BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN　VOL. 42　411—416 (1969)

# Stability Constants of Some Uranyl Complexes. II

S. RAMAMOORTHY and M. SANTAPPA

*Department of Physical Chemistry, University of Madras, Madras-25, India*

(Received April 10, 1968)

Stability constants of complexes of uranyl ion with various carboxylic acids were determined by the pH titration method at 31°C and $\mu=0.1$ ($NaClO_4$) in the pH range 2.5—3.5. The 1 : 1 and 1 : 2 complexes were formed with crotonic, pyruvic, malonic, and diglycolic acids and only the 1 : 1 complex with formic, propionic, succinic, adipic, maleic, fumaric acids. The effect of ring size and presence of oxygen atom as keto or ether oxygen or that of double bonds in the ligand acids on the stabilities of the corresponding complexes are discussed.

Recently Rajan and Martell[1] in a potentiometric study of chelates of uranyl perchlorate with carboxylic acids reported the stability constants of uranyl ion-maleate complexes (1 : 1 and 1 : 2), uranyl ion-succinate complex (1 : 1) and uranyl ion-maleate complex (1 : 1) in the pH range 2—4 at 25°C and $\mu=1$ M($KNO_3$). As a part of our studies on the complexes of uranyl ion with various organic acids, systems of uranyl ion with formic, propionic, crotonic, pyruvic, malonic, succinic, adipic, maleic, fumaric and diglycolic acids were studied by the pH titration method at 31°C ±0.1°C and $\mu=0.1$ ($NaClO_4$) with a view to determine the

---

[1] K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.*, **29**, 523 (1967).

TABLE 1. VALUES OF $v'$, $v''$ AND $v'''$ FROM THE pH TITRATION DATA AND EVALUATION OF $\bar{n}_H$, $\bar{n}$ AND p$L$ FOR THE URANYL ION-FORMIC ACID SYSTEM

$v'$, $v''$ and $v'''$ are volumes of sodium hydroxide (0.9416 M) added for the titration of (i) 0.022 M $HClO_4$ (100 m*l*), (ii) 0.022 M $HClO_4$ + 0.025 M formic acid (100 m*l*), and (iii) 0.022 M $HClO_4$ + 0.025 M formic acid + 0.00497 M uranyl ion (100 m*l*) respectively for the same pH values, as obtained from an enlarged graph.

$\mu=0.1$ ($NaClO_4$)
$T=31 \pm 0.1$°C

| pH | $v'$ | $v''$ | $v'''$ | $\bar{n}_H$ | $\bar{n}$ | p$L$ |
|---|---|---|---|---|---|---|
| 2.4 | 2.063 | 2.213 | 2.413 | 0.944 | 0.411 | 2.860 |
| 2.5 | 2.200 | 2.365 | 2.563 | 0.939 | 0.414 | 2.792 |
| 2.6 | 2.300 | 2.500 | 2.700 | 0.925 | 0.424 | 2.701 |
| 2.8 | 2.425 | 2.725 | 2.963 | 0.887 | 0.522 | 2.532 |
| 2.9 | 2.475 | 2.838 | 3.100 | 0.864 | 0.594 | 2.453 |
| 3.1 | 2.525 | 3.100 | 3.375 | 0.783 | 0.687 | 2.310 |
| 3.2 | 2.550 | 3.225 | 3.500 | 0.746 | 0.723 | 2.230 |
| 3.4 | 2.575 | 3.550 | 3.800 | 0.633 | 0.777 | 2.100 |
| 3.6 | 2.600 | 3.900 | 4.125 | 0.510 | 0.869 | 1.996 |
| 3.7 | 2.600 | 4.075 | 4.333 | 0.444 | 1.056 | 2.274 |

p$K$ of formic acid from the plot of $\bar{n}_H$ *versus*$-\log[H^+]=3.539$
$\log K_{ML_1}$ from the plot of $\bar{n}$ *versus* p$L$ (Fig. 1)$=2.61$

compositions and stability constants of the complexes in the pH range 1.5—3.5 in which hydrolysis of uranyl ion may completely be neglected2) and the effect of ring size on stabilities of the complexes and coordinating tendencies of ligands containing oxygen atoms as keto or ether oxygen. The effects of various oxygen donor compounds on the stabilities of the metal chelates are compared with the chelating behaviour of compounds containing no additional coordinating group other than carboxylate group.

## Experimental

**Materials.** Preparation of uranyl perchlorate as well as other reagents and their estimations have been given earlier.3) Formic (M and B; AnalaR), propionic (B.D.H.; AnalaR), crotonic (Chem. pure; AnalaR), pyruvic (Ingelheim, Germany; pure), malonic (Fluka; purum), succinic (Riedel; pure), adipic (Fluka; purum), maleic (Riedel; pure), fumaric (Fluka; purum) and diglycolic (Fluka; purum) acids were used as such for ligands. These acids were standardized with sodium hydroxide solution (0.1 M).

**Procedure.** The details of apparatus and of experimental technique used to obtain the Bjerrum-Calvin titration curves and methods of calculation of dissociation constants of ligand acids, and stability constants of complexes by Irving and Rossotti's difference method4) were outlined in our earlier paper.3) Acid dissociation constants, p$K$, of monobasic acids were evaluated from the value of $-\log[H^+]$ at $\bar{n}_H=0.5$, utilising a value of 0.83 for the activity coefficient5) of 0.1 N $[H^+]$ (Table 1 and Fig. 1A) and $K_1$ and $K_2$ of dibasic acids were determined more conveniently by the method of slope and intercept due to Irving and Rossotti6) (Table 2 and Fig. 2). Stability constants of the complexes, $\log K_{ML_1}$ and $\log K_{ML_2}$ evaluated from the values of p$L$ ($-\log$ [Ligand]) at $\bar{n}$ (formation function)$=0.5$ and 1.5 respectively from the formation curves of the systems (Table 1 and Fig. 1B) were only approximate when they did not differ greatly in magnitude (<2.5 log units)6); exact values were determined by Eq. (1) according to Irving and Rossotti6) (Table 3).

$$\frac{\bar{n}}{(\bar{n}-1)[L]}=K_{ML_1}+K_{ML_1}\cdot K_{ML_2}\cdot\frac{(2-\bar{n})[L]}{(1-\bar{n})}+\sum_{n=3}^{N}K_{ML_1},K_{ML_2}\ldots\ldots K_{ML_n}\cdot\frac{(n-\bar{n})[L]^{n-1}}{(1-\bar{n})} \qquad (1)$$

where $K_{ML_1}$, $K_{ML_2}$,..., $K_{ML_n}$ are successive stability constants, $[L]$=free ligand anion concentration, $\bar{n}$= formation function of the system. The formation of only 1 : 1 complex was obvious from the plots of $\bar{n}/(1-\bar{n})[L])$ *versus* $((2-\bar{n}))[L]/(1-\bar{n})$ which was parallel to abscissa (Fig. 2) and in the plots of p$L$ *versus* $\bar{n}$ (Fig. 1B) magnitude of the latter was less than unity, even when $[T_L]/[T_M]$ was 1 to 10, $T_L$ and $T_M$ being total

---

2) J. Sutton, *J. Chem. Soc.*, (Suppl) 2, S-275 (1949); St. Ahrland, S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **8**, 1907 (1954); S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **13**, 1828 (1959); M. Bartusek and L. Sommer, *Z. Phys. Chem.*, **226**, 309 (1964).

3) S. Ramamoorthy and M. Santappa, This Bulletin, **41**, 1330 (1968).

4) H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, **1954**, 2904.

5) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

6) H. Irving and H. S. Rossotti, *J. Chem. Soc.*, **1953**, 3397; F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

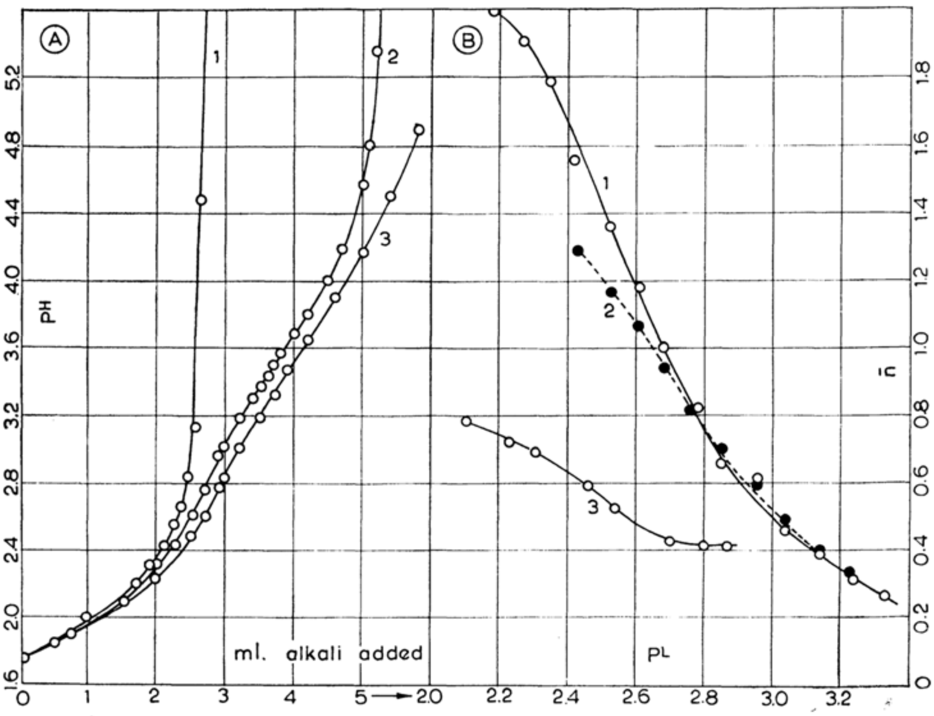

Fig. 1.

(A) uranyl ion-formic acid system.
Plot of pH *versus* ml of alkali added.
(i) $HClO_4$ (0.022 M) + $NaClO_4$ (0.1 M)
(ii) $HClO_4$ (0.022 M) + $NaClO_4$ (0.1 M) + formic acid (0.025 M)
(iii) $HClO_4$ (0.022 M) + $NaClO_4$ (0.1 M) + formic acid (0.025 M) + uranyl ion (0.005 M)

(B) (1) Plot of $\bar{n}_{exp.}$ *versus* p$L$ for the uranyl ion-crotonic acid system.
(2) Plot of $\bar{n}_{calcd.}$ *versus* p$L$ for the uranyl ion-crotonic acid system.
(3) Plot of $\bar{n}$ *versus* p$L$ for theuranyl ion-formic acid system.

TABLE 2. ACID DISSOCIATION CONSTANTS OF THE LIGANDS AND THE STABILITY CONSTANTS OF URANYL COMPLEXES

$\mu=0.1(NaClO_4)$
$T=31\pm0.1$°C

| | Ligand | Authors' value | | | | Literature | |
|---|---|---|---|---|---|---|---|
| | | p$K_1$ | p$K_2$ | log $K_{ML_1}$ | log $K_{ML_2}$ | log $K_{ML_1}$ | log $K_{ML_2}$ |
| 1 | Formic acid | 3.54 | | 2.61 | | | |
| 2 | Benzoic acid | 4.01 | | 2.57 | | | |
| 3 | Phenylacetic acid | 4.12 | | 3.21 | | | |
| 4 | Propionic acid | 4.62 | | 3.03 | | | |
| 5 | Phenoxyacetic acid | 2.96 | | 2.59 | | | |
| 6 | Pyruvic acid | 2.39 | | 2.15 | 0.59 | | |
| 7 | Malonic acid | 2.81 | 5.14 | 5.28 | 4.01 | 5.66 | 4.00[1] |
| 8 | Succinic acid | 3.87 | 5.12 | 4.48 | | 3.68[1] | |
| 9 | Adipic acid | 4.12 | 5.04 | 4.08 | | | |
| 10 | Itacoic acid | 3.61 | 4.98 | 4.86 | | | |
| 11 | Thiomalic acid | 2.95 | 4.45 | 3.71 | | | |
| 12 | Maleic acid | 1.95 | 6.16 | 5.15 | | 4.46[1] | |
| 13 | Fumaric acid | 2.89 | 4.11 | 3.05 | | | |
| 14 | Diglycolic acid | 2.77 | 3.88 | 4.90 | 2.84 | | |
| 15 | Crotonic acid | 4.53 | | 2.74 | 2.53 | | |

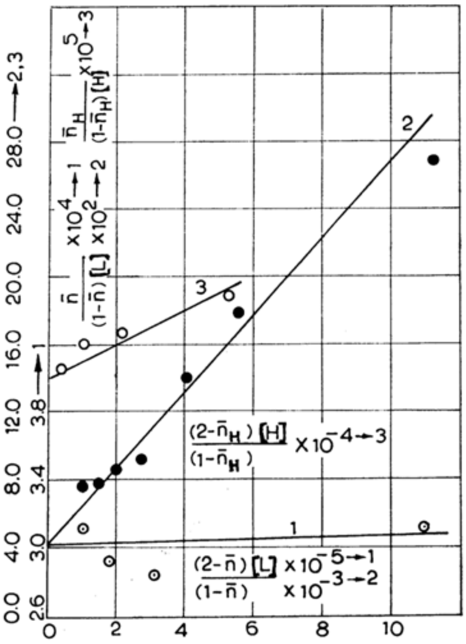

Fig. 2.

(1) Plot of $\frac{\bar{n}}{(1-\bar{n})[\mathrm{L}]}$ *versus* $\frac{(2-\bar{n})[\mathrm{L}]}{(1-\bar{n})}$ for the uranyl ion-succinic acid systems.

(2) Plot of $\frac{\bar{n}}{(1-\bar{n})[\mathrm{L}]}$ *versus* $\frac{(2-\bar{n})[\mathrm{L}]}{(1-\bar{n})}$ for the uranyl ion-crotonic acid system.

(3) Plot of $\frac{\bar{n}_{\mathrm{H}}}{(1-\bar{n}_{\mathrm{H}})[\mathrm{H}]}$ *versus* $\frac{(2-\bar{n}_{\mathrm{H}})[\mathrm{H}]}{(1-\bar{n}_{\mathrm{H}})}$ for the uranylion-malonic acid system.

TABLE 3. EVALUATION OF STABILITY CONSTANTS ($K_{\mathrm{ML}_1}$, $K_{\mathrm{ML}_2}$) FOR THE URANYL ION-CROTONIC ACID SYSTEM

$\mu=0.1$ ($NaClO_4$) $T=31\pm0.1$°C

| $\frac{\bar{n}}{(1-\bar{n})[\mathrm{L}]} \times 10^{-2}$ | $\frac{(2-\bar{n})[\mathrm{L}]}{(1-\bar{n})} \times 10^{3}$ | $\frac{\bar{n}}{(1-\bar{n})[\mathrm{L}]} \times 10^{-2}$ | $\frac{(2-\bar{n})[\mathrm{L}]}{(1-\bar{n})} \times 10^{3}$ |
|---|---|---|---|
| 7.603 | 1.111 | −25.880 | −11.890 |
| 7.447 | 1.434 | −12.350 | − 5.352 |
| 8.407 | 1.914 | − 7.372 | −22.914 |
| 9.105 | 2.597 | − 5.037 | − 1.225 |
| 14.090 | 4.027 | − 3.866 | − 0.563 |
| 17.840 | 5.489 | − 3.059 | − 0.250 |
| 26.350 | 11.230 | − 2.517 | − 0.109 |

Intercept $=5.5\times10^{2}$; $\log K_{\mathrm{ML}_1}=2.74$
Slope $=1.9\times10^{5}$; $\log K_{\mathrm{ML}_2}=2.53$

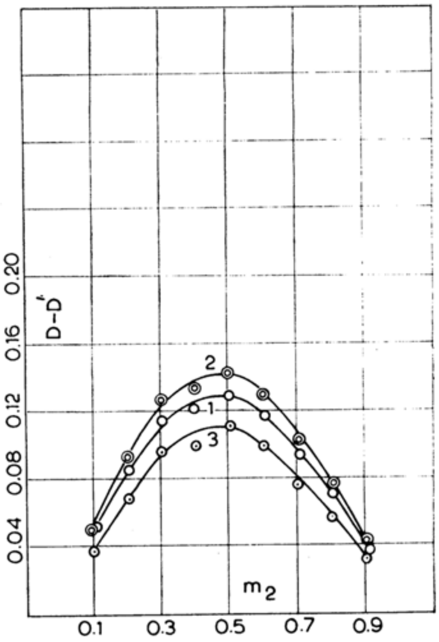

Fig. 3.

Plot of $D-D'$ (observed optical density-optical density calculated for no complexation) *versus* $m_2$, mole fraction of the uranyl ion.
Total Concentration = [uranyl ion + diglycolic acid] = 0.04 M.
$\mu=0.1$ $T=31\pm0.1$°C
$\lambda=430$ m$\mu$ (curve 1),
440 m$\mu$ (curve 2), and 460 m$\mu$ (curve 3).

concentrations of the ligand and the uranyl ion respectively. In such cases, the log $K_{\mathrm{ML}_1}$, calculated graphically from the $\bar{n}$ *versus* p$L$ curves agreed very well with those calculated from Eq. (1). The formation of higher complexes was indicated by the value of $\bar{n}$ going beyond unity in some of the systems studied (uranyl ion-malonic, uranyl ion-pyruvic, uranyl ion-crotonic and uranyl ion-diglycolic acids) (Fig. 1B). In such cases, $K_{\mathrm{ML}_1}$ and $K_{\mathrm{ML}_2}$ were evaluated from Eq. (1) by the least squares treatment (Table 3). It may be mentioned that since the pH measurements and consequently log $K_{\mathrm{ML}}$ values are accurate to ±0.02 units, the log $K_{\mathrm{ML}_1}$ and log $K_{\mathrm{ML}_2}$ values from half integral values of p$L$ will also be accurate7) to −log 0.02 units even if log $(K_1/K_2)$ is $<2.5$. The $K_{\mathrm{ML}}$ values reported (Table 2) are concentration (stoichiometric) stability constants as concentrations were used in place of activities. The data at values of pH$>$3.5 were not used in the calculation of stability constants. Formation curves which were constructed from the values of p$L$ and $\bar{n}_{\mathrm{calculated}}$ using values of log $K_{\mathrm{ML}_1}$ and log $K_{\mathrm{ML}_2}$ obtained from Irving and Rossotti's equation (1) showed very slight deviations from the formation curves of p$L$ *versus* $\bar{n}_{\mathrm{exp.}}$ within the limits of experimental errors. For values of pH$>$3.5, $\bar{n}_{\mathrm{exp.}}$ deviated greatly from $\bar{n}_{\mathrm{calc.}}$ probably due to considerable hydrolysis of uranyl ion (Fig. 1B).

## Results

The titration curves for (i) perchloric acid-

---

7) K. E. Jabalpurwala, K. A. Venkatachalam and M. B. Kabadi, *J. Inorg. Nucl. Chem.*, **26**, 1011, 1027 (1964).

sodium perchlorate, (ii) perchloric acid-ligand acid-sodium perchlorate and (iii) uranyl perchlorate - ligand acid - perchloric acid - sodium perchlorate systems against sodium hydroxide are presented for the uranyl ion - formic acid system in Fig. 1A. The $\bar{n}_H$, $\bar{n}$ and pL values are given in Table 1.

## Discussion

Most of the data reported in the present paper were obtained for the first time, though reported data on the stability constants in the case of malonic, succinic and maleic acids were obtained under somewhat different experimental conditions of ionic strength (1 M $KNO_3$) and temperature (25°C). Results for systems of uranyl ion with itaconic, thiomalic, benzoic, phenylacetic and phenoxyacetic acids are taken from the previous paper[3] for comparison and discussion.

**(a) Uranyl Ion-Simple Monocarboxylic Acids (Formic, Propionic, Benzoic and Phenylacetic Acids).** Dissociation constants of ligand acids are listed in Table 2. The p$K$ of the ligand acid increases in the order formic$<$benzoic$<$phenylacetic$<$propionic acids and $K_{ML_1}$ increases in the order, formic$=$benzoic$<$phenylacetic$>$propionic acids (Table 2). It may be mentioned that $\bar{n}$ did not exceed unity even when $[T_L]/[T_M]$ was 1 to 10 in all the four systems. The formation of only 1 : 1 complex was also obvious from the plots of $\bar{n}/((1-\bar{n})\ [L])$ *versus* $((2-\bar{n})([L])/(1-\bar{n})$ which was parallel to the abscissae (Fig. 2). The stability constants calculated from $\bar{n}$ *versus* p$L$ curve agreed very well with those calculated from Eq.(1). The substitution of H atom in formic acid by a phenyl group caused no change in the stability of the corresponding uranyl complex, while substitution by a benzyl group as well as an ethyl group increases the stability of the respective complexes. This kind of increase was not observed in the case of copper(II) complexes (formic, acetic and propionic acids)[8] and there the alkyl substitution caused no detectable effect on the values of stability constants of the complexes.

**b) Uranyl Ion-Monocarboxylic Acid Containing-O-and-CO-linkages (Phenoxyacetic and Pyruvic Acids).** From acid dissociation constants (Table 2), it is obvious that p$K$'s of phenoxyacetic and pyruvic acids are very much lower than the corresponding acids, phenylacetic acid and acetic acid[9] (p$K$=4.64 at $\mu$=0.2 (KCl) and $T$=20°C) (without –O– and –CO– groups). The stability constants were obtained from the plots of $\bar{n}$ *versus* p$L$ as well as from $\bar{n}/(1=\bar{n})\ [L])$ versus $((2-\bar{n})\ [L])/(1-\bar{n})$ since the difference between log $K_{ML_1}$ and log $K_{ML_2}$ determined from half integral values was less than 2.5 log units. However the half integral values would be in error by $-0.02$ log units, when the difference in $\log(K_1/K_2)$ is 1.78. The system of uranyl ion-phenoxyacetic acid differed very much from the uranyl ion-pyruvic acid system in number of complexes formed as well as the stability range of the latter; for the former, the value of $\bar{n}$ did not exceed unity even with excess of ligand, [ligand]/[uranyl ion]$=$1 to 10, indicating the absence of formation of higher complexes, while for the latter, the value of $\bar{n}$ was as high as 0.7 at pH 1.80 and reached 2.0 at pH 3.00. The log $K_{ML_1}$ value of the uranyl ion pyruvic acid system in consistent with the fact that p$K$ of pyruvic acid is lower than that of phenoxyacetic acid. From the orders of stability constants (log $K_{ML_1}$) of the systems uranyl ion-pyruvic acid, uranyl ion-phenoxyacetic acid, uranyl ion-benzoic, uranyl ion-formic acid complexes etc., it is obvious that neither the phenoxy oxygen in phenoxy-acetic acid nor keto oxygen in pyruvic acid was involved in complexation. However, from the observation that precipitation in the system uranyl ion-pyruvic acid did not occur till pH 10.5, coupled with the fact that complexation was considerable even at low p$H$, it might be inferred that the keto oxygen stabilized the complex probably through coordination to the uranyl ion. The ether oxygen atom of phenoxyacetic acid has very little tendency for coordination with uranyl ion compared with carbonyl oxygen atom of keto group of pyruvic acid.

**c) Uranyl Ion-Simple Dicarboxylic Acids (Malonic, Succinic and Adipic Acids).** It may be seen that the difference between p$K_1$ and p$K_2$ of the ligand acids (Table 2) decreases as the number of carbon atoms separating the two COOH groups increases *i. e.* malonic→succinic→adipic acids. In other words, the basicity of the first COOH group increases in the same order. It is evident from the log $K_{ML_1}$ values (Table 2) that, of the three ligands malonic acid forms the most stable chelate with uranyl ion with a six membered ring and the stability of the chelate ring decreases with the increase in ring size *i. e.*, from six→seven→nine memered ring, from malonic→succinic→adipic acids. Though the basicity of the first carboxyl group increases from malonic acid to adipic acid as evident from the p$K_1$ values, the increasing ring size from malonic acid to adipic acid decreases the stabilities of the chelates in the same order (*i. e.* malonic acid→adipic acid). The formation of the 1 : 2 complex was favoured only in the uranyl ion-malonic acid system (six membered rings), but not in the uranyl ion-succinic acid or uranyl ion-adipic acid system. The difference between the authors' values and those of Rajan

---

[8] S. Ramamoorthy and M. Santappa, *J. Inorg. Nucl. Chem.*, **30**, 2393 (1968).

[9] R. K. Cannan and A. Kibrick, *J. Am. Chem. Soc.*, **60**, 2314 (1938).

and Martell (Table 2) may be due to the somewhat different experimental conditions; the latter were measured in 1 M $KNO_3$ and at 25°C, while authors' values were at 0.1 M $NaClO_4$ and at 31°C. The stability decrease in the series, uranyl ion-malonic acid→uranyl ion-succinic acid→uranyl ion-adipic acid, is consistent with the earlier observations with other metal ions.[10]

**d) Uranyl Ion-Substituted Dicarboxylic Acids (Thiomalic and Itaconic Acids).** From the results with succinic acid, it was obvious that the formation of the 1 : 2 complex was not indicated with thiomalic (mercapto succinic) and itaconic (methylene succinic) acids. Moreover, from comparison of stability order of thiomalic acid and malic acid complexes, and then itaconic acid and succinic acid complexes, it is believed that the chelate ring is stabilized by the presence of a double bond or by an SH group, and more so by the former.

**e) Uranyl Ion-*cis* and *trans* Dicarboxylic Acids (Maleic and Fumaric Acids).** The $pK_1$ and $pK_2$ values for maleic and fumaric acids (Table 2) calculated by the least squares treatment of Irving and Rossotti's equation indicate the obvious fact that the two COOH groups are well separated in maleic acid, while they are overlapping in fumaric acid. Both the ligands form only 1 : 1 complexes with uranyl ion. From the results (Table 2) of stability of the uranyl ion-maleic acid and uranyl ion-fumaric acid complexes, it was evident that maleic acid formed a seven membered chelate ring with uranyl ion through the two carboxyl groups, while fumaric acid being a trans isomer of maleic acid with two COOH groups separated farther away, formed only a complex (not a chelate) with uranyl ion through one COOH group only. The stability range of the uranyl ion-fumaric acid complex ($\log K_{ML_1}=$ 3.05) (*cf.* $\log K_{ML_1}$ of the uranyl ion-formic acid complex, 2.61) also supported this argument. If there were no chelate ring in the uranyl ion-maleic acid complex, the stability of the uranyl ion-maleate complex would have been lower than the uranyl ion-fumarate complex from considerations of different $pK_1$ values of these two ligand acids. On the other hand, the stability of the uranyl ion-maleate system is comparable to any seven-membered chelate ring structure such as the uranyl ion-succinic acid system.

**f) Uranyl Ion-Diglycolic Acid System (Dicarboxylic Acid Containing–O–Linkage).** The $pK_1$ and $pK_2$ values obtained from the slope and intercept method are given in Table 2. Successive formation of the 1 : 1 and 1 : 2 complexes of the uranyl ion-diglycolic acid system was evident from the fact that $\bar{n}$ value reached 1.5 at pH 3.50. It is very interesting that $\log K_{ML_1}$ (4.90) is very high for the chelate structure with the eight-membered ring involving two $COO^-$ groups for coordination to metal (*cf.* $\log K_{ML_1}$ of the uranyl ion-adipic acid system$=4.08$ or the uranyl ion-glutaric acid system) and it is comparable to the stabilities of the chelates with five or six-membered rings (*cf.* $\log K_{ML_1}$ of the uranyl ion-malonic acid system$=5.28$). The most probable structure for the uranyl ion-diglycolic acid chelate, therefore, might involve two $COO^-$ groups with additional stabilisation through the –O– group. In fact, Suzuki and Yamasaki[11] showed that diglycolic acid chelates were much more stable than the glutaric acid chelates (absence of –O– groups). The Job's method of continuous variations (Fig. 3) for the uranyl ion-diglycolic acid system gave a peak at $m_2$ (mole fraction of uranyl ion)$=0.5$, indicating the 1 : 1 complex. The formation of a higher complex (1 : 2) was shown by a slight shoulder at $m_2=0.33$. This observation indicated the absence of free carboxylate ion in the uranyl ion-diglycolic acid chelate. It is to be noted that in the copper(II)-malic acid system a 2 : 1 complex was formed as the second carboxylate group was free.[12] **g) Uranyl Ion-Unsaturated Carboxylic Acids; Crotonic Acid.** The values of $pK$ and $\log K_{ML_1}$ and $K_{ML_2}$ are listed in Tables 2 and 3. The higher stability of the uranyl ion-crotonic acid complex is due to the hig her basicity of the ligand (*cf.* $\log K_{ML_1}=2.61$ for the uranyl ion-formic acid complex) due to the inductive effect of the methyl group as well as the presence of the double bond in the structure.

From the results, it may be concluded that basicities of the monodentate ligands have very little influence on the stabilities of the corresponding uranyl ion complexes. Steric factors and ring size presumably determine the metal chelate stabilities with bidentate ligands. In general, the uranyl-carboxylate chelates are more stable than the corresponding copper chelates conforming to the extended Irving-Williams order in which uranyl ion occupies a higher place over copper(II).[13]

---

10) H. Irving, R. J. P. Williams, D. J. Ferret and A. E. Williams, *J. Chem. Soc.*, **1954**, 3494.

11) K. Suzuki and K. Yamasaki, *J. Inorg. Nucl. Chem.*, **28**, 473 (1966); K. Yasuda, K. Yamasaki and H. Ohcaki, This Bulletin, **33**, 1077 (1970).

12) S. Ramamoorthy and M. Santappa, *J. Inorg. Nucl. Chem.*, **30**, 1855 (1968).

13) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Willey & Sons, Inc., New York (1958), p. 16.