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## Hydrolysis of Uranium(VI): Ultracentrifugation and Acidity Measurements in Chloride Solutions<sup>1</sup>

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Equilibrium ultracentrifugations and e.m.f. (acidity) measurements were carried out in chloride solutions for hydroxyl numbers  $n$  (average number of hydroxyls bound per uranyl) up to 1.4. Weight average degrees of polymerization between 1 and 2 were found for  $n < 0.8$ , and from 2 to somewhat less than 3 for higher values of  $n$ . A few centrifugations of uranyl perchlorate and nitrate solutions indicate that polymerization is similar in these media. These results indicate that hydrolysis schemes proposed in the literature which include species no higher than dimers cannot be complete. Further, the interpretation earlier reported of e.m.f. (acidity) data by a core-link mechanism, whether a continuous or limited series of polymers is involved, conflicts with present results. An interpretation involving polymers no larger than trimers which is compatible with ultracentrifugation and e.m.f. measurements is presented. Comparison of acidity measurements in chloride and perchlorate solutions suggests that there is some difference in the hydrolysis schemes for the two media. Volume and refractive index increments for U(VI) in chloride are presented as a function of  $n$ .

Although about a score of studies of the hydrolysis of U(VI) have been published in the last fifteen years, many of the schemes postulated by various authors agree in little more than the fact that polymeric species are formed; even this has been disputed by some.<sup>2</sup> Even when several authors agree on the presence of a given species, as for example  $(\text{UO}_2)_2(\text{OH})_2^{+2}$  (also written as  $\text{U}_2\text{O}_5^{+2}$ , which is equivalent in the present discussion), stability constants quoted vary sometimes by a factor of 10,<sup>3</sup> or even 100, as in the case of  $\text{UO}_2\text{OH}^+$ .<sup>4</sup> Among the polymeric species which at one time or another have been postulated are  $(\text{UO}_2)_2(\text{OH})^{+3}$ ,<sup>5,6</sup>  $(\text{UO}_2)_2(\text{OH})_2^{+2}$ ,<sup>3,4a, 6-11</sup>

$(\text{UO}_2)_3(\text{OH})_4^{+2}$ ,<sup>6,8,9</sup> (or  $\text{U}_3\text{O}_8^{+2}$ ),  $(\text{UO}_2)_3(\text{OH})_5^+$ ,<sup>9</sup> and  $(\text{UO}_2)_4(\text{OH})_2^{+6}$ .<sup>11</sup>

In an attempt at a more general scheme, Ahrland, Hietanen, and Sillén<sup>12</sup> reinterpreted earlier e.m.f. (acidity) data of Ahrland,<sup>5</sup> which had been measured in perchlorate media, by the core-link hypothesis of Sillén.<sup>13</sup> In this interpretation, all hydrolyzed species are postulated to have the formula  $(\text{UO}_2)[\text{UO}_2(\text{OH})_2]_L^{+2}$ , where  $L$  is the number of  $\text{UO}_3$  "links,"  $\text{UO}_2^{+2}$  being the "core." Three possibilities were offered: a limited series, the hydrolyzed species being a dimer and a tetramer; a limited series, having a dimer, a tetramer, and a pentamer; and an unlimited series, *i.e.*, species having all values of  $L$  being represented. The latter, the continuous polymerization scheme, was preferred by the authors. The picture was slightly modified later by introduction of the additional species  $(\text{UO}_2)_2(\text{OH})^{+3}$  by two of the authors<sup>6</sup> to account for e.m.f. measurements in concentrated, only slightly hydrolyzed uranyl solutions. Very recently, the core-link hypothesis has been invoked to interpret e.m.f. data in U(VI) sulfate solutions, measured by Peterson<sup>14</sup> in Sillén's laboratory. That this model of uranium hydrolysis has not been universally convincing is evidenced by the many papers since 1954 proposing other schemes.

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(2) (a) N. P. Komar and Z. A. Tretyak, *Zhur. Anal. Khim.*, **10**, 236 (1955); (b) S. A. Brusilovskii, *Doklady Akad. Nauk S.S.S.R.*, **120**, 305 (1958); (c) I. I. Chernyaev, V. A. Golovnya, and G. V. Ellert, *Zhur. Neorg. Khim.*, **5**, 1481 (1960); see also (d) G. Jander and K. F. Jahr, *Kolloid-Beih.*, **43**, 295 (1936).

(3) (a) J. A. Hearne and A. G. White, *J. Chem. Soc.*, 2168 (1957); (b) H. Guiter, *Bull. soc. chim. France*, 64 (1947).

(4) (a) R. L. Gustafson, C. Richard, and A. E. Martell, *J. Am. Chem. Soc.*, **82**, 1526 (1960); (b) W. E. Harris and I. M. Kolthoff, *ibid.*, **69**, 446 (1947); see also ref. 2a; (c) J. Rydberg, *Arkiv Kemi*, **8**, 113 (1956).

(5) S. Ahrland, *Acta Chem. Scand.*, **3**, 374 (1949).

(6) S. Hietanen and L. G. Sillén, *ibid.*, **13**, 1828 (1959).

(7) D. A. MacInnes and L. G. Longworth, U. S. Atomic Energy Comm., MDDC-911, 1947.

(8) J. Faucherre, *Compt. rend.*, **227**, 1367 (1948); *Bull. soc. chim. France*, 253 (1954).

(9) J. Sutton, *J. Chem. Soc.*, S275 (1949).

(10) R. A. Robinson and C. K. Lim, *ibid.*, 1840 (1951).

(11) E. Orban, M. K. Barnett, J. S. Boyle, J. R. Heiks, and L. V. Jones, *J. Phys. Chem.*, **60**, 413 (1956).

(12) S. Ahrland, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **8**, 1907 (1954); see also F. J. C. Rossotti, H. Rossotti, and L. G. Sillén, *ibid.*, **10**, 203 (1956).

(13) L. G. Sillén, *ibid.*, **8**, 299, 318 (1954).

(14) A. Peterson, *ibid.*, **15**, 101 (1961).

Some of the conflicts may stem from the fact that not all work was done at the same temperature or in the same medium; different media, both with respect to ionic strength and anion, were involved. We do not believe it reasonable to suppose, however, that all differences stem from these sources. The techniques used in most of these studies have been measurement of the acidity of hydrolyzed U(VI) solutions or measurement of some other property primarily sensitive to number of particles. It seemed worthwhile to see what information might be gained from equilibrium ultracentrifugation, a technique primarily sensitive to the weight of solute particles, which has been helpful in similar situations involving polymeric species.<sup>15,16</sup> In addition to ultracentrifugations, this paper presents acidity measurements of hydrolyzed U(VI) solutions in chloride media.

### Experimental and Computational Procedure

1. **Centrifugations.**—Details of centrifugation technique and interpretation have been presented earlier.<sup>17</sup> Centrifugations were carried out with a Spinco Model E ultracentrifuge at 25°. Sedimentation was followed by the interference optical system standard with the machine. Most centrifugations were carried out with a five-cell rotor, equipped with 12-mm. cells; a few of the dilute solutions (0.01 M U(VI)) were centrifuged in a single cell rotor with a 30-mm. cell. Speeds varied from 17,250 to 27,690 r.p.m.

Results were computed with the equation<sup>15b,17</sup>

$$N_w = \frac{d \ln c_2'/d(x^2)}{A_2' - (z'/2) d \ln \left\{ \left[ 1 + \frac{(z'c_2'/2c_3)}{[1 - (z'c_2'/2c_3)]} \right] / d(x^2) \right\}} \quad (1)$$

where  $N_w$  is weight average degree of polymerization;  $c$  is concentration (moles/l.);  $x$ , radius;  $z$ , charge;  $A_2 = [M_2(1 - \bar{v}_2\rho)\omega^2]/2RT$ ;  $M$ , molecular weight;  $\bar{v}$ , partial specific volume;  $\rho$ , solution density;  $\omega$ , angular velocity;  $R$ , gas constant;  $T$ , absolute temperature; primes refer to quan-

(15) (a) K. A. Kraus and J. S. Johnson, *J. Am. Chem. Soc.*, **75**, 5769 (1953); (b) J. S. Johnson, K. A. Kraus, and R. W. Holmberg, *ibid.*, **78**, 26 (1956); (c) J. S. Johnson and K. A. Kraus, *ibid.*, **78**, 3937 (1956).

(16) R. W. Holmberg, K. A. Kraus, and J. S. Johnson, *ibid.*, **78**, 5506 (1956).

(17) J. S. Johnson, G. Scatchard, and K. A. Kraus, *J. Phys. Chem.*, **63**, 787 (1959) and earlier references cited therein. One minor change has been made in the computational procedure outlined in this paper. In eq. 7, the background contribution to the total refractive index integral,  $n_0^*(x\omega^2 - x\alpha^2)$ , was evaluated as  $k_0 c_{BG}^\dagger (x\omega^2 - x\alpha^2)$ , in view of the unsymmetrical interference mask on the upper collimating lens (Section 3(e)iii(b)). Symbols are the same as in the reference. This term now is computed as

$$k_0 \int_{x\alpha^2}^{x\omega^2} c_{BG}^\dagger d(x^2),$$

*i.e.*, the concentrations of the background solutions are computed for the radius from which light interferes with light from the solution compartment, and by trapezoid rule, the integral is evaluated over the radial limits of the solution. This procedure is more nearly correct, but in practice little change in the value of  $N_w$  is involved.

ties in terms of monomer units; subscript 2 to the polymer component; and subscript 3 to the supporting electrolyte. The degree of hydration assumed for the solute does not affect appreciably the values of  $N_w$  computed with eq. 1; the differences in  $M_2'$  for different degrees of hydration will be compensated by differences in the values of  $\bar{v}_2$  computed from the densities of the solutions.

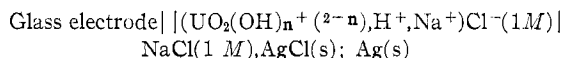
The components are defined by the convention of Scatchard.<sup>17</sup> For example, the "primed" component, 2, is, for maximum charge  $(2 - n)$ ,  $[\text{UO}_2(\text{OH})_n \text{Cl}_{2-n} - \left(\frac{2-n}{2}\right) \text{NaCl}]$ . The symbol  $n$  represents hydroxyl number, or the number of hydroxides bound per uranyl; it is obtained from the stoichiometry of the solution with a correction for free acid. The slopes,  $d \ln c_2'/dx^2$ , were evaluated at that radius at which the uranyl concentration had its initial value; at this point, the solution has essentially its initial composition.

Variations of activity coefficients have been neglected. The uncertainty introduced is difficult to estimate; however, the results to be presented for the experimentally obtained molecular weights for the (known) unhydrolyzed solutions indicate that this effect probably is not serious. For polydisperse systems as are dealt with here, eq. 1 is exact only if the value of  $z'$  (charge per monomer unit) is the same for all species,<sup>15b</sup> which is not the case here. However, this approximation usually will not introduce a serious error, because the maximum average charge used in the computations, in general, is reasonably close to the maximum charge of the predominant species.

A few other sources of uncertainty should be mentioned. Since U(VI) concentrations vary with radius while acidity is constant to a good approximation, the hydroxyl number,  $n$ , will vary with radius; this can be seen from the acidity data to be presented. The specific volumes, specific refractive index increments (see below), as well as the weight  $M'$  of the monomer unit,  $\text{UO}_2(\text{OH})_n \text{Cl}_{2-n}$ , will vary correspondingly. The effect of these variations can be estimated; it turns out to be negligible for computations made on the assumption of maximum charge ( $z' = 2 - n$ ), as we have done here, since the refractive index increment for the Scatchard component turns out to be essentially invariant with hydroxyl number for U(VI) in NaCl. If computations had been carried out for  $z' = 0$ , correction for this effect would have affected  $N_w$  by less than 5%.

Densities were measured with a *ca.* 24-ml. pycnometer, and refractive index increments with a Brice-Phoenix differential refractometer. Computations were carried out on digital computers, the ORACLE and an IBM 7090.

2. **E.m.f. Measurements.**—Acidity measurements were carried out with a vibrating reed electrometer.<sup>18</sup> The cell was



A Beckman No. 41262 glass electrode, which has a silver-silver chloride inner electrode, was used; the inner buffer solution was replaced with 0.1 M HCl. A Leeds and Northrup dual-glass junction was used. The silver-silver chloride reference electrode was of the thermal-electrolytic type, prepared generally by the procedure of Taniguchi

(18) K. A. Kraus, R. W. Holmberg, and C. J. Borkowski, *Anal. Chem.*, **22**, 341 (1950).

and Janz.<sup>19</sup> Temperature of the measurements was 25.0°. There was a slight drift of the electrode potentials of standards (from 0.1–0.2 mv./day); consequently, standard acids (*ca.* 0.003 or 0.001 *M* H<sup>+</sup> with NaCl added to give 1 *M* total chloride) were measured each day, usually both before and after a series. The acidity  $c_H$  (moles/l.) of the uranium solutions was taken to be given by

$$\log c_H = \log (c_H)_{\text{standard}} + \frac{(E_{U(VI)\text{Soln.}} - E_{\text{standard}})/59.16}{2} \quad (2)$$

The potential,  $E$ , expressed in millivolts, increases with acidity in this convention. The slope,  $\Delta E/\Delta \log c_H$ , was found to approach the ideal value, 59.16 mv., as the acidity decreased, and this value therefore was used to compute the acidities of the uranium solutions (which were mostly between  $10^{-8}$  and  $10^{-5}$  *M* H<sup>+</sup>) from the potentials and the concentrations of the standards. No attempt was made to correct for differences in junction potential between U(VI) solutions and standards. The most concentrated (0.1 *M*) U(VI) solutions were prepared by weight from unhydrolyzed U(VI) chloride, NaOH, and NaCl stock solutions, and the other concentrations were prepared by weight dilution with 1 *M* NaCl. The total stoichiometric chloride concentration was  $0.999 \pm 0.002$  *M*.

**3. Materials.**—Uranium stock solutions were prepared from  $\text{UO}_2 \cdot \text{H}_2\text{O}$ . Analysis of U(VI) stocks was carried out by precipitation with ammonia, followed by ignition to  $\text{U}_3\text{O}_8$ . Chloride in the uranyl stocks was determined by AgCl precipitation. In some of the earlier centrifugations, it was found that the  $\text{UO}_2 \cdot \text{H}_2\text{O}$  used in preparing solutions contained *ca.* 0.025 mole nitrate per mole U(VI), and a correction of hydroxyl number was made for this. The  $\text{UO}_2 \cdot \text{H}_2\text{O}$  used in the acidity measurements and in later centrifugations contained less than 0.003 mole nitrate per mole U(VI). Sodium hydroxide solutions were prepared by dilution of saturated NaOH with demineralized water. Standardizations were carried out with potassium acid phthalate and by titration with HCl, which in turn had been analyzed by AgCl precipitation.

The upper limit of the hydroxyl numbers investigated by ultracentrifugation was set by the stability of solutions against precipitation for times long enough for attainment of centrifugation equilibrium. With 0.1 *M* U(VI) we found that  $n$  *ca.* 1 was the highest that could be reached, but with 0.01 *M* U(VI),  $n$  *ca.* 1.4 was attained. Even at this concentration the solution was not stable indefinitely and, in time, precipitation occurred. However, stable potentials and centrifugation equilibrium usually could be attained before precipitation started. Precipitation behavior was rather odd; in preparation of a solution, a precipitate frequently would form on addition of base to uranium stock, which would readily redissolve. The solution then would remain clear, would give stable potentials, or would reach an equilibrium distribution in a centrifugal field, and then after days or weeks, would deposit a precipitate. When precipitation began, it was indicated clearly by drift of potential, or a decrease in the number of interference fringes in the centrifuge. Such behavior was not always reproducible, and seemed to depend on procedure in preparation and other factors not altogether understood. Similar observations were reported by Sutton.<sup>9</sup>

(19) H. Taniguchi and G. J. Janz, *J. Electrochem. Soc.*, **104**, 123 (1957).

## Results and Discussion

**1. Apparent Volumes and Refractive Index Increments.**—In interpretation of ultracentrifugation results, the partial specific volumes of solutes are necessary; in addition, refractive index increments of solutes are needed for conversion of interference fringe patterns to concentration distributions. Apparent molal volumes of the hydrolyzed uranium component,  $\text{UO}_2(\text{OH})_n\text{Cl}_{2-n}$ , are presented in Fig. 1 as a function of hydroxyl

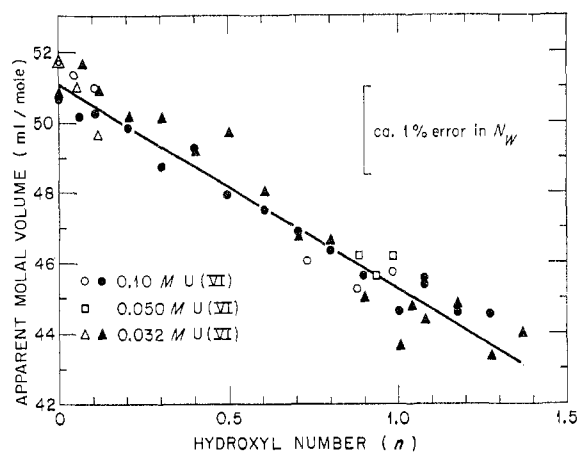


Fig. 1.—Apparent molal volume of hydrolyzed uranyl chloride: solid symbols, 1 *M* total chloride; open symbols, 1 *M* NaCl.

number  $n$ . In computation of apparent volumes, the volume of “solvent” (a solution having the same number of moles of NaCl and HCl per kg. water as the U(VI) solution) was obtained from the mixing rule of Young and Smith,<sup>20</sup> based on the density measurements reported previously by Wirth.<sup>21</sup>

The volume of the uranium component is seen to decrease with degree of hydrolysis. As one would expect, there is no significant difference between the volume measured in 1 *M* NaCl solutions (the media for the centrifugations) and solutions 1 *M* in total chloride (the media of the acidity measurements). The less precise values obtained at lower concentrations scatter about the higher concentration values, and no significant concentration dependence of apparent volumes is evident. Apparent volumes therefore were used for partial volumes in computation of centrifugation results; the values taken from the line drawn through the 0.1 *M* U(VI) points in Fig. 1 were used. An estimate of the effect of error in volume

(20) T. F. Young and M. B. Smith, *J. Phys. Chem.*, **58**, 716 (1954).

(21) U. E. Wirth, *J. Am. Chem. Soc.*, **62**, 1128 (1940).

on error in computed molecular weight (represented in Fig. 1 as the error in volume approximately equivalent to an error of 1% in  $N_w$ ) indicates that the uncertainties in volume are not important for present purposes.

Refractive index increments ( $(n_{\text{solution}} - n_{\text{solvent}})/c$ ) of the uranium solute,  $\text{UO}_2(\text{OH})_n\text{Cl}_{2-n}$ , are presented in Fig. 2. These were

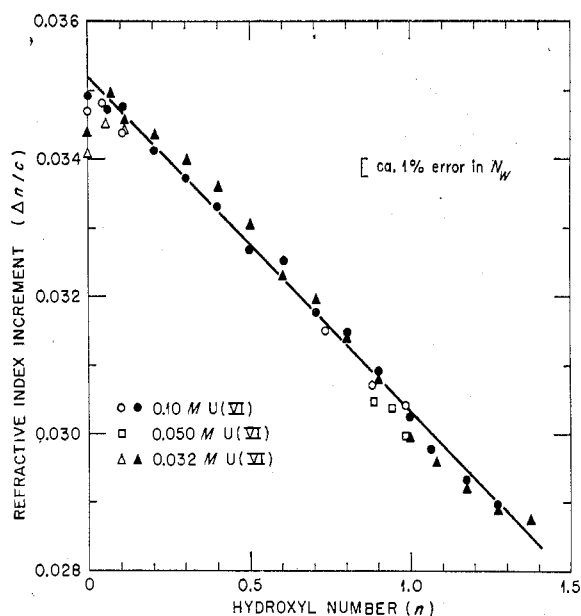


Fig. 2.—Refractive index increment at 546  $m\mu$  of hydrolyzed uranyl chloride: solid symbols, 1  $M$  total chloride; open symbols, 1  $M$  NaCl.

measured in a differential refractometer against about the same concentration of NaCl (or NaCl-HCl in the unhydrolyzed cases). Corrections for the small differences in supporting electrolyte concentrations were computed from literature data<sup>22</sup> for NaCl and measurements in this Laboratory for HCl.<sup>23</sup> The increment of HCl (significant only for the unhydrolyzed U(VI) solutions) in 1  $M$  total HCl-NaCl was taken to be the same as the increment in 1  $M$  HCl. These literature values also were used in the interpretation of the ultracentrifugation results.

Refractive index increments of the hydrolyzed uranium component decrease with increasing degree of hydrolysis. As with the volumes, values used in interpretation of ultracentrifugations were taken from the line in the figure drawn through the 0.1  $M$  U(VI) points. Scatter of the results obtained with more dilute solutions about

this line indicates no significant dependence of refractive index increment on uranium concentration under these conditions. Increments seem to be the same in 1  $M$  NaCl and in solutions 1  $M$  in total chloride. Uncertainties in degree of polymerization stemming from uncertainties in refractive index increments (depicted in Fig. 2), though somewhat greater than those from uncertainties in volumes, are small.

Apparent molal volumes for hydrolyzed uranium perchlorate solutions were computed by adding to the volumes of the U(VI)-chloride component  $(2 - n)$  times the difference in volume of NaClO<sub>4</sub> and NaCl,<sup>20</sup> both taken for 1  $M$  solutions. The corresponding refractive index increments were computed analogously, with the data of Kohner<sup>24</sup> for NaClO<sub>4</sub>. The corresponding quantities for the nitrate centrifugation were obtained in the same way with literature volumes<sup>25</sup> and refractive index increments.<sup>22,26</sup>

**2. Ultracentrifugation Results.**—Equilibrium ultracentrifugations were carried out for 38 U(VI)-chloride solutions with  $0 \leq n \leq 1.4$ . All solutions except the unhydrolyzed were 1  $M$  in NaCl; for  $n = 0$ , the supporting electrolyte was 1  $M$  HCl. The U(VI) concentration range was 0.01 to 0.1  $M$  up to  $n = 1.0$ ; from  $n = 1.0$  to 1.4, the U(VI) concentration was 0.01  $M$ . The results are presented in Fig. 3 as a plot of weight average degree of polymerization,  $N_w$ , vs.  $n$ . A few centrifugations of solutions 1  $M$  in NaClO<sub>4</sub> and a single result on a 0.5  $M$  KNO<sub>3</sub> solution also are included in Fig. 3. The results were computed with eq. 1 on the assumption of maximum charge per monomer unit,  $z' = 2 - n$ . A brief discussion of the significance of this perhaps is worthwhile.

Distribution of an ionized solute in a gravitational field is a function of charge, as well as of molecular weight; the effect of charge is repressed, but not completely, by the presence of excess slightly sedimenting supporting electrolyte. The effect of charge is in the direction of decreasing sedimentation, *i.e.*, molecular weights computed from equilibrium distributions, without correction for this effect, will tend to be low. In the case of monodisperse solutes, estimates of the charge can be made from centrifugations carried out at varying polymer concentration,

(24) H. Kohner, *Z. physik. Chem.*, **B1**, 427 (1928).

(25) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958, p. 361.

(26) W. Geffcken, *Z. physik. Chem.*, **B5**, 81 (1929).

(22) A. Kruis, *Z. physik. Chem.*, **B34**, 13 (1936).

(23) R. M. Rush and G. Scatchard, *J. Phys. Chem.*, **65**, 2240 (1961).

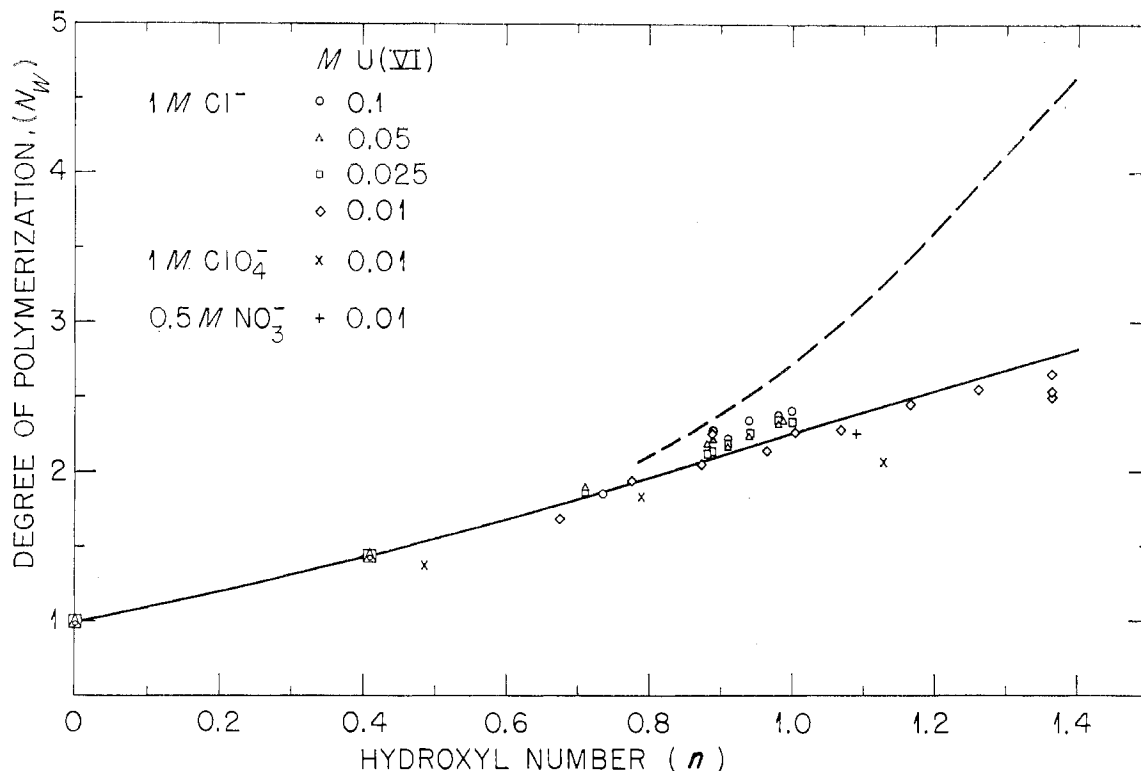


Fig. 3.—Equilibrium ultracentrifugation of U(VI), computed for charge  $z = (2 - n)$ : dashed line computed for core-link scheme; solid line computed with  $k_{2,2} = 6.7 \times 10^{-7}$ ,  $k_{3,4} = 4.7 \times 10^{-13}$ , and  $k_{3,5} = 1.0 \times 10^{-17}$ .

since part of the charge effect increases with concentration.<sup>17,27</sup> The results for hydrolyzed U(VI) however, indicated a polydisperse distribution (concavity upward of plots of  $\ln n^*$  vs.  $x^2$ , where  $n^*$  is the difference in refractive index between solution and background, and  $x$  is radius), and estimates of charge directly from the centrifuge results therefore were difficult. For this reason, the charge was assumed to be  $(2 - n)$ , which is equivalent to the assumption of no chloride complexing by the U(VI) species. The results in Fig. 3 are therefore, so far as they are influenced by charge effect, upper limits of  $N_w$ . The fact that higher concentrations of U(VI) at constant  $n$  tend to give slightly higher values of  $N_w$  suggests that the assumed charge is too large and that there is some chloride complexing by the uranium species.

The results in Fig. 3 show that polymeric species are formed on U(VI) hydrolysis, that species larger than dimeric must be present, but there is no indication of the presence in important amounts of species larger than trimeric, even at  $n = 1.4$ .

### 3. Comparison with Degrees of Polymeriza-

(27) J. S. Johnson, K. A. Kraus, and G. Scatchard, *J. Phys. Chem.*, **58**, 1034 (1954).

**tion Given by the Core-Link Hypothesis**—Ahrland, *et al.*,<sup>12</sup> do not list values of  $N_w$ , but estimates of this quantity may be made from their values of  $g$  and  $u$ , which are functions evaluated from the acidity measurements. The weight average degree of polymerization may be represented by<sup>28</sup>

$$N_w = \left( \sum_{N=1} N^2 c_N \right) / \left( \sum_{N=1} N c_N \right) \quad (3)$$

where  $N$  is the number of uranium atoms per species (including unhydrolyzed species) and the summation includes all uranium species. In the core-link theory  $N = (L + 1)$  where  $L$  is the number of links. Thus

$$N_w = \frac{\sum_{L=0} (L+1)^2 c_L}{\sum_{L=0} (L+1) c_L} = \frac{c_0 + \sum_{L=1} L^2 c_L + \sum_{L=1} 2L c_L + \sum_{L=1} c_L}{c_0 + \sum_{L=1} L c_L + \sum_{L=1} c_L} \quad (3a)$$

$c_0$  being the concentration of  $\text{UO}_2^{++}$ . The formation constant,  $k_L$ , for the  $L^{\text{th}}$  species is given by

$$k_L = \frac{c_L}{c_0 u^L} \quad (4)$$

(28) F. Granér and I. G. Sillén, *Acta Chem. Scand.*, **1**, 631 (1947).

where  $u = c_0/(H^+)^2$  for the core-link scheme  $UO_2-[UO_2(OH)_2]_L^{+2}$ . When the core-link mechanism applies<sup>12</sup>

$$c_0 g = \sum_{L=1}^{\infty} c_L = c_0 \sum_{L=1}^{\infty} k_L u^L \quad (5a)$$

$$\frac{dg}{du} = \sum_{L=1}^{\infty} L k_L u^{L-1} = \frac{1}{c_0 u} \sum_{L=1}^{\infty} L c_L \quad (5b)$$

$$\frac{d^2 g}{du^2} = \frac{1}{c_0 u^2} \left[ \sum_{L=1}^{\infty} L^2 c_L - \sum_{L=1}^{\infty} L c_L \right] \quad (5c)$$

By substitution into eq. 3a, expression (6) is obtained

$$N_w = 1 + \frac{d \ln(1 + d(gu)/du)}{d \ln u} \quad (6)$$

Equation 6 holds if all species are of the core-link type, whether the series is limited or unlimited. It should be noted that, since  $g$  and  $u$  in this scheme are independent of U(VI) concentration,  $N_w$  also is concentration independent. By fitting the functions to be differentiated to a power series<sup>29</sup> in  $u$ , the curve of  $N_w$  vs.  $n$  presented in Fig. 3 was computed. The curve was insensitive to values of  $\delta$  (a residual term in the integrations to obtain  $g$  and  $u$  introduced by Ahrlund, *et al.*)<sup>12</sup> over the range of values of  $\delta$  they imply is reasonable; it is about the same for the two sets of  $g$  and  $u$  values they list (their curves I and II). We also have computed  $N_w$  vs.  $n$  curves using their constants for the limited series, and for the unlimited series including species up to  $L = 14$ ; these agreed with the dashed curve in Fig. 3 very well for the unlimited, and within 15% for the limited, series. Agreement should be complete but their uncertainties in evaluation of constants from the  $g$  vs.  $u$  data, and our uncertainties in the differentiations required by eq. 6 give rise, of course, to some discrepancy. The "core-link" curve in Fig. 3 gives, however, a fairly good representation of the values of  $N_w$  implied by their interpretations of U(VI) hydrolysis.

The ultracentrifugation results clearly are in conflict with the core-link interpretation of Ahrlund's results. It seems possible, of course, that the values of  $N_w$  of U(VI) are vastly different in chloride and perchlorate media. However, centrifugations in 1 M NaClO<sub>4</sub> (Fig. 3) indicate that this is not the case.

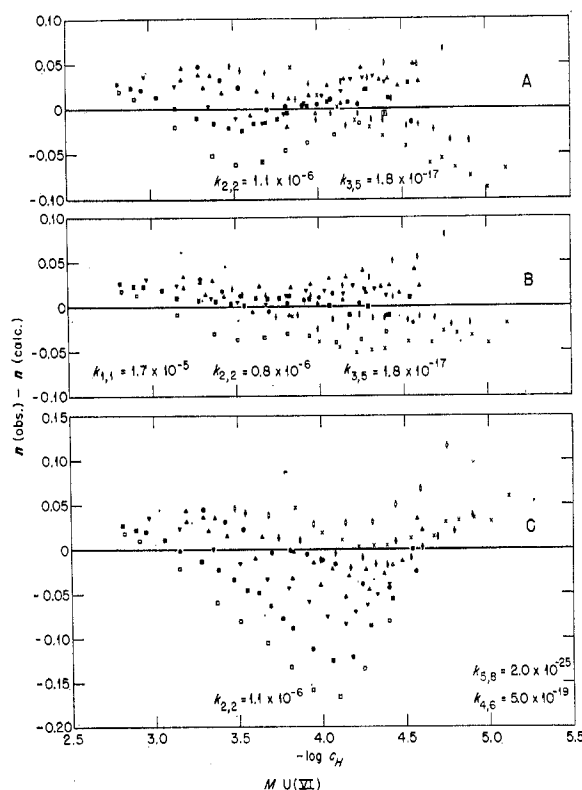
**4. Reinterpretation of Ahrlund's Acidity Measurements.**—The question arises whether there is a scheme alternate to core-link for U(VI) hydrolysis which is compatible both with the

ultracentrifugation results and with Ahrlund's acidity measurements. One possibility would include the species  $(UO_2)_2(OH)_2^{+2}$ , which a preponderance of previous investigators have postulated, and  $(UO_2)_3(OH)_5^+$ , since a trimer is necessary to explain the ultracentrifugation results and at least one relatively low molecular weight species having a degree of hydrolysis greater than 1.4 is needed, in view of the hydroxyl numbers reached for  $N_w < 3$ .

Formation constants

$$k_{i,j} = \frac{((UO_2)_i(OH)_j^{+(2i-j)})(H^+)^j}{(UO_2^{+2})^i} \quad (7)$$

were computed for this scheme to give the minimum least square deviation for Ahrlund's experimental points.<sup>30</sup> We compare in a deviation plot, Fig. 4, the agreement with experimental results



M U(VI)		
GLASS ELECTRODE	QUINHYDRONE ELECTRODE	
• 0.00389 - 0.00370	• 0.00150 - 0.00136	• 0.0118 - 0.0102
• 0.0117 - 0.0102	• 0.00397 - 0.00377	• 0.0232 - 0.0182
• 0.0466 - 0.0300	• 0.00790 - 0.00722	• 0.0446 - 0.0274

Fig. 4.—Hydrolysis of U(VI) in 1 M NaClO<sub>4</sub>. Deviations of experimental points (Ahrlund, ref. 5) from computed curves. For A and B, constants obtained by least squares fit of all points; for C, constants taken from ref. 12.

(29) We are indebted to M. P. Lietzke and M. H. Lietzke for use of their Fortran least squares subroutine, Polfit II.

(30) We are indebted to H. A. Levy and W. R. Busing for use of their Fortran least squares program and for assistance in programming these computations.

of this dimer (2,2)–trimer (3,5) scheme<sup>31</sup> with the agreement of one of the core-link limited series proposed in reference 12 (dimer (2,2)–tetramer (4,6)–pentamer (5,8)) and computed for the constants listed there. The agreement is, if anything, better for the (2,2)–(3,5) scheme ( $k_{2,2} = 1.1 \times 10^{-6}$  and  $k_{3,5} = 1.8 \times 10^{-17}$ ) than for the core-link scheme. Addition of the species  $\text{UO}_2\text{OH}^+$  (1,1) to the (2,2)–(3,5) scheme ( $k_{1,1} = 1.7 \times 10^{-5}$ ,  $k_{2,2} = 0.8 \times 10^{-6}$ , and  $k_{3,5} = 1.8 \times 10^{-17}$ ) gave slightly closer agreement, especially at the lowest concentration, though perhaps not significantly better. Degrees of polymerization computed for either the (1,1)–(2,2)–(3,5) or the (2,2)–(3,5) scheme are in much better agreement with the ultracentrifugation values than the core-link scheme. The computed values of  $N_w$  (not shown in Fig. 3) would fall somewhat below the points of Fig. 3 though well above the centrifuge results computed for zero charge.

There thus appears to be at least one hydrolysis scheme consistent with Ahrlund's acidity measurements which is not in conflict with degrees of polymerization obtained by ultracentrifugation and which does not require a core-link system nor a continuous polymerization scheme.

**5. Acidity Measurements of Hydrolyzed U(VI) Solutions in Chloride Media.**—In order to provide a more pertinent correlation with the ultracentrifugation results, we have carried out acidity measurements on hydrolyzed U(VI) solutions in 1 *M* total chloride. Curves for five U(VI) concentrations, covering the range from 0.001–0.1 *M*, were determined; measurements were made up to *n ca.* 1.4 for the lowest U(VI) concentration, and to somewhat lower degrees of hydrolysis at the higher concentrations.

The results are given in Fig. 5. In an attempt to represent the data as we described in the previous section, it was found that a scheme with only the species  $\text{UO}_2\text{OH}^+$ ,  $(\text{UO}_2)_2(\text{OH})_2^{+2}$ , and  $(\text{UO}_2)_3(\text{OH})_5^{+3}$  did not give satisfactory agreement with the data. This is illustrated in a plot of deviations (top, Fig. 6) of observed results from values computed for constants obtained by a least square fit of all the data.

Several other schemes were found to be more or less unsuccessful; those tried include the schemes (1,1)–(2,2)–(2,3)–(3,5); (2,2)–(3,3)–(3,5); and (2,2)–(3,4)–(4,6). Satisfactory agreement was

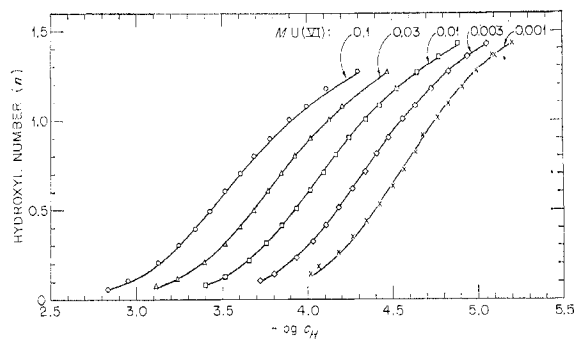


Fig. 5.—Hydrolysis of U(VI) in 1 *M* chloride. Curves computed with constants obtained by least squares fit of all data points ( $k_{2,2} = 6.7 \times 10^{-7}$ ,  $k_{3,4} = 4.7 \times 10^{-13}$ ,  $k_{3,5} = 1.0 \times 10^{-17}$ ).

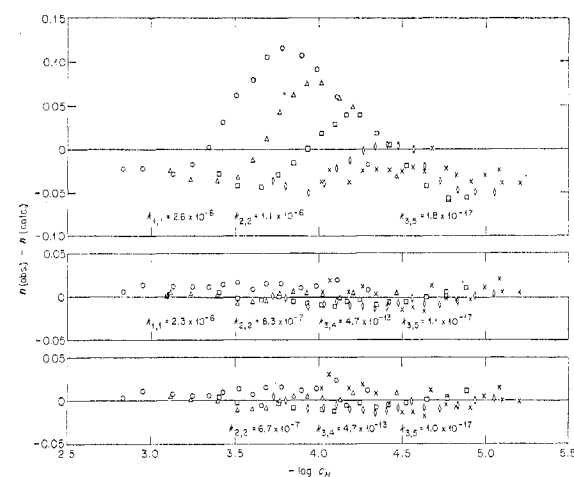


Fig. 6.—Comparison of schemes for U(VI) hydrolysis in 1 *M* total chloride. Deviations of observed values from values computed with constants obtained by least squares fit of all data points. Symbols represent *M* U(VI) as: O, 0.1; Δ, 0.03; □, 0.01; ◇, 0.003; and ×, 0.001.

found, however, if three hydrolyzed species were postulated to be (2,2)–(3,4)–(3,5) (bottom, Fig. 6). Addition of a (1,1) species did not noticeably improve the fit (middle, Fig. 6). In both cases, the standard deviation was *ca.* 0.01 in *n*. The curves computed for polymers with *i, j* of (2,2), (3,4), and (3,5) ( $k_{2,2} = 6.7 \times 10^{-7}$ ,  $k_{3,4} = 4.7 \times 10^{-13}$ , and  $k_{3,5} = 1.0 \times 10^{-17}$ ) are compared directly with the titration curves in Fig. 5.

It should be remembered that, since chloride complexing occurs, the constants listed are not strictly the  $k_{i,j}$  values defined by eq. 7, but involve also factors for the formation of the chloride complexes of the various species and the free chloride concentration raised to an appropriate power. Since the concentration of free chloride does not vary greatly in these experiments, the values of the constants as given should apply over the experimental range.

(31) The species are identified by the values of *i* and *j* of eq. 7; e.g., (2,2) corresponds to the species  $(\text{UO}_2)_2(\text{OH})_2^{+2}$  and (3,5) to the species  $(\text{UO}_2)_3(\text{OH})_5^{+3}$ .

Average degrees of polymerization computed on this scheme are shown in Fig. 3. (Concentration dependence of  $N_w$  is small between 0.01 and 0.1  $M$  U(VI), the range of the ultracentrifugation experiments, and the average curve for these concentrations is presented.) Agreement is satisfactory; with the exception of some 0.01  $M$  U(VI) points, the experimental points fall somewhat above the computed curve. It was pointed out earlier that this would be expected if the species charges were not the maximum, as assumed, *i.e.*, if some chloride complexing occurs. The 0.01  $M$  U(VI) points which tend to fall below the computed curve are experimentally the least precise.

**6. Discussion.**—Our conclusions are in general agreement with those of many earlier workers, in that many have postulated the species  $(UO_2)_2(OH)_2^{2+}$ . Of the many schemes which have been proposed, our scheme is most in accord with Sutton's.<sup>9</sup> He suggests additional species having higher degrees of hydrolysis, though no larger than trimeric, apparently from measurements at higher values of  $n$  than we reached.

We believe the value of a weight-sensitive technique in the study of equilibria involving polymers again is demonstrated in this study. When aggregates are formed, there is such a large number of possibilities for interpretation of, *e.g.*, acidity data that arriving at a unique scheme is very difficult. Use of a weight-sensitive method at least strongly limits the molecular weights of species which comprise important fractions of the hydrolyzed solute.

With respect to the mechanism of hydrolysis, both unlimited and limited series of core-link species are excluded by the present results. In two cases besides the present one, Bi(III) and Zr(IV), for which continuous polymerization had been claimed,<sup>28,32</sup> we concluded from ultracentrifugation<sup>15a,c,16</sup> that the mechanism was not applicable; these findings now seem to be generally accepted.<sup>33,34</sup> In a fourth case, Th(IV), our conclusion so far is indefinite, though the core-link mechanism, on which the unlimited scheme is based, clearly is inadequate for the early stages of hydrolysis.<sup>35</sup> In the case of Bi(III), X-ray studies

of concentrated solutions<sup>36</sup> have contradicted the basic structural arguments which originally were advanced to support the continuous polymerization scheme.<sup>28</sup> In view of this history, we believe that the hydrolysis of other ions for which continuous polymerization has been suggested<sup>37</sup> (Sc(III), In(III), U(IV)) should be reexamined.

Although we hope that the scheme presented here for hydrolysis in chloride solution delineates the species present in important amounts, the exact values of the constants given should not be taken too seriously. For example, the least square fit of our acidity data for the scheme with the (1,1) species included assigned a value for its formation constant which is significant by the criteria of some, *i.e.*, the value of  $k_{1,1}$  is different from zero by about three standard deviations in its value. On the other hand, comparison of the fit to experiment with and without inclusion of this species (Fig. 6) does not in our opinion support an unambiguous conclusion concerning its presence or absence. However, its inclusion modifies the  $k_{2,2}$  by 6%. Similarly, uncertainty concerning presence or absence of other species in minor amounts makes the precise values of a given set of constants doubtful. Even if one had much more accurate data than we present, uncertainties as to constancy of activity coefficient ratios, junction potentials, and complexing reactions (particularly of polymers) would make unambiguous decisions difficult.

There is a strong suggestion on the basis of the acidity measurements that the hydrolytic schemes of U(VI) in chloride and perchlorate media differ. Inclusion of the species  $(UO_2)_3(OH)_4^{+2}$  did not improve the agreement with Ahrlund's data for uranyl perchlorate, even though this was tried both with all his points and with his glass electrode and quinhydrone electrode points separately. Scatter of the points is too great for an unambiguous conclusion, but it appears most likely that the principal hydrolytic species in 1  $M$   $NaClO_4$  are  $(UO_2)_2(OH)_2^{+2}$  and  $(UO_2)_3(OH)_6^+$ . In chloride solution, there appears to be the additional species  $(UO_2)_3(OH)_4^{+2}$ . Its stability in chloride *vs.* perchlorate solutions implies that this (3,4) species is complexed by chloride ions. Perhaps the differences in the hydrolysis schemes (and the implied differences in complexing) account for the large differences in the phase diagrams in these media<sup>38</sup>; much higher values of  $n$  can be realized for a

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(38) C. A. Kraus, U. S. Atomic Energy Comm., A-360, 1942.



given U(VI) concentration in chloride than in perchlorate solutions.

On the basis of recent acidity measurements by other workers in this Laboratory,<sup>39</sup> it was concluded that the (3,4) species also is not important in nitrate solutions. From this point of view, nitrate media seem more similar to perchlorate than chloride media, a conclusion which is consistent with the phase diagrams.<sup>38</sup> The degrees of polymerization are, of course, (Fig. 3) not very

(39) C. F. Baes, Jr., and N. J. Meyer, Paper No. 105, Inorganic Div., 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961.

sensitive to these differences in hydrolysis in the various media, since only different trimers are involved.

A report is in preparation containing the acidity data, information on the least squares fitting program, and other details relative to this article. The report, ORNL-3278, will be available from the Office of Technical Services, Department of Commerce, Washington 25, D.C.

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## Chemistry of the Metal Carbonyls. XVI. Synthesis of Dicarboxyldinitrosyliron(0)<sup>1,2</sup>

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Nitrosyl chloride and iron pentacarbonyl react to give dicarboxyldinitrosyliron(0) in good yields. Some new phosphine and arsine complexes derived from dicarboxyldinitrosyliron(0) are reported, and their infrared spectra are discussed and compared with those of related complexes.

As part of a study of reactions between metal carbonyls and compounds having *pseudo*-halogen properties, we investigated the action of nitrosyl chloride on iron pentacarbonyl. We found that this reaction gives dicarboxyldinitrosyliron(0) in good yield. Since both iron pentacarbonyl and nitrosyl chloride are obtainable readily this represents a much easier route to the compound  $\text{Fe}(\text{CO})_2(\text{NO})_2$  than the previously known syntheses from triiron dodecacarbonyl or iron enneacarbonyl and nitric oxide,<sup>3a</sup> or *via* the carbonyl hydride and sodium nitrite.<sup>3b</sup> With relatively large quantities of dicarboxyldinitrosyliron(0) available, we were led to investigate some of its reactions with ligands having a Group V element as the donor atom, and with unsaturated organic compounds.

A few complexes derived from dicarboxyldi-

nitrosyliron(0) and Group V ligands have been reported previously,<sup>4</sup> including the compounds  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Fe}(\text{NO})_2$ ,  $(\text{C}_6\text{H}_5)_3\text{AsFe}(\text{CO})(\text{NO})_2$ , and  $(\text{C}_6\text{H}_5)_3\text{SbFe}(\text{CO})(\text{NO})_2$ . We describe the related compounds  $(\text{C}_6\text{H}_5)_3\text{PFe}(\text{CO})(\text{NO})_2$  and  $[(\text{C}_6\text{H}_5)_3\text{As}]_2\text{Fe}(\text{NO})_2$ , substances not obtained by the previous investigators, as well as the chelate complex  $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2]\text{Fe}(\text{NO})_2$  (Table I).

Several attempts were made to replace the carbonyl groups in dicarboxyldinitrosyliron(0) with various unsaturated organic ligands in the hope of obtaining diene-iron dinitrosyl compounds, analogous to the many known diene-iron tricarbonyl complexes. Reactions with bicycloheptadiene, diphenylacetylene, cyclooctatetraene, and cycloheptatriene were investigated. All gave evidence of reaction, but in every case the solutions of product were found to be extremely unstable and air-sensitive, and no iron containing products were isolated.

(1) Previous article in this series, R. B. King, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3604 (1961).

(2) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

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