Values of $H_0$ were measured for two concentrations of perchloric acid ($2.38 \times 10^{-3}$ and $4.76 \times 10^{-3}$ $M$) in a series of acetic acid–water mixtures. From these results and also from the data of Fig. 1 average $H_0$ values for $1.00 \times 10^{-3}$ $M$ perchloric acid were calculated with the aid of equation 2. These values are summarized in Table I. From a graph of these data $H_0$ for other water concentrations up to 5 wt. % may be interpolated and for other perchloric acid concentrations within the range $10^{-2}$ to $10^{-5}$ $M$ may be computed from equation 2. For the anhydrous solvent Smith and Elliott have reported an $H_0$ value of −1.58 for $5.0 \times 10^{-3}$ $M$ perchloric acid. This corresponds to a value of −0.88 for $10^{-3}$ $M$ acid, in complete agreement with our value. Their value for acetic acid containing 0.12% water (−0.44 for $1 \times 10^{-3}$ $M$ $HClO_4$) lies slightly above our curve (Fig. 2). The data of Lemaire and Lucas[5a] for the anhydrous solvent also are in agreement with these results, the

---

[1] Army Chemical Center, Maryland. This note is abstracted from a portion of the Ph.D. Dissertation of Frederick J. Ludwig, St. Louis University, June, 1953.

[2] H. J. Gebhart, Jr., and K. H. Adams, THIS JOURNAL, in press.

[3] R. J. O'Neill, F. J. Ludwig, D. Melillo and K. H. Adams, Abstracts of Papers, 124th Meeting of the American Chemical Society, Sept. 6–11, 1953, Chicago, Ill., p. 81-O.

[4] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721, 4239 (1932); L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter IX.

[5] (a) H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951); (b) T. L. Smith and J. H. Elliott, *ibid.*, **75**, 3566 (1953).

[6] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 983 (1927).

[7] D. S. Noyce and P. Castelfranco, THIS JOURNAL, **73**, 4482 (1951).

[8] J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

[9] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2785 (1939).

[10] E. A. Braude, *J. Chem. Soc.*, 1971 (1948).

[11] M. A. Paul and L. P. Hammett, THIS JOURNAL, **58**, 2182 (1936); N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940).