these studies, then, is why the two proteins behave so differently in this regard. In the case of O the streaming birefringence behavior[10] indicates that this change is the same typical denaturation produced also by heat and by urea. The absence of such changes in the case of A suggests that either (1) binding in this case does not involve a similar structural change or (2) the change is a readily reversible one. The identical behaviors of native and heat denatured A tend to rule out the first explanation. Furthermore, the pronounced changes in specific viscosity and optical rotation imply a pronounced structural alteration. This change is evidently produced by the low *p*H, even in the absence of detergent. In a more detailed study of this behavior considerable evidence has been presented for the ready reversibility of the changes in both viscosity and optical rotation observed.[17] The conclusion, then, is that the failure to observe an all-or-none type of reaction in the case of serum albumin is due to the reversibility of the structural changes produced in this protein either by acid or by the cationic detergent.

Acknowledgments.—The authors are indebted to Armour and Company, Chicago, for generous donations of crystalline bovine plasma albumin. Mr. Joseph Kucera performed the electrophoretic analyses.

[17] J. T. Yang and J. F. Foster, Abstracts 124th Meeting of the American Chemical Society (1953); THIS JOURNAL, in press.

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NOTES

The System: Silver Perchlorate–Dioxane[1]

BY ALAN E. COMYNS AND HOWARD J. LUCAS

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Few complexes in which silver ion is coördinated with an oxygen atom have been isolated.[2] Evidence has been obtained for the formation of a solid complex between silver nitrate and dioxane,[3] and for this complex the authors tentatively assigned the formula $C_4H_8O_2\cdot 8AgNO_3$, on the basis of silver determinations. Silver perchlorate was found to be insoluble in dioxane by Salomon,[4] who deduced from this that silver perchlorate did not react with dioxane. In the complexes of silver nitrate with pyrone,[5] phenol[6] and cyclooctatetraenyl phenyl ketone,[7] it is not known whether the silver ions are attached to the oxygen atoms or to other parts of the molecules, since similar compounds not containing oxygen also form silver complexes.

We have found that although silver perchlorate is insoluble in dioxane, it reacts slowly with dioxane to produce a white powder of composition $3(C_4H_8O_2)\cdot AgClO_4$, which occupies about six times the volume of the original silver perchlorate. The reaction between the well-dried reactants at 25° is very slow: it is accelerated by traces of water (with 0.5% water, reaction is complete within five days) and by heat. The conversion of silver perchlorate, in the presence of excess moist dioxane, to this complex is quantitative (99%); and dioxane may quantitatively (97%) be removed from the complex by high-vacuum distillation. The same complex may be produced in the form of large crystals by dissolving silver perchlorate in a warm mixture of equal volumes of dioxane and acetone, and cooling to room temperature. When heated the crystalline complex does not melt, but evolves dioxane and is converted to a powdery solid rapidly at 120°. Further heating causes this solid to shrink and finally to melt to a bubbling brown liquid above 400°. On heating in a flame, the complex burns quietly with occasional bright spurting: it does not appear to be explosive.

Experimental

Dioxane and anhydrous silver perchlorate were both of "reagent" grade. Silver analyses were by conventional thiocyanate titration; carbon, hydrogen and chlorine analyses were by Dr. A. Elek.

Preparation of Powdered Complex.—Silver perchlorate (1.81 g.), dioxane (10 ml.) and water (0.05 ml.) were shaken together at 25° for 5 days. Filtration yielded 4.42 g. of white powder. Adhering dioxane was removed by pumping to 5 mm. mercury pressure for 1 min. The product weighed 4.10 g., and evacuation for another minute resulted in the further loss of only 0.01 g.

Anal. Calcd. for $(C_4H_8O_2)_3\cdot AgClO_4$: C, 30.6; H, 5.10; Cl, 7.52; Ag, 22.9. Found: C, 30.1; H, 5.14; Cl, 8.57; Ag, 23.0, 23.1.

Preparation of Crystalline Complex.—Silver perchlorate (2.2 g.), dioxane (15 ml.) and acetone (15 ml.) were warmed until the solid had dissolved, and then cooled to room temperature. The resulting crystals were filtered off, washed with dioxane, and freed from excess dioxane by a current of dry air; yield 3.4 g.

Anal. Found: C, 29.9; H, 5.13; Cl, 7.60; Ag, 23.0, 23.1.

Recovery of Dioxane from Complex.—A wide, inverted U-tube, connected to a high-vacuum line *via* a stopcock, connected the flask containing the crystalline complex (3.35 g.) with the receiver. High-vacuum distillation from the flask at 70° to the receiver cooled in liquid nitrogen yielded, after 3 hours, 1.85 g. of colorless liquid. A negligible amount collected after a further 45 min. The distillate was treated with sodium until the slight effervescence had ceased, and redistilled in the same apparatus. The distil-

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[1] The research herein reported has been made possible by support extended the California Institute of Technology by the ONR, under Contract Nonr-270 (00).

[2] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, Oxford, Eng., 1950, p. 141.

[3] J. A. Skarulis and J. E. Ricci, THIS JOURNAL, **63**, 3429 (1941).

[4] G. Salomon, *Rec. trav. chim.*, **68**, 905 (1949); "Cationic Polymerisation and Related Complexes," edited by P. H. Plesch, Heffer, Cambridge, Eng., 1953, p. 59.

[5] R. Willstätter and R. Pummerer, *Ber.*, **37**, 3747 (1904).

[6] C. R. Bailey, *J. Chem. Soc.*, 1534 (1930).

[7] A. C. Cope and D. J. Marshall, THIS JOURNAL, **75**, 3208 (1953).

ate had $n^{25}D$ 1.4198, m.p. 11.3°; dioxane has[8,9] $n^{25}D$ 1.4201, m.p., 11.6°.

Solubility of Silver Perchlorate in Dioxane.—Silver perchlorate (*ca.* 1 g.), contained in a glass tube integral with a vacuum system, was dried by evacuation to 10^{-3} mm. mercury pressure for 18 hours. Dioxane (10 ml.), dried over sodium, was distilled through the vacuum system directly on to the silver perchlorate, and the tube then sealed and removed from the system. The tube and contents were left to stand at room temperature (25 ± 5°), with occasional shaking, for 20 days. The tube was then opened and 5 ml. of the supernatant liquid removed. This was evaporated to dryness under vacuum, the residue dissolved in water (2 ml.) and hydrochloric acid (2 ml. of 0.1 *N*) added; the solution remained quite clear, showing the absence of silver in the supernatant dioxane.

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[8] C. H. Schneider and C. C. Lynch, THIS JOURNAL **65**, 1063 (1943).

[9] J. Gillis and A. Delaunois, *Rec. trav. chim.*, **53**, 186 (1934).

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Racemization of Tris-(ethylenediamine)-cobalt(III) Ion in the Presence of Decolorizing Carbon

BY BODIE E. DOUGLAS

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The use of decolorizing carbon as a catalyst in the preparation of hexamminecobalt(III) salts prompted the investigation of the effect of decolorizing carbon on the racemization of tris-(ethylenediamine)-cobalt(III) ion. Optically active tris-(ethylenediamine)-cobalt(III) ion is very stable toward racemization. No change in rotation is observed for an aqueous solution of the complex after 24 hours on a steam-bath. However, in the presence of decolorizing carbon, racemization is complete in 2 minutes at 90°.

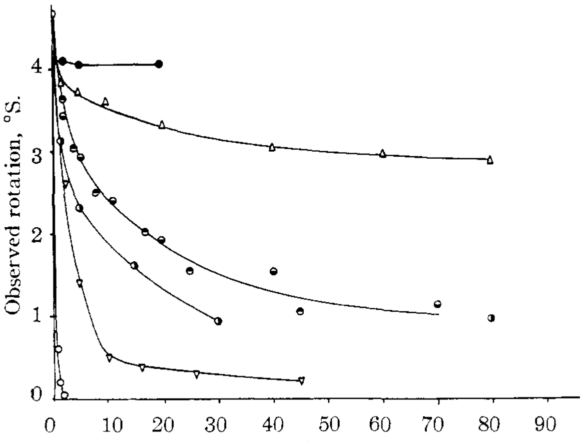

Fig. 1.—Rate of racemization of $Co(en)_3Cl_3$ in the presence of decolorizing carbon. The composition of the samples represented by circles was 1 g. of $Co(en)_3Cl_3$ and 1 g. of decolorizing carbon in 100 ml. of water at various temperatures: ●, 20.5°; ◒, ◓ and ◑, 57°; ○, 90°. The initial rotation for the curves represented by ● and ◑ was 4.1°S. because of incomplete resolution of the sample of the complex used. The samples represented by the triangles were maintained at 57° and differed only in the amount of decolorizing carbon present: △, 0.5 g. of carbon; ▽, 2.0 g. of carbon.

Experimental

Tris-(ethylenediamine)-cobalt(III) chloride was prepared according to the method of Work[1] and resolved by fractional crystallization of the chloro-*d*-tartrate salt as described by Werner.[2] The *d*-complex is less soluble as the chloro-*d*-tartrate salt and can be obtained in a very pure form. The *l*-form of the complex is very soluble as the chloro-*d*-tartrate salt and a solution of the complex tends to form a gel rather than crystals. The *l*-form of the complex was precipitated as the chloride salt with concentrated hydrochloric acid and recrystallized twice to separate it from the less soluble *dl*-form. The specific rotations using a sodium lamp as the light source were +159° and −155° as compared to Werner's values of +152° and −154°, respectively. The first optical rotations were obtained with a Schmidt and Haensch polarimeter which read to 0.01° by means of a vernier scale. The rate studies were carried out using a Bausch and Lomb saccharimeter which read to 0.1°S. (International Sugar scale) by means of a vernier scale. The readings obtained with the saccharimeter could be converted to circular degrees by means of the relationship 100°S. = 34.62° circular. Readings were made with both instruments on the same sample and found to be reproducible to within the reproducibility of the saccharimeter, or about 0.03° circular. Rotations were observed at room temperature for solutions containing 0.100 g. of tris-(ethylenediamine)-cobalt(III) chloride dissolved in enough water to give 10.00 ml.

The racemization rate studies were carried out as follows. The weighed sample of the complex was dissolved in the required volume of water and the solution was allowed to reach a constant temperature in a water-bath before the weighed sample of decolorizing carbon was added. A typical sample for the studies of the effect of temperature contained 1.00 g. of tris-(ethylenediamine)-cobalt(III) chloride, 1.00 g. of carbon and 100 ml. of water. Samples of the stirred suspension were removed with a pipet and filtered as rapidly as possible through a sintered glass filter using suction. The filtrate was then evaporated under an infrared lamp with an air stream blowing over the surface of the solution. Alcohol was added just before the water had been completely evaporated to give a powder on drying rather than a glassy solid. Samples of the active complex were subjected to the same treatment with the omission of the active carbon without change in rotation. Each observation at 90° was carried out with an individual sample of 0.15 g. of complex, 0.15 g. of carbon and 15 ml. of water because of the short and closely spaced time intervals.

Baker and Adamson decolorizing carbon was heated to 700° in a loosely covered crucible for 1 hour in a muffle furnace and bottled for future use. Carbon treated in this way gave reproducible results after 2 or 3 months.

Discussion of Results

The results are presented in Fig. 1. It is apparent that the rate of racemization of tris-(ethylenediamine)-cobalt(III) ion is dependent on the presence of relatively large amounts of active carbon and on the temperature. Samples heated with active carbon for 5 minutes at over 90° were optically inactive, but the absorption spectrum of a solution of the complex in the range of 330 to 725 mμ was the same as for a fresh sample of the complex. Therefore, the decrease in rotation is due to racemization, not decomposition. Samples which had stood in contact with carbon at room temperature for one-half hour or more showed practically no change in rotation on further standing. Samples heated to boiling for an hour or more after standing for at least a day at room temperature in the presence of carbon showed a slight decrease in rotation, but the decrease was never as great as 50% of the original rotation.

Additional data were obtained under somewhat

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[1] J. B. Work, "Inorganic Syntheses," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 221.

[2] A. Werner, *Ber.*, **45**, 121 (1912).