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Coördination of Silver Ion with Unsaturated Compounds. IX. Solid Complexes of Silver Salts with Cyclohexene, α-Pinene and β-Pinene[1]

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Silver perchlorate with cyclohexene, α-pinene and β-pinene forms crystalline complexes which contain two molecules of hydrocarbon to one of silver perchlorate. Silver nitrate forms a similar complex with cyclohexene but none with the pinenes. By means of silver perchlorate the pinenes can be separated from each other, and both α-pinene and β-pinene can be obtained optically pure from optically impure specimens of the respective hydrocarbons.

The first complexes of silver salts with alkenes to be isolated[4] were those of silver nitrate with cyclopentadiene dimer and of silver perchlorate with biallyl and cyclopentadiene dimer. Many complexes of silver nitrate with cyclic olefins have since been prepared and have been used to purify and characterize the olefins.[5] The melting points of a number of olefin–silver nitrate complexes have been compared by Salomon,[6] and some unusual "liquid complexes" of silver nitrate with propene and 1-butene have been described.[7]

When silver perchlorate is added to cyclohexene, α-pinene and β-pinene finely divided solid compounds are formed in the ratio of one mole of silver perchlorate to two of the hydrocarbon. When the mixture of solid with excess of hydrocarbon (plus acetone in the case of cyclohexene) is cautiously warmed,[8] the solid dissolves and crystallizes on cooling. The cyclohexene complex was prepared for study by X-ray diffraction.[9]

The pinene complexes are of interest because they enable the two pinenes to be separated from each other and to be obtained optically pure. The separations are effected by mixing less than one mole of silver perchlorate with two moles of the pinene mixture, letting them react, removing uncomplexed pinene by high vacuum distillation and recovering pinene from the complex by the addition of water. The separations probably depend on differences in the solubilities of the complexes in the pinene mixtures.

The best sample of α-pinene[10] obtained had $[\alpha]^{25}_{\mathrm{D}}$ $+52.4°$ and n^{25}_{D} 1.4632. Two other methods have been described for the preparation of "optically pure" α-pinene, namely, crystallization of the nitrosochloride[10a] and isomerization of "optically pure" β-pinene,[10b] but the present method is easier and more effective. The best sample of β-pinene[11] had $[\alpha]^{25}_{\mathrm{D}}$ $-22.7°$ and n^{25}_{D} 1.4764; the rotation is higher than any previously reported value.

It is necessary to employ pure samples of pinenes. α-Pinene which had been exposed to the air for several days gave a sticky black mass with silver perchlorate. Negligible optical fractionation of α-pinene was obtained with a "practical" grade, although the complex was formed as usual.

Experimental

Materials.—Silver perchlorate (anhydrous) was used as purchased from G. F. Smith and Co. The cyclohexene had been prepared from cyclohexanol by Dr. N. Koenig in this Laboratory and had n^{25}_{D} 1.4441. The pinenes, prepared specially for this work by the Glidden Co. and stated to be of better than 99.9% purity, were stored before use under vacuum in sealed ampoules. α-Pinene[10] had $[\alpha]^{25}_{\mathrm{D}}$ $+30.0°$ (in 1 dm. tube),[12] n^{25}_{D} 1.4631, and β-pinene[11] had $[\alpha]^{25}_{\mathrm{D}}$ $-21.0°$, n^{25}_{D} 1.4765.

Analyses.—Silver determinations on the cyclohexene complexes were by thiocyanate titration in the presence of the hydrocarbon; other analyses were by A. Elek, Los Angeles, Calif.

Preparation of Silver Perchlorate–Cyclohexene Complex.—An excess of cyclohexene, 12 ml., was added to crystalline silver perchlorate, 2.63 g. A rapid exothermic reaction occurred, and the silver perchlorate was converted into a voluminous white powder which was filtered off; yield 4.28 g.

Anal. Calcd. for $AgClO_4 \cdot 2C_6H_{10}$: C, 38.78; H, 5.42; Cl, 9.54; Ag, 29.03. Found: C, 38.91; H, 5.53; Cl, 9.77; Ag, 28.97, 28.93.

Crystallization of Silver Perchlorate–Cyclohexene Com-

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(2) Arthur Amos Noyes Fellow, 1952–1953.

(3) To whom requests for reprints should be sent.

(4) S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

(5) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 11 (1948); A. C. Cope and M. R. Kintner, THIS JOURNAL, **72**, 630 (1950); A. C. Cope, C. L. Stevens and F. A. Hochstein, *ibid.*, **72**, 2510 (1950); A. C. Cope and F. A. Hochstein, *ibid.*, **72**, 2515 (1950); A. C. Cope and H. C. Campbell, *ibid.*, **74**, 179 (1952); A. C. Cope and D. J. Marshall, *ibid.*, **75**, 3208 (1953); A. C. Cope, R. H. Pike and C. F. Spencer, *ibid.*, **75**, 3212 (1953); A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955); A. C. Cope and W. R. Moore, *ibid.*, **77**, 4939 (1955); A. C. Cope and C. L. Bumgardner, *ibid.*, **78**, 2812 (1956); C. Grundmann, G. Ottmann and G. Gollmer, *Ann.*, **582**, 178 (1953); W. O. Jones, *J. Chem. Soc.*, 2036 (1953); 312, 1808 (1954).

(6) G. Salomon in "Cationic Polymerisation and Related Complexes," P. H. Plesch, ed., Heffer, Cambridge, England, 1953, p. 62.

(7) A. W. Francis, THIS JOURNAL, **73**, 3709 (1951).

(8) Rapid or excessive heating could cause decomposition. A Dewar vessel containing liquid N_2 should be handy in order to freeze the mixture rapidly in case any darkening is observed.

(9) This investigation is being made in these laboratories by Albert E. Smith. The complexes of silver nitrate and silver perchlorate with cyclopentadiene dimer have been investigated similarly but with meager results; J. J. Arlen, private communication to G. Salomon and C. Konigsberger, *J. Polymer Sci.*, **2**, 535 (1947).

(10) Lit. rotations: (a) $[\alpha]^{20}_{\mathrm{D}}$ $+51.14°$, $-51.28°$; (b) $[\alpha]^{27}_{\mathrm{D}}$ $-47.4°$. (a) F. H. Thurber and R. C. Thielke, THIS JOURNAL, **53**, 1030 (1931); (b) R. N. Moore, C. Golumbic and G. S. Fisher, *ibid.*, **78**, 1173 (1956). Lit. n^{25}_{D}: (c) 1.4631; (d) 1.4631–1.4632. (c) R. E. Fuguitt, W. D. Stallcup and J. E. Hawkins, *ibid.*, **64**, 2978 (1942); (d) J. E. Hawkins and G. E. Armstrong, *ibid.*, **76**, 3756 (1954).

(11) Lit. $[\alpha]^{25}_{\mathrm{D}}$: (a) $-21.49°$, (b) $-18.54°$, (c) $-21.5°$. (a) Ref. 10c; (b) ref. 10d; (c) G. Widmark, *Acta Chem. Scand.*, **9**, 938 (1955). Lit. n^{25}_{D}: (d) 1.4768, (e) 1.4762. (d) Ref. 10c and 10d; (e) ref. 11c.

(12) Specific rotations were calculated from observed rotations using the densities of α-pinene and β-pinene, namely, d^{25}_{4} 0.8542 and 0.8666, respectively, given by Fuguitt, *et al.*[10c]

plex.—Silver perchlorate, 4.05 g., was dissolved in a warm mixture of cyclohexene, 5 ml., with acetone, 5 ml., and the solution was cooled in ice. The complex crystallized in the form of rectangular plates, which were filtered off; yield 5.02 g.

Anal. Found: C, 37.97; H, 5.41; Cl, 9.66; Ag, 29.00, 28.93.

Recovery of Cyclohexene from Silver Perchlorate Complex.—The powdered complex, 3.64 g., was shaken with water, 15 ml., until all the solid had dissolved. The upper liquid layer, 1.6 ml., was separated, dried overnight with sodium and then distilled under vacuum; yield 1.21 g. (75%) of liquid having $n^{25}\mathrm{D}$ 1.4438. The lower aqueous layer yielded only a trace of second liquid phase when treated with an excess of ammonium hydroxide.

Solubility of Silver Perchlorate Complex in Cyclohexene.—Silver perchlorate, *ca.* 0.2 g., contained in an ampoule fused to the vacuum system, was dried by pumping for 24 hr. with a mercury-vapor diffusion pump followed by a liquid-air trap. Cyclohexene, 25 ml., over sodium in a flask attached to the vacuum system, was distilled directly onto the silver perchlorate, and the ampoule was then sealed and removed from the apparatus. After having been shaken at 25.0° for 4 days, the ampoule was opened, and a 10-ml. portion of the clear supernatant liquid was withdrawn. This was evaporated. Titration of the silver in the residue against thiosulfate showed the solubility to be 0.003 g. of $AgClO_4$/100 ml. of solution. A similar experiment in which the silver perchlorate had been dried for only 4 hr. gave a solubility of 0.005 g./100 ml.

Preparation of Silver Perchlorate-α-Pinene Complex.—When silver perchlorate was left to stand with α-pinene at 25° for several hours, a voluminous white powder formed. It was not possible to obtain a solid of reproducible silver content by removing adhering liquid by high-vacuum distillation from room temperature to a trap cooled by liquid air. For the preparation of the crystalline complex, silver perchlorate, *ca.* 0.2 g., was left with α-pinene, 10 ml., at room temperature for 3 hr., and the mixture was then warmed[8] to dissolve the complex thus formed. Cooling to room temperature yielded small hexagonal plates; yield 0.1 g.

Anal. Calcd. for $AgClO_4 \cdot 2C_{10}H_{16}$: C, 50.06; H, 6.72; Cl, 7.39; Ag, 22.48. Found: C, 50.36; H, 6.72; Cl, 7.26; Ag, 22.64.

When these crystals were heated in a melting-point tube, they broke up into a liquid and a solid phase at 76 ± 1°, and on further heating this mixture blackened suddenly at 125°. Observation of these processes under a hot-stage microscope showed that at 74° the edges of the crystals started to become etched with the formation of liquid drops and that at 80° the crystalline form had been lost entirely. Again, further heating to 125° caused sudden blackening. When heated in a test-tube, the complex exploded mildly. The crystals were not stable in air at room temperature; a sample that had been kept for 3 days in the dark in a well-corked tube had become gray, and microscopic examination showed liquid drops to be present on the faces of the crystals. No attempt was made at storage in the absence of oxygen.

The crystalline complex was prepared in better yield by the use of acetone. Silver perchlorate, *ca.* 4 g., was dissolved in a mixture of α-pinene, 6 ml., and acetone, 1.4 ml., thereby forming a system of two liquid phases. Most of the acetone was removed by standing in a continuously evacuated desiccator. Filtration yielded crystals 2.3 g., m.p. 77–78°, dec. *ca.* 150°.

Anal. Found: Ag, 22.6, 22.9.

Preparation of Silver Perchlorate-β-Pinene Complex.—Silver perchlorate reacted rapidly with β-pinene at room temperature, the mixture becoming warm and much white powder being produced. As in the case of the α-pinene complex, a pure product could not be obtained using this procedure. The crystalline complex was obtained by allowing silver perchlorate, *ca.* 0.4 g., to stand with β-pinene, 10 ml., for 5 min., heating[5] to dissolve the complex so formed, cooling to room temperature and filtering; yield 0.4 g. of small rectangular plates, m.p. 108–109°. The molten complex underwent violent decomposition at 125°.

Anal. Found: C, 49.00; H, 6.56; Cl, 7.21; Ag, 22.40.

The same complex was obtained in better yield by the addition of acetone to the β-pinene. An excess of silver perchlorate was warmed with a mixture of β-pinene, 3.5 ml., having $[\alpha]^{25}\mathrm{D}$ −20.6°, $n^{25}\mathrm{D}$ 1.4763, and acetone, 0.5 ml., "reagent" grade. The liquid was decanted and allowed to cool slowly to 4°. Filtration yielded rectangular plates, 0.42 g., m.p. 107–109°, decomposing at 126°.

The crystalline complex, 0.32 g., was decomposed by water, 0.4 ml., the β-pinene phase was separated and dried with a small lump of calcium sulfate and then distilled in the vacuum system. The distillate, *ca.* 0.1 g., had $[\alpha]^{25}\mathrm{D}$ −22.4°, $n^{25}\mathrm{D}$ 1.4763.

Optically Pure α-Pinene from Optically Impure α-Pinene.—α-Pinene, 12.75 g., having $[\alpha]^{25}\mathrm{D}$ +30.0°, $n^{25}\mathrm{D}$ 1.4631, and crushed silver perchlorate, 4.83 g., were shaken together in a stoppered flask at 25° for 24 hr. Although less than half the α-pinene had reacted, the product was a semi-solid white mass. Unreacted α-pinene was removed from the mixture by high-vacuum distillation at room temperature into a receiver cooled in liquid air. Pinenes volatilize very slowly from their complexes with silver perchlorate under these conditions, and this quantity of unreacted α-pinene distilled completely in about 1 hr.[13] The distillate was dried over calcium sulfate (the trace of water present probably originated in the silver perchlorate), decanted and redistilled in the same apparatus under the same conditions: yield 6.08 g. (48%) of α-pinene, $[\alpha]^{25}\mathrm{D}$ +16.2°, $n^{25}\mathrm{D}$ 1.4630. The solid complex was decomposed by water, 10 ml., and the upper layer of α-pinene was separated. This was dried over calcium sulfate and distilled as before: yield 4.52 g. (36%), $[\alpha]^{25}\mathrm{D}$ +50.7°, $n^{25}\mathrm{D}$ 1.4630.

The sample of α-pinene obtained from the complex was fractionated again by the same procedure: 4.27 g. was shaken with silver perchlorate, 2.33 g., at 25° for 24 hr. In this experiment, however, little reaction occurred in this period, and the mixture was warmed in a water-bath at 95° for 0.5 min. to initiate the reaction. After a further 24 hr. little more reaction had occurred, so the mixture was warmed in a water-bath at 60° for several minutes, and then left to stand at 25° for a further 24 hr., by which time the mixture had become a semi-solid white mass. The products were separated, and the complex decomposed by water, 0.5 ml., as in the previous experiment. The unreacted α-pinene, 2.21 g. (52%), had $[\alpha]^{25}\mathrm{D}$ +49.6°, $n^{25}\mathrm{D}$ 1.4633; the α-pinene, 1.31 g. (30%), obtained from the solid complex had $[\alpha]^{25}\mathrm{D}$ +52.4°, $n^{25}\mathrm{D}$ 1.4632. The constancy of the refractive index throughout showed that no chemical change was taking place.

Optically Pure β-Pinene from Optically Impure β-Pinene.—β-Pinene, 8.59 g. having $[\alpha]^{25}\mathrm{D}$ −21.0°, $n^{25}\mathrm{D}$ 1.4765, reacted exothermally with silver perchlorate, 2.93 g., to produce a semi-solid white mass in several minutes; the mixture was then left at 25° for 18 hr. The product was treated in the same manner as the α-pinene complex. The unreacted β-pinene, 3.34 g. (39%), had $[\alpha]^{25}\mathrm{D}$ −20.6°, $n^{25}\mathrm{D}$ 1.4763. The β-pinene, 2.93 g. (34%), obtained by treating the solid complex with water, 10 ml., had $[\alpha]^{25}\mathrm{D}$ −22.7°, $n^{25}\mathrm{D}$ 1.4764.

Separation of α-Pinene from β-Pinene.[14]—The initial mixture was prepared by mixing α-pinene, 1.11 g., $\alpha^{25}\mathrm{D}$ +44.7°, $n^{25}\mathrm{D}$ 1.4632, with β-pinene, 1.13 g., $\alpha^{25}\mathrm{D}$ −19.7°, $n^{25}\mathrm{D}$ 1.4764. The mixture had $\alpha^{25}\mathrm{D}$ +12.8°, $n^{25}\mathrm{D}$ 1.4699. The percentage of α-pinene in this mixture, as calculated from the quantities taken, is 49.6. Assuming linear relations, the measured optical rotation of the mixture corresponds with that of a mixture containing 50.5% α-pinene, and the

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[13] On one occasion an attempt was made to hurry this process by warming the reaction mixture in a water-bath at 90°; an explosion occurred which shattered the apparatus.

[14] Mixtures were analyzed by measurement of optical activity and refractive index, the results of these two methods agreeing within the limits of accuracy of the refractive index measurements. In this experiment the optical activities are expressed as measured rotations in a 1-dm. tube, the measured rotations of mixtures of α-pinene and β-pinene being approximately linear functions of relative concentration. The error involved in assuming refractive indices to be linear functions of concentration is only 1.5% at equal concentrations; the accuracy of our measurements did not warrant the more accurate treatment given by Fuguitt, *et al.*[10] Optically pure pinenes, prepared by the methods described in the preceding two sections, were employed in order to avoid simultaneous fractionation of optical isomers which would vitiate the simple optical method of analysis. Other experiments in which optically pure pinenes were not employed gave similar results, as shown by the refractive index method.

refractive index corresponds with that of a mixture containing 51.1% α-pinene.

The mixture, 2.05 g., was treated with silver perchlorate, 0.75 g., and left to stand at 25° for 7 hr., when the products were separated by the method described above. The liquid, 1.00 g. (49%), distilled from the mixture had $\alpha^{25}\text{D}$ +30.7°, $n^{25}\text{D}$ 1.4662. These figures correspond with those of a mixture of α-pinene with β-pinene containing 78.3 and 78.2% α-pinene, respectively. The liquid, 0.60 g. (29%), obtained by treating the solid phase with water, 2 ml., had $\alpha^{25}\text{D}$ −14.7°, $n^{25}\text{D}$ 1.4756. These figures correspond with those of a mixture containing 92.2 and 93.1% β-pinene, respectively. The agreement between the two methods of analysis for both fractions confirms that no chemical change had occurred and that the recovered liquids consisted of only the mixed pinenes.

Behavior of α-Pinene and β-Pinene toward Aqueous Silver Perchlorate.—A solution of silver perchlorate, 6 g., in water, 5 ml., was shaken with β-pinene, 0.5 ml., for several minutes at 25°. The β-pinene was thereby completely converted to a white solid, which was not analyzed but was probably the same complex as that formed in the absence of water. An identical experiment in which α-pinene was substituted for the β-pinene did not produce any solid, the α-pinene remaining instead as a separate liquid phase. A further experiment, in which a mixture, 0.5 ml., of equal volumes of the two pinenes was taken, gave a mixture of solid and two liquid phases. This might be a promising method for the separation of α-pinene and β-pinene from each other.

Preparation of Silver Nitrate–Cyclohexene Complex.[15]—Silver nitrate, 3.6 g., was dissolved in a warm mixture of cyclohexene, 15 ml., and ethanol, 2 ml. At room temperature a system of two colorless phases was formed, and at 0° the lower phase gave a mass of needle-shaped crystals. Filtration at *ca.* 4° gave 4.6 g. of product, m.p. 24–32°.

Anal. Calcd. for $AgNO_3 \cdot 2C_6H_{10}$: Ag, 32.3. Found: Ag, 33.2, 33.3.

Pinenes and Silver Nitrate.—Attempts to obtain a solid complex were unsuccessful with pinene (practical) or pinene diluted with a solvent, for example, acetone, methanol or ethanol.

Miscellaneous Observations.—Silver perchlorate dissolves readily in 2-pentene, in 1-hexene and in 4-methyl-2-pentene to form systems consisting of two colorless liquid phases.[16] Crystals form when the 2-pentene system is cooled below room temperature. Silver nitrate dissolves to some extent in 2-pentene and in 4-methyl-2-pentene, but no second liquid phase results.

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(15) The complex, but not its preparation, has previously been described by Salomon.[6]

(16) Francis[7] found that silver nitrate gave two liquid phases with propene and 1-butene but not with mixed pentenes.

PASADENA, CALIF.

[CONTRIBUTION NO. 2191 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Coördination of Silver Ion with Unsaturated Compounds. X. Complexes of Silver Perchlorate and Silver Nitrate with Alkynes[1]

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Systems of silver nitrate and silver perchlorate with 2-butyne, 2-pentyne and 3-hexyne have been studied. Solid complexes are formed, and their solubilities in the alkynes have been measured at 25°.

Previous investigations in this series[4,5] of the coordination[6] of alkynes with silver ion were devoted to measuring equilibrium constants in aqueous solution. We now report studies on systems formed in the absence of added solvent. As before, only dialkylacetylenes have been studied in order to obviate complications from the presence of acidic hydrogen atoms on 1-alkynes.

Silver perchlorate and silver nitrate differ markedly in their solubilities in the three alkynes, as shown in Table I. Except in the case of the silver perchlorate–2-butyne system, where a solid complex is rapidly and quantitatively formed, the solids in contact with the "saturated" solutions were mixtures of unreacted silver salt with solid complexes. This was due to the slowness with which solid complexes were formed, and in consequence the solubilities given in Table I are not true equilibrium values.

TABLE I

SOLUBILITIES OF $AgClO_4$ AND $AgNO_3$ COMPLEXES IN ALKYNES AT 25°

	2-Butyne	2-Pentyne	3-Hexyne
$AgClO_4$[a]	0.10	68	65
$AgClO_4$[b]	.10	211	185
$AgNO_3$[a]	.28	0.22	0.24

[a] Grams of $AgClO_4$ or $AgNO_3$ per 100 g. of solution.
[b] Grams of $AgClO_4$ per 100 g. of solvent.

Silver Perchlorate Complexes.—The solubility of silver perchlorate in 2-pentyne and 3-hexyne is about two thousand times that in 2-butyne. This is probably a consequence of the symmetry of the 2-butyne molecule, which favors packing into a crystal lattice, rather than the formation of concentrated solutions. Similar behavior is found in related systems: thus silver perchlorate is insoluble in dioxane[7] but very soluble in tetrahydropyran[8] and is sparingly soluble in cyclohexene but very soluble in 1-hexene.[9] In each of these systems the solvents of more symmetrical structure readily form solid complexes with silver perchlorate but are poor solvents for these complexes.

The compositions of the "saturated" solutions of silver perchlorate in 2-pentyne and 3-hexyne at 25° correspond with molal ratios of alkyne to silver perchlorate of 1.4:1. Partial evaporation of the

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(2) Arthur Amos Noyes Fellow, 1952–1953.

(3) To whom requests for reprints should be sent.

(4) W. S. Dorsey and H. J. Lucas, THIS JOURNAL, **78**, 1665 (1956).

(5) G. K. Helmkamp, F. L. Carter and H. J. Lucas, *ibid.*, **79**, 1306 (1957).

(6) The reaction is considered to be complexing; J. G. Traynham and M. F. Sehnert, *ibid.*, **78**, 4024 (1956).

(7) A. E. Comyns and H. J. Lucas, *ibid.*, **76**, 1019 (1954).

(8) A. E. Comyns and H. J. Lucas, unpublished results.

(9) A. E. Comyns and H. J. Lucas, THIS JOURNAL, **79**, 4339 (1957).