the character of the absorption spectra of the aldehydes[22] and the total primary process quantum yields of decomposition.

At 3130 Å. the total primary process quantum yields increase in the order of decreasing fine structure and fluorescence of the compounds. The change in the absorption spectrum of each of these aldehydes, from a banded region at 3130 Å., through a region of diffuse bands around 2804 Å. and into an apparent continuum around 2654 Å., is accompanied in each case by an increase in the sum of the primary yields of decomposition.

(b) **Secondary Reactions.**—The uninhibited photolysis of each of these aldehydes has been shown to involve chain processes accompanied by a number of free radical reactions. Of particular interest are the association and disproportionation reactions of alkyl and formyl radicals, and the dissociation of the acyl and formyl radicals in thermal and "hot-atom" processes.

The necessity of including an association reaction between alkyl radicals in the mechanisms for aldehyde photolyses is evident, since the formation of ethane in the photolysis of acetaldehyde was shown by Blacet and Brinton,[23] while butane, hexane, and diisopropyl were identified as products of the photodecomposition of propionaldehyde and the butyraldehydes,[11,12] respectively. Evidence also has been accumulated for disproportionation reactions between the ethyl and propyl radicals.[12] Disproportionation is considerably less probable than the association reaction with the ratio $\Phi_{\text{disproportionation}}/\Phi_{\text{association}}$ being 0.10 for both ethyl and *n*-propyl radicals, and 0.33 for isopropyl radicals.

Studies of the yields of hydrogen *vs.* temperature led to the calculation of activation energies for the decomposition of formyl radicals from the several aldehydes. The value of E was found to be 13 kcal. for propionaldehyde, 14 kcal. for the butyraldehydes,[12] and 13.5 kcal. for formaldehyde.[21] In addition to the dissociation reaction of formyl radicals there is good analytical evidence that these radicals can disproportionate to form formaldehyde and carbon monoxide[7,12,17] or associate to give glyoxal.[7,17]

Acknowledgment.—The second named author was the E. I. du Pont fellow in chemistry in the years 1947–1949 and his research was aided also by a grant-in-aid from the Research Corporation, New York. The mass spectrometer used in this investigation was a gift to the University of California by the Signal Gas and Oil Company.

LOS ANGELES 24, CALIFORNIA

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[22] F. E. Blacet, *J. Phys. Chem.*, **52**, 534 (1948).

[23] F. E. Blacet and R. K. Brinton, THIS JOURNAL, **72**, 4715 (1950).

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. VII. Complexes Formed between Silver(I) Ions and Triethylenetetramine

BY HANS B. JONASSEN AND PAUL C. YATES[1]

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When aqueous or alcoholic solutions of silver(I) nitrate are allowed to react with triethylenetetramine (abbrev. trien) several complexes are formed. Spectrophotometric and conductometric studies of their aqueous and alcoholic solutions indicate that complex ions with the composition $[\text{Ag trien}]^+$ and $[\text{Ag}_2\text{ trien}]^{+2}$ are present in both media. Although the complex compound $[\text{Ag trien}]\text{NO}_3$ has been isolated from alcoholic solutions, it has been impossible to isolate salts of the $[\text{Ag trien}]^+$ complex ion present in aqueous solution. Hydrolysis–e.m.f. studies show that the 1:1 complex isolated from alcohol slowly hydrolyzes to that present in water. The observation can be best explained by assuming a coördination number of four for silver(I) complexes.

Introduction

Although many silver(I) complexes containing two, three or four coördinating groups have been reported, investigations have usually been confined to the collection of analytical data. Thus, even when four coördinating groups are present in a complex, it is often impossible to state that they are all coördinated to the silver(I) ion.

The silver(I) complexes containing the polydentate dipyridyl, tripyridyl and tetrapyridyl groups[2-4] have more than two groups available for coördination. In the latter two compounds, however, excessive strain in the coördinating groups would result from the adoption of the tetrahedral structure normally exhibited in four coördinated silver(I) complexes. For this reason Morgan and Burstall[4] believe that these compounds are polynuclear with the coördinating agents acting as bridging units between several metal ions. Only the bis-dipyridyl complex is postulated as a mononuclear four coördinated complex.

It has been claimed in some instances[5] that polydentate groups do not utilize all available coördination positions in complexes with silver(I) even when no steric factors intervene. Job investigated the complexes formed between silver(I) ions and ethylenediamine. Although a stable complex is formed between two molecules of the diamine and one silver(I) ion, the magnitude of the instability constant indicates that the coördination number of silver in the bis-ethylenediamine complex is two rather than four. The fact that one molecule of the amine

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[1] Presented in part before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1949.

[2] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 2594 (1930).

[3] G. T. Morgan and F. H. Burstall, *ibid.*, 1649 (1937).

[4] G. T. Morgan and F. H. Burstall, *ibid.*, 1672 (1938).

[5] P. Job, *Ann. chim.* [10], **9**, 166 (1928).

replaces only one ammonia molecule in the complex $[Ag(NH_3)_2]^+$ is cited as a further substantiation of this conclusion.

This investigation was undertaken to determine the nature of complex ions formed between silver(I) and triethylenetetramine ($H_2NC_2H_4NHC_2H_4NH$-$C_2H_4NH_2$) (abbrev. trien) in aqueous and alcoholic media. Trien offers several interesting features as a coördinating agent for the study of chelation effects. It can function as a mono-, di-, tri- or quadridentate group with the formation of one, two or three five-membered chelate rings and it can act also as a bridging unit in polynuclear complexes. Furthermore, it can adopt either a four coördinate tetrahedral or square planar structure with little difference in strain. If trien occupies all positions in a four coördinated tetrahedral structure, the complex should be asymmetric, and might be resolved into optical isomers if the bonds are covalent.

Experimental

Preparation of Materials.—A technical grade of the trien obtained from Carbide and Carbon Chemicals Co., was purified by the method of Jonassen, LeBlanc, Meibohm and Rogan.[6] Aqueous and alcoholic solutions of trien were standardized potentiometrically against a standard acid using a Beckman model G *p*H meter.

Alcoholic solutions of Ag^+ were prepared by stirring absolute ethyl alcohol with excess silver nitrate for four hours in a darkened room. The excess $AgNO_3$ was filtered off and the solution standardized volumetrically against aqueous HCl using dichlorofluorescein as an indicator.

All other reagents were prepared by weight from C.P. materials.

(a) **Preparation of** $[Ag(trien)]NO_3$.—One hundred ml. of a solution 0.8485 *M* in trien dissolved in absolute ethyl alcohol was treated dropwise with 400 ml. of 0.1697 *M* $AgNO_3$ solution in alcohol. To this was added 500 ml. of diethyl ether and a white precipitate resulted. After several washings with 50 ml. of ether the precipitate was dried over $CaCl_2$ in a vacuum desiccator.

Anal. Calcd. for $[Ag(trien)]NO_3$: Ag, 34.13; N, 22.14. Found: Ag, 34.0; N, 22.2.

(b) **Attempted Preparation of the Hydrate of** Ag(trien)-NO_3.—The $[Ag(trien)]NO_3$ prepared above was allowed to stand for several weeks in a black desiccator over water at about 25°. The complex hardened slowly and was ground to a fine powder repeatedly. Repeated analysis showed that the amount of H_2O present in the complex increased slowly. However, before the per cent. of silver was reduced to that present in $Ag[(trien)]NO_3 \cdot 2H_2O$ the complex completely dissolved. Attempts to prepare $[Ag(trien)]$-$NO_3 \cdot 2H_2O$ by dehydration of the solution of the hydrated complex in a desiccator over various dehydrating agents were unsuccessful. Heating in an oven always led to decomposition of the complex.

The light scattering studies were made on a model DU Beckman spectrophotometer at 24° at 450 mμ.

In the conductance studies the temperature was maintained at 25 ± 0.1° by a water-bath and thermal regulator. Resistance values were determined using a Wheatstone bridge and are accurate to 0.5 ohm. A 1,000-cycle generator was used as the current source and a telephone headset for null-point detection.

Results

A. **Light Scattering Studies.**—It was observed that solutions containing trien and Ag^+ at a ratio smaller than one to one reacted when exposed to light. A Tyndall effect became apparent after 15 minutes and the solution turned brown. After standing for two days in the light, a black precipitate had settled which is a mixture of silver and silver oxide. Solutions containing trien and Ag^+ at ratios larger than one to one stayed perfectly clear and showed no Tyndall effect after more than two hours of exposure to light.

It was decided to investigate this Tyndall effect spectrophotometrically by the method of continuous variation.[7] The total concentration of solute was held constant at 0.002 molar for all solutions with varying proportions of Ag^+ and trien. A Tyndall effect was produced by placing each solution in the light for 15 minutes and immediately afterwards determining the changes in optical density due to scattering. Figure 1 is a plot of optical density difference against mole fraction of trien in the mixture at the wave length of 450 mμ.

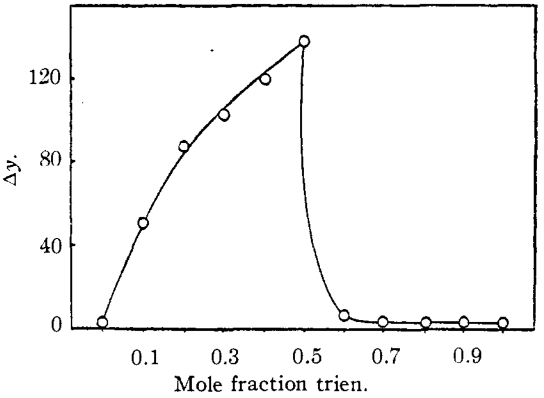

Fig. 1.

This study shows that the scattering and therefore the optical density increases until a ratio of one Ag^+ ion to one trien has been reached. As soon as the concentration of trien exceeds the one-to-one ratio the solution stays clear with a corresponding drop in optical density and a disappearance of the Tyndall effect indicating a one-to-one complex between Ag^+ and trien.

B. **Conductance Studies.**—The data obtained from the titration of 200 ml. of 0.099 molar aqueous trien with 0.100 molar aqueous Ag^+ are presented graphically in Fig. 2.

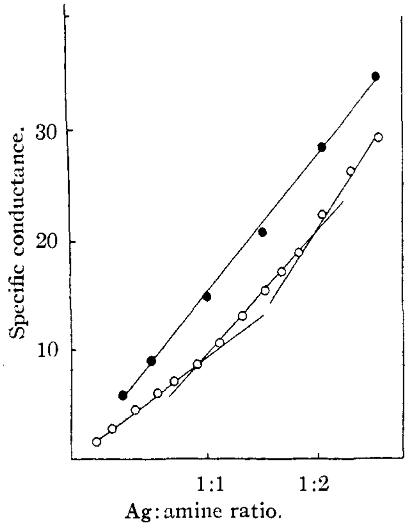

Fig. 2.

Two distinct breaks are shown: one corresponding to a one to one and the other to a one to two trien to silver(I) ion ratio.

While the conductance method is not too sensitive to changes in mobility on the formation of complex ions in a medium of high dielectric constant, the weighting effect of such a heavy group as trien is apparently sufficiently large to cause a perceptible decrease in cation mobility.

The data for the titration of 200 ml. of 0.0130 molar alcoholic trien with 0.1514 molar in alcoholic Ag^+ are shown in Fig. 3.

A very sharp maximum corresponding to a one-to-one ratio of trien to Ag^+ is evident. A minimum in conduct-

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[6] H. B. Jonassen, R. B. LeBlanc, A. W. Meibohm and R. M. Rogan, THIS JOURNAL, **72**, 2430 (1950).

[7] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

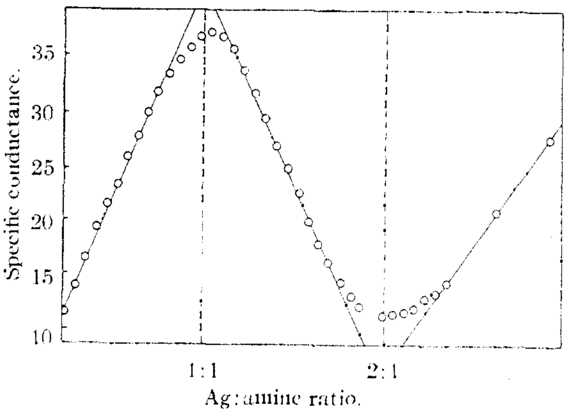


Fig. 3.

ance accompanied by the appearance of a heavy white flocculent precipitate occurs after the addition of Ag$^+$ in alcoholic solution corresponding to a 1:2 trien to Ag$^+$ ratio. Beyond this point the conductance again increases and the value of the slope is the same as that obtained by adding Ag$^+$ in alcoholic solution to pure alcohol. This indicates that no further amine–silver ion interaction occurs.

C. Hydrolysis Studies of [Ag(trien)]NO$_3$.—A solution 0.05 *M* in AgNO$_3$ and 0.11 *M* in KNO$_3$ in H$_2$O was opposed in a concentration cell to a solution containing 0.05 *M* [Ag(trien)]NO$_3$ in H$_2$O, 0.11 *M* in KNO$_3$ and 0.005 *M* in free trien, and the cell e.m.f. measured as a function of time. For comparison, a solution containing exactly the same total amounts of AgNO$_3$, trien and KNO$_3$ but mixed in the form of their aqueous solutions, was measured against the same reference solution.

The data obtained are plotted in Fig. 4. They show that the complex prepared from alcoholic solution develops initially a much lower e.m.f. than that prepared in water solution. However, upon hydrolysis under a nitrogen atmosphere the e.m.f. developed by the aqueous [Ag(trien)]$^+$ in equivalent concentration is reached after one hour and 48 minutes. An inert atmosphere is essential since the complex is oxidized in the presence of air as shown in Fig. 4.

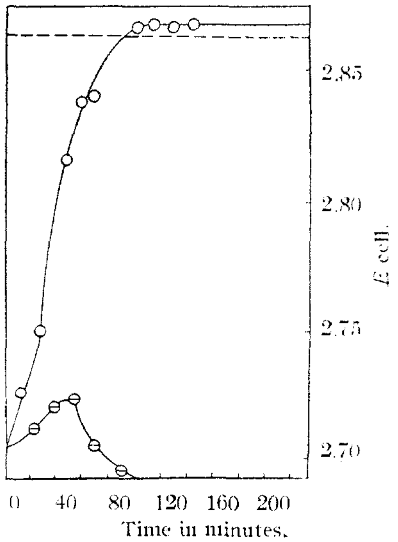


Fig. 4.

Discussion

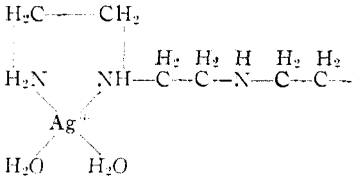
One rather unexpected property of this compound is its low solubility in water, about 0.05 mole per liter. In view of the fact that aqueous solutions containing one mole of trien and one mole AgNO$_3$ show no signs of precipitation, the low solubility of the one-to-one complex isolated from alcoholic solution indicates that some difference must exist between the one-to-one complexes formed in the two solvents.

This is also indicated by the fact that the molar conductivity of the alcoholic [Ag(trien)]$^{+1}$ complex is much greater than that of the solvated silver(I) ion of the same concentration in alcoholic solution. The reverse is true for the aqueous system.

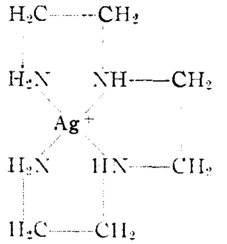
It is difficult to reconcile this difference in behavior of the complex ion in different solvents on the basis of the usually accepted two-coördinate structure for silver(I) amine complex ions. Some possible coördinate structures of trien with silver(I) in a one-to-one ratio are (a) two structures involving coördination of two adjacent nitrogens with the formation of a five-membered chelate ring, (b) a structure involving a primary and a non-adjacent secondary amine with the formation of an eight-membered chelate ring, and (c) a structure involving coördination of the two primary amine groups forming an eleven-membered ring.

The two structures involving the coördination of adjacent nitrogens seem unlikely from steric considerations, for the bond directions of two coördinated silver(I) complexes are at angles of 180° to one another.[8]

Although the structures involving eight and eleven membered rings might arrange themselves to fit bond angles of 180° between the coördinating groups through the formation of puckered rings, no stabilization through chelation would occur. If, however, a four coördinate structure is postulated for silver(I) with this amine, it is easily possible to present a reasonable explanation for the observed variation of properties with the nature of solvent.



Structure I



Structure II

In the tetrahedral bond structure, little strain would be involved in fusing a five-membered ring (bond angles 108°) onto the tetrahedral angles between adjacent coördinating groups (109°). Such chelation would result in a considerable increase of stability in the complex.

Although it was possible to partially hydrate [Ag(trien)]NO$_3$ the extreme solubility of the hydrated complex prevented structural proof by analytical means. The unsuccessful dehydration stud-

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[8] Hultgren, *Phys. Rev.*, **40**, 891 (1932).

ies indicate only the small thermal stability of these complexes.

The hydrolysis–e.m.f. studies, however, prove that the [Ag(trien)]$^+$ ion isolated from alcoholic solution slowly hydrolyzes to the one-to-one complex present in aqueous solution. The most logical explanation for this is to assume a coördination number of four for the Ag$^+$ ion as shown in structures I and II.

The participation of the solvent in the coördination sphere in structure I also explains the high solubility of the aqueous [Ag(trien)]$^+$ form of the complex while the highly blocked nature of structure II would explain the insolubility in water of the compound from alcoholic solution.

This same symmetrical highly blocked structure would greatly increase cation size and decrease ion pair association in a solvent with a low dielectric constant such as alcohol. This would account for the increase of the molar conductance in alcohol of the complex ion over that of alcoholic silver nitrate.

Acknowledgment.—The authors are indebted to the Office of Naval Research for the sponsorship of this and continuing investigations.

NEW ORLEANS 18, LOUISIANA

[CONTRIBUTION NO. 305 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

Compositional Relationships in the Copolymerization of Ethylene with Carbon Monoxide

BY D. D. COFFMAN, P. S. PINKNEY, F. T. WALL, W. H. WOOD AND H. S. YOUNG

The compositions of polyketones synthesized by the copolymerization of ethylene with carbon monoxide have been found to depend upon the temperature, pressure and composition of the reacting mixture. It has been predicted theoretically and has been confirmed experimentally that a particular mixture of monomers will copolymerize to give a product of the same composition. This "azeotropic" composition has been determined for the system ethylene–carbon monoxide as a function of temperature. In addition, the temperature dependence of copolymer composition has been used to determine the difference between the activation energies of certain polymer chain growth steps.

The synthesis and properties of a new family of linear polyketones obtained by the free radical-initiated copolymerization of ethylene with carbon monoxide under pressure have recently been described.[1] These polyketones are heterogeneous with respect to molecular weight and composition, and the average composition of the polymer formed generally differs considerably from that of the reaction mixture employed. The present paper describes a study of the relationship between the composition of the copolymers and that of the reacting comonomers.

Relationship between Monomer and Polymer Composition

The copolymerization of ethylene with carbon monoxide can be accomplished by introducing the mixed gases under pressure into a reactor containing a peroxide initiator. Since it is observed that the monomers do not combine in the ratio in which they are present, except under special circumstances to be indicated later, it follows that the composition of the monomer mixture, as well as that of the polyketones formed therefrom, must change throughout a batch polymerization. Accordingly, the average composition of the polyketones must depend in part upon the duration of the reaction.

To study these effects quantitatively, the copolymerizations were carried out in a 400-ml. reactor at temperatures ranging from 120 to 130° under pressures of 850–1000 atm. for 16 to 19 hours, employing 0.5 ml. of diethyl peroxide as initiator. Unless otherwise indicated, a solvent was not used. The relationship between the composition of the mixed monomers and the average composition of the copolymers formed during a standard polymerization schedule is shown in Table I. The composition of the monomer mixtures can be read as mole per cent. or weight per cent. since carbon monoxide and ethylene are of identical molecular weight.

TABLE I

COPOLYMERIZATION OF ETHYLENE WITH CARBON MONOXIDE

Carbon monoxide in monomer mixture, %	Carbon monoxide in polyketone, %	Yield, g.
1[a]	2.2	77
2[a]	3.8	67
4[a]	7.9	49
10	20	69
20.1	38.4[c]	90
28.4	42.6[c]	102
30[a]	42	104
45[b]	45.9	20
47[b]	45.0	58
48	45.7	92
70[b]	47	32

[a] 0.1 ml. of initiator was used. [b] 100 ml. of benzene was present as a medium. [c] Composition of polymer initially formed on reactor wall.

With low percentages of carbon monoxide in the monomer mixture, it was found, under the conditions employed, that carbon monoxide reacted at a relatively higher rate than did ethylene; however, the rate at which carbon monoxide reacted approached that of ethylene when the ratio of ethylene to carbon monoxide in the monomer mixture approximated unity. Copolymers containing more than 50% carbon monoxide were not formed under the conditions discussed here. This implies that under the conditions used, two carbon monoxide units do not add successively in the chain propagation, but must always be separated by one or more ethylene units. (Under these conditions, carbon monoxide resembles maleic anhydride, which heteropolymerizes[2] with many other monomers, but

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[1] M. M. Brubaker, D. D. Coffman and H. H. Hoehn, THIS JOURNAL, **74**, 1509 (1952).

[2] P. D. Ritchie, "A Chemistry of Plastics and High Polymers" Cleaver-Hume Press, Ltd., London, 1949, Chapt. IV, p. 74.