TABLE I

| Reactive methylene compound | Alkylating agent | | Catalyst | % Yield of product[a] |
|---|---|---|---|---|
| Cyanoacetic ester | Ethyl chloroacetate | 1. | 1 mole of $AlCl_3$ | 50% |
| | | 2. | 2 moles of $AlCl_3$ | Quantitative |
| | | 3. | 1 mole of $NaOC_2H_5$ | 50% mono-condensation product + 10% dicondensation product |
| | | 4. | 2 moles of $NaOC_2H_5$ | 35% dicondensation product + 10% mono-condensation product |
| α-Cyanosuccinic ester | Ethyl chloroacetate | 5. | 1–7 moles of $AlCl_3$ | Nil |
| | | 6. | 1 mole of $NaOC_2H_5$ | 30% dicondensation product |

[a] The yield depends on the freshness of the $AlCl_3$.

**lyst** (1 *M*).—To 13 g. (0.1 mole) of coarsely powdered anhydrous aluminum chloride was added dropwise a solution of 11.3 g. (0.1 mole) of cyanoacetic ester and 12 g. (0.1 mole) of ethyl α-chloroacetate in 25 ml. of dry chloroform with constant shaking of the externally cooled reaction mixture. The addition of the solution was attended with evolution of hydrogen chloride followed by dissolution of the catalyst. The brown reaction mixture was left at room temperature till gas evolution had ceased. After careful decomposition of excess aluminum chloride with ice the reaction mixture was worked up in the usual manner. The residual liquid after removal of the solution was fractionated under vacuum.

The yield of colorless liquid product, b.p. 105° (10 mm.), was 11.5 g. (50%). *Anal.* Calcd. for $C_9H_{13}NO_4$: C, 54.27; H, 6.5; N, 7.03. Found: C, 53.97; H, 6.63; N, 7.32.

A portion (2 g.) of the distillate on hydrolysis with 20% hydrochloric acid and subsequent crystallization proved to be succinic acid (0.8 g.), m.p. 185°, singly and on admixture.

The catalyst even if increased to 2 moles or more always gave the above monocondensation product alone in quantitative yield but never any dicondensation product.

**Sodium Ethoxide Catalyst.**—To sodium ethoxide (prepared from 1 g. (less than 0.05 mole) of sodium metal and 12 ml. of absolute alcohol) was added 5.65 g. (0.05 mole) of cyanoacetic ester with constant shaking and external cooling. The sodio salt formed was left at room temperature for an hour or so after which 6 g. (0.05 mole) of ethyl chloroacetate in 5 ml. of absolute alcohol was dropped in with external cooling and constant shaking of the reaction mixture. Eight to ten hours reflux on a water-bath and subsequent working up in the usual manner gave 4.9 g. (50%) of the monocondensation product and 1.4 g. (10%) of a glycerol-like dicondensation liquid product, b.p. 145° (10 mm.). Calcd. for $C_{13}H_{19}NO_6$: C, 54.73; H, 6.66; N, 4.91. Found: C, 54.52; H, 6.77; N, 4.83.

Acid hydrolysis of the dicondensation product (3 g.) gave tricarballylic acid (1.5 g.), m.p. 165°; on admixture with an authentic sample the m.p. was 164–165°.

As already pointed out the acid catalyst yielded no dicondensation product under any of the above experimental conditions. It could be prepared only when a base catalyst was employed as described below.

**In One Step.**—2.3 g. (0.1 mole) of sodium metal was dissolved in 30 ml. of absolute alcohol. To the cold sodium ethoxide was added 5.7 g. (0.05 mole) of cyanoacetic ester. The resulting mixture was intermittently warmed on a water-bath for about an hour. A solution of 12 g. (0.1 mole) of ethyl α-chloroacetate in 10 ml. of absolute alcohol was added dropwise to the cold sodio salt. After leaving overnight the mixture was refluxed on a steam-bath for 10 hours. The reaction mixture was cooled and worked up in the usual way to get 1 g. (10%) of monocondensation product, b.p. 105° (10 mm.), and 4.9 g. (35%) of dicondensation product, b.p. 145° (10 mm.).

**Monocondensation to Dicondensation Product.**—Three grams (0.025 mole) of ethyl α-chloroacetate was added to the sodio salt of ethyl α-cyanosuccinate prepared from 4.98 g. (0.025 mole) of the ester and 0.681 g. (0.025 mole) of sodium metal. The reaction mixture was colored violet. The usual processing gave (30%) of the ethyl α-cyanotricarballylate, b.p. 145° (10 mm.).

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## Mechanism of Aquotization of Carbonato Complex Ions

BY FRANZ A. POSEY AND HENRY TAUBE

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Stranks and Harris[1] have reported that there is no carbon isotope discrimination in the reaction

$$Co(NH_3)_4CO_3^+ + H_2O + 2H^+ = Co(NH_3)_4(H_2O)_2^{+++} + CO_2 \quad (1)$$

In an oxygen tracer study on a related reaction

$$Co(NH_3)_5CO_3^+ + 2H^+ = Co(NH_3)_5H_2O^{+++} + CO_2 \quad (2)$$

Hunt, Rutenberg and Taube[2] showed that in release of carbonate, the Co–O bond is not severed, but rather the C–O bond. Since reaction (2) is analogous to what can reasonably be supposed to be a stage in the net reaction (1)

$$Co(NH_3)_4(H_2O)CO_3^+ + 2H^+ = Co(NH_3)_4(H_2O)_2^{+++} + CO_2 \quad (3)$$

there is an apparent inconsistency in the two observations which, while it can be resolved by one of several assumptions, forces none as a conclusion. We have therefore undertaken an oxygen tracer study of reaction (1), for comparison with the results obtained in reaction (2), similar to that conducted for this reaction, but have increased the power of the tracer results by examining also the isotopic composition of the carbon dioxide liberated both in reactions (1) and (2). The method for isotopic assay of the water bound in $Co(NH_3)_4(H_2O)_2^{+++}$ was developed during the course of other research on the ion, and will be described more fully when these results are published.

### Experimental

The salt $(Co(NH_3)_4CO_3)NO_3 \cdot {}^1/_2H_2O$ was prepared according to the method of Grubitsch.[3] The purity was checked by electrolytic determination of the cobalt content (calculated, 22.84%; observed, 22.86%). The salt $(Co(NH_3)_5CO_3)NO_3 \cdot H_2O$ was part of a preparation used previously.[2]

The tracer experiments with $(Co(NH_3)_4CO_3)NO_3 \cdot {}^1/_2H_2O$ were performed by preparing a solution of this compound in water enriched in $H_2O.^{18}$ Perchloric acid in water of isotopic composition very near to that in the solution was

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(1) D. R. Stranks and G. W. Harris, *J. Phys. Chem.*, **56**, 906 (1952).

(2) J. P. Hunt, A. C. Rutenberg and H. Taube, THIS JOURNAL, **74**, 268 (1952).

(3) H. Grubitsch, "Anorganisch-präparative Chemie." Springer Verlag, Vienna, 1950, p. 441.

then added. During this operation, a rapid stream of nitrogen passed through the solution to carry off the carbon dioxide released. This was stripped from the gas by means of a trap immersed in liquid nitrogen. The ion $Co(NH_3)_4(H_2O)_2^{+++}$ was precipitated from the solution with $Co(CN)_6^{\equiv}$, and the salt $(Co(NH_3)_4(H_2O)_2)(CO(CN)_6)$ was removed, washed, dried, and finally heated *in vacuo* to remove the complex-bound water. The isotopic composition of the water was determined by equilibrating it with carbon dioxide, and analyzing the carbon dioxide in a mass spectrometer. The necessary blank determinations were conducted as indicated by the procedures described. Separate experiments were also conducted in which the solid carbonato salts were dusted into perchloric acid in enriched water, and the carbon dioxide swept out with nitrogen as before.

All operations were performed as rapidly as possible to minimize exchange of $Co(NH_3)_4CO_3^+$ and $Co(NH_3)_4(H_2O)_2^{+++}$ with the environment. The solutions before addition of the acid were cooled to 0°, and maintained there for precipitation of $Co(NH_3)_4(H_2O)_2(Co(CN)_6)$. In a typical experiment, 1.5 g. of salt was used in 30 ml. of solution.

## Results

$N$ represents the mole fraction of $O^{18}$ in the species under consideration. All results were normalized to $2.000 \times 10^{-3}$ as the mole fraction of $O^{18}$ in a sample of ordinary $CO_2$ kept as a standard.

The method of isotopic assay of $Co(NH_3)_4(H_2O)_2^{+++}$ was tested by precipitating the cobalticyanide from water enriched in $O^{18}$, after leaving the aquo ion in contact under conditions and for a time comparable to those obtaining in the experiments with the carbonato ion. The results were: $N \times 10^3$ for inner sphere water of $Co(NH_3)_4(H_2O)_2^{+++}$ precipitated from normal water = 2.235; $N \times 10^3$ for normal water = 1.928; $N \times 10^3$ for inner sphere water when precipitated from enriched solvent = 2.348; $N \times 10^3$ for $H_2O$ in enriched solvent = 7.163. The results show 2.3% exchange of the aquo ion during the operation.

To learn the exchange to be expected for $CO_2$ liberated by acid under the conditions of our experiments, a solution of $Na_2CO_3$ (of normal isotopic composition) was added to enriched water containing acid, with the following results: $N \times 10^3$ for $CO_2$ from $Na_2CO_3$ in ordinary water = 1.996; $N \times 10^3$ for $CO_2$ from $Na_2CO_3$ in enriched water = 2.077; $N \times 10^3$ for enriched water = 5.985; exchange of $CO_2$ = 2.0%.

To provide the necessary base values for the interpretation of the tracer experiments, the aquotization of $Co(NH_3)_4CO_3^+$ was conducted in water of normal isotopic composition ($N \times 10^3 = 1.928$). $N \times 10^3$ for $CO_2$ from aquotization = 2.009; $N \times 10^3$ for inner sphere water = 1.985.

The results on the aquotization in enriched water are: $N \times 10^3$ for water in solution = 8.263; $N \times 10^3$ for inner sphere water = 5.147. Base value ($1.985 \times 10^{-3}$ corrected for exchange expected in this environment = $2.129 \times 10^{-3}$. Fraction of inner sphere water derived from environment = 0.493. The carbon dioxide collected in this experiment was found to have undergone 5.4% exchange with the environment, somewhat in excess of that observed using $Na_2CO_3$. A third experiment proved this exchange not to be reproducible ($\sim$ 8%), and the method of adding the solid was adopted.

With $(Co(NH_3)_4CO_3)NO_3 \cdot {}^1/_2H_2O$, the results were: $N \times 10^3$ for $H_2O$ in enriched solvent = 6.923; $N \times 10^3$ for $CO_2$ released = 2.069. The value 2.069 compared with 2.009 for the release of $CO_2$ in normal water shows 1.2% enrichment.

With $(Co(NH_3)_5CO_3)NO_3 \cdot H_2O$ the results were: $N \times 10^3$ for $CO_2$ released from normal water = 1.972; $N \times 10^3$ for $CO_2$ released from enriched water = 2.048; $N \times 10^3$ for $H_2O$ in enriched solution = 5.665. In this experiment, the carbon dioxide underwent 1.5% exchange with the solvent.

## Discussion

It is necessary for the success of an experiment of this type that the resulting aquo ion not exchange rapidly with the solvent. The blank experiments with $Co(NH_3)_4(H_2O)_2^{+++}$, as well as proving the method of isotopic analysis of the bound water, prove the formula of this ion in water to be $Co(NH_3)_4(H_2O)_2^{+++}$, and demonstrate its exchange with the solvent to be sufficiently slow for the present purposes.

The experiments show that the ion $Co(NH_3)_4(H_2O)_2^{+++}$, formed from $Co(NH_3)_4CO_3^+$, derives only $^1/_2$ of the oxygen from the solvent, the other $^1/_2$ being left by the carbonate when $CO_2$ is removed. The possibility that the 50% exchange appears equally distributed between the two positions, as an accidental value on the way to complete exchange, can be excluded by considering the isotopic composition of the liberated $CO_2$. Such enrichment could only take place with some form of the carbonato ion ($Co(NH_3)_4(H_2O)_2^{+++}$ does not exchange sufficiently rapidly) and would necessarily result in enrichment of the $CO_2$ which is liberated. The slight enrichment of the $CO_2$ observed ($\sim$1%) is attributable to exchange following its release.

Stranks and Harris have suggested the mechanism

$$Co(NH_3)_4CO_3^+ + H^+ + H_2O = Co(NH_3)_4H_2O\ CO_3H^+ \text{ (rapid)} \quad (4)$$

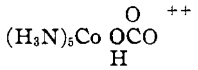
$$Co(NH_3)_4H_2O\ CO_3H^{++} \longrightarrow Co(NH_3)_4(H_2O)OH^{++} + CO_2 \quad (5)$$

The stepwise feature of the mechanism is certainly reasonable, and is to some extent confirmed by providing an explanation for our oxygen tracer results. Applying our observations to this mechanism, it can be concluded that the Co–O bond is severed in step (4), otherwise $CO_2$ would appear at least 33% exchanged with solvent. Reaction 5, involving $Co(NH_3)_4H_2O^*\ CO_3H^{++}$, then takes place as demonstrated for the analogous ion $Co(NH_3)_5CO_3H^{++}$, severing the C–O bond. The fractionation experiments of Stranks and Harris, obtained for the reaction in acid, find an explanation if reaction (4) under these conditions is formulated not as an equilibrium, but as a rate determining step; no large carbon fractionation can be expected in step (4) since the Co–O bond is severed there, and none can take place in (5), since the ion is completely decomposed to products.

It is interesting to note that the major conclusions are indicated also by the experiments on aquotization in ordinary water, the isotopic composition of the inner sphere water ($1.985 \times 10^{-3}$) lying fairly near the mean of that of the solvent ($1.928 \times 10^{-3}$) and of the carbon dioxide ($2.009 \times 10^{-3}$). The dependability of such a conclusion drawn from this experiment, however, is reduced not only because of the slight difference between the extreme values, but also because fractionation effects interfere. These can take place due to discrimination by Co(III) between $O^{16}$ and $O^{18}$ in water, and in the attached carbonate. The results show that a slight excess of $O^{18}$ is left on the Co(III).

If it is assumed that precisely 50% of the $H_2O$ in the inner sphere is derived from the solvent, the isotopic composition expected for this water in the experiment using enriched solvent is the mean of $8.263 \times 10^{-3}$ and $2.009 \times 10^{-3}$ or $5.136 \times 10^{-3}$. When this is corrected for the exchange to be expected for the aquo ion, the value $5.208 \times 10^{-3}$ is obtained, to be compared with the experimental value of $5.147 \times 10^{-3}$. The result may indicate a slightly greater rate of reaction of $H_2O^{16}$ compared to $H_2O^{18}$.

A conclusion about mechanism which applies to the results for $CO_3^=$ attached as a chelate, bound at one position, or not bound at all, is that there is no transfer of oxygen from the solvent to C at any stage on the release of $CO_2$. Thus it seems likely that the activated complex which in the case of $Co(NH_3)_5CO_3^+$ has the composition $Co(NH_3)_5CO_3H^{++}$, does not have the structure reasonable for this complex ion, but rather has the proton on the oxygen bridging cobalt and carbon



$$(H_3N)_5Co\underset{H}{O}\overset{O}{C}O^{++}$$

Since new Co(III) bonds are established during the release of $CO_2$ from $Co(NH_3)_4CO_3^+$, it will be of interest to learn whether groups besides water (*e.g.*, $Cl^-$, $SO_4^=$) can enter during this rapid process. It was this possibility that attracted interest to the aquation of $Co(NH_3)_5CO_3^+$, but could not be realized in this reaction since oxygen is left attached to Co(III).

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## Some Esters of Unsaturated Acids

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In connection with a study of the preparation of co-polymers of acrylic esters, various esters of unsaturated acids (listed in Table I) were required. Though several of these esters are available commercially, their physical properties are either not found in the permanent chemical literature or these are insufficiently reported. *n*-Butyl maleate[2,3] and fumarate[2,3] and 2-chloroethyl maleate[4] and fumarate[5] have been most completely reported; for butyl fumarate, however, the previously reported constants and those of this paper are not in good agreement. The patent literature reports only the boiling point of 2-ethylhexyl maleate,[3] and the refractive index for *n*-butyl aconitate[6] and 2-ethylhexyl aconitate.[7] This paper reports the preparation, boiling point, refractive index and density of various esters of several unsaturated acids.

### Experimental

Samples of 2-chloroethyl crotonate, butyl maleate, 2-ethylhexyl maleate, butyl itaconate, butyl aconitate and 2-ethylhexyl aconitate were available commercially; these were redistilled and the constants determined.

The other esters of Table I were prepared by the usual esterification procedure, glass equipment with ground glass joints being employed.[8] A mixture of acid or anhydride, an excess of the alcohol, sulfuric acid catalyst and entraining agent was refluxed, and water was continuously removed in a separating trap. Benzene or toluene was used as the entraining agent except in the preparation of the butyl esters, in which the excess of butyl alcohol served as the entraining agent. After esterification was complete, the catalyst was neutralized with sodium acetate, and the ester isolated by vacuum distillation. A 35-mm. by 50-cm. Vigreux or an alembic-type still,[9] mounted to permit agitation of the still pot contents, was used in the distillation. Center fractions were collected for determination of the various constants. Results are shown in Table I.

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TABLE I

PROPERTIES OF SOME ESTERS OF UNSATURATED ACIDS

| Ester | Yield, % | B.p., °C. | B.p., mm. | $n^{20}D$ | $d^{20}_4$ | Carbon, % Found | Carbon, % Calcd. | Hydrogen, % Found | Hydrogen, % Calcd. | Chlorine, % Found | Chlorine, % Calcd. | Sapn. equiv. Found | Sapn. equiv. Calcd. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Chloroethyl crotonate[a] | | 58–60 | 3.5 | 1.4599 | 1.1185 | | | | | 23.72 | 23.86 | | |
| *n*-Butyl maleate[a] | | 124–125 | 3.4 | 1.4451 | 0.9964 | | | | | | | | |
| *n*-Hexyl maleate | 97 | 127 | 0.7 | 1.4499 | .9583 | 68.20 | 67.57 | 10.48 | 9.92 | | | 142.1 | 142.2 |
| 2-Ethylhexyl maleate[a] | | 156 | 0.7 | 1.4548 | .9437 | | | | | | | | |
| 2-(2-Chloroethoxy)-ethyl maleate | 86 | 197 | 1.0 | 1.4858 | 1.2738 | | | | | 21.70 | 21.54 | | |
| *n*-Butyl fumarate | 80 | 117 | 2.5 | 1.4429 | 0.9775 | 63.12 | 63.13 | 8.77 | 8.77 | | | 113.9 | 114.1 |
| 2-Ethylhexyl fumarate | 87 | 160 | 0.5 | 1.4570 | 0.9398 | 70.53 | 70.55 | 10.58 | 10.66 | | | 171.4 | 170.2 |
| 2-(2-Chloroethoxy)-ethyl fumarate | 83 | 182 | 0.3 | 1.4863 | 1.2673 | | | | | 21.83 | 21.54 | | |
| *n*-Butyl chloromaleate | 83 | 112 | 1.2 | 1.4558 | 1.0756 | 54.86 | 55.10 | 7.29 | 7.23 | 13.50 | 13.31 | | |
| 2-Chloroethyl chloromaleate | 75 | 138 | 1.2 | 1.4983 | 1.4047 | | | | | 38.44 | 38.60 | | |
| *n*-Butyl itaconate[a] | | 82 | 0.2 | 1.4450 | 0.9839 | | | | | | | | |
| *n*-Butyl aconitate[a] | | 155 | .5 | 1.4553 | 1.0184 | | | | | | | | |
| 2-Ethylhexyl aconitate[a] | | 170[b] | .07[b] | 1.4620 | 0.9589 | | | | | | | | |

[a] The commercially available esters were redistilled. [b] Distilled in an alembic-type still.

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[1] Foreign trainee from Italy.

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## Sulfatoalkyl Amines

BY WILSON A. REEVES AND JOHN D. GUTHRIE

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Although a number of investigators have reported the preparation and use of 2-aminoethyl sulfuric acid[1,2] other aminoalkyl sulfates have received very little attention. Apparently, most interest in these sulfates has been for the production of

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[1] Sigmund Fränkel and Martha Cornelius, *Ber.*, **51**, 1654 (1918).

[2] John D. Guthrie, *Textile Research J.*, **17**, 625 (1947).