of the respective aldehydes and ethylenediamine. The Schiff bases were then recrystallized to constant melting points.

Measurements.—The spectra were measured with a Beckman model DU spectrophotometer, using fused-silica cells. The solvent was commercial ethanol in all cases. The wet melting points were determined in sealed glass tubes from Size 7 glass tubing, with one end drawn to a 2-cm. capillary of about 1 mm. i.d. Several measurements were made for each compound with varying amounts of water and the value chosen that was the most reproducible. The proportion of water used was found to have only a small effect on the melting range.

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[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL CO., INC.) RESEARCH AND DEVELOPMENT DEPARTMENT]

Liquid Complexes of Lower Olefins with Anhydrous Metal Salts[1]

BY ALFRED W. FRANCIS

Anhydrous silver nitrate forms liquid complexes with propylene and 1-butene containing over 1.3 moles of olefin to one of salt. These are stable only under pressure near the vapor pressure of the olefin, and below 36 and 25°, respectively. At lower pressures or higher temperatures evolution of the olefin is complete. Propylene forms an equimolar liquid complex with anhydrous mercuric acetate. This liquid does not evolve propylene on evacuation or moderate heating, but does so with addition of hydrochloric acid.

The solvent power of aqueous solutions of silver, mercury, and cuprous salts for the lower olefins is well known[2a,b] although the decided differences in properties and operation for different solutions are not so well understood. For example, it is not generally realized[2a,b,3,4] that the absorption of olefins by most mercury solutions is irreversible[5,6] except with destruction of the reagent by addition of certain substances such as hydrochloric acid.

Solid anhydrous cuprous chloride has been shown to form solid complexes with ethylene,[7,8,9] propylene,[8,9] and isobutene[8,9] and cuprous bromide with ethylene.[8] These have definite equimolar compositions, but are stable only under high partial pressures of the respective olefins. Soday[4] suggested that many other solid dry salts of monovalent copper, mercury and silver might form similar complexes with olefins and diolefins. There seems to be no mention in the literature of a *liquid* complex of an olefin with an anhydrous metal salt (excluding halides of amphoteric elements like aluminum).

In this investigation anhydrous crystalline silver nitrate was agitated with liquid propylene under pressure and was found to give a separate liquid phase of unusual properties.

The new liquid phase is colorless, not very viscous, insoluble in excess of propylene, but miscible with water (with slight decrease in its propylene content). Its density is 1.83 to 1.95 depending on its composition. It is stable only under pressure approaching the vapor pressure of the olefin, since at lower pressure it dissociates quantitatively to propylene and crystalline silver nitrate. Even in contact with pure liquid propylene it dissociates with rising temperatures, and is not stable above 36° although it may be superheated for a few seconds up to 60° or for several hours at 40°. The lower layer reappears when it is cooled and shaken. The liquid thus shows the paradoxical behavior of seeming to freeze on warming and to remelt on cooling. A tube containing a sample in contact with liquid propylene has been kept more than five years. It shows only a slight yellow color in spite of frequent exposure to light and in spite of previous heating to complete dissociation and cooling to regeneration.

Phase relations in the binary system are shown in Fig. 1, and observations of the points are recorded in Table I. The liquid complex exists in the area ABC. The line AB shows the composition of this liquid in equilibrium with pure liquid propylene. It has metastable extensions above 36° and below the freezing point, −26°, both of which are readily observable because of superheating and subcooling. The line AC shows the composition of the liquid in equilibrium with silver nitrate crystals. This equilibrium can be readily subcooled, but not superheated. The straightness of the lines is due to the short range in composition.

When the liquid complex is frozen, crystals may appear as rapidly growing seemingly regular tetrahedra, as much as a centimeter on a side, but these are usually interfered with by conglomerates. These crystals must be solid solutions of at least two different propylates because they melt over a nine or ten degree range except when the composition is above 60 mole % propylene. The composition is non-stoichiometric in spite of well formed crystals, and the crystal shape is independent of composition. They are probably not mixtures of different crystals because on gradual melting from the top down without agitation no trace of crystals (*e.g.*, silver nitrate) remains. Free silver nitrate is not a physical component of the solid solution since

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 117th Meeting of the American Chemical Society, Detroit, Mich., April, 1950.

[2] (a) C. Ellis, "The Chemistry of Petroleum Derivatives," Chem. Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1934, pp. 142, 582. There are at least twenty-one patents for absorbing olefins in solutions of cuprous salts, seven for silver salts, and one for mercury salts. (b) R. N. Keller, *Chem. Revs.*, **28**, 229, especially p. 245 (1941).

[3] J. Chatt, *ibid.*, **48**, 32 (1951).

[4] F. J. Soday, U. S. Patents 2,373,715; 2,389,647 (1945); 2,395,956 (1946).

[5] A. W. Francis and S. J. Lukasiewicz, *Ind. Eng. Chem., Anal. Ed.*, **17**, 703 (1945).

[6] A. W. Francis and co-workers, U. S. Patents 2,077,041 (1937); 2,377,221 (1945); 2,463,482 (1949).

[7] H. Tropsch and W. J. Mattox, THIS JOURNAL, **57**, 1102 (1935).

[8] E. R. Gilliland, J. E. Seebold, J. R. Fitz Hugh and P. S. Morgan, *ibid.*, **61**, 1960 (1939).

[9] E. R. Gilliland and Standard Oil Development Co., U. S. Patents 2,209,452 (1940); 2,289,773 (1942); British Patents 537,468; 537,497 (1941).

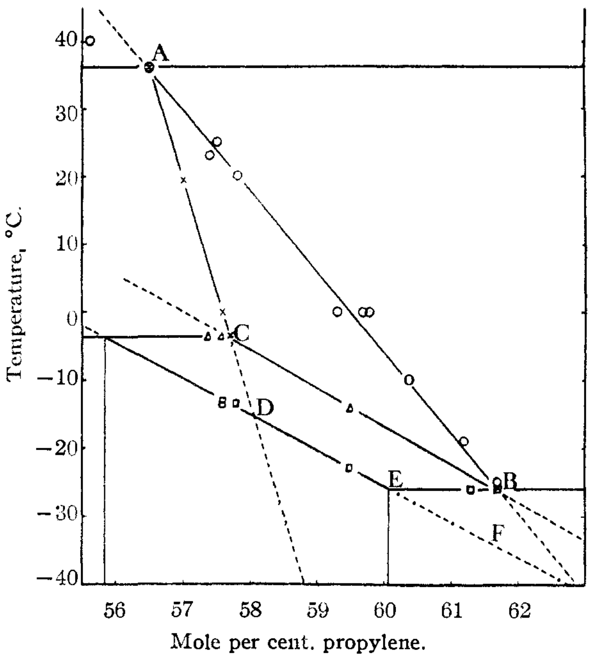

Fig. 1.—Binary system, silver nitrate–propylene.

TABLE I

BINARY SYSTEM, SILVER NITRATE–PROPYLENE

AB: Composition of liquid complex in equilibrium with pure liquid propylene, calculated as in Table II.

AC: Composition of liquid complex in equilibrium with silver nitrate crystals, obtained by isothermal distillation of propylene from the liquid until silver nitrate began to crystallize.

BC: Composition of liquid complex (calculated as in Table II) after freezing it and warming about 0.1° per minute with gentle agitation until the last crystals melted.

BE and ED: Composition of solid complex, with temperature observed while warming about 0.1° per minute without agitation until a trace of liquid was observed.

ED*: The last point was observed by isothermal distillation of propylene until the liquid complex had entirely crystallized.

Temp., °C.	Composition, mole % C_3H_6	Equilibrium	Temp., °C.	Composition, mole % C_3H_6	Equilibrium
−25	61.7	AB	− 3.5	57.7	AC
−19	61.2	AB	0	57.6	AC
−10	60.4	AB	19.4	57.0	AC
			36	56.5	AC
0	59.8	AB			
0	59.7	AB	−26	61.7	BC
0	59.3	AB	−14	59.5	BC
			− 3.5	57.6	BC
19.4	57.8	AB	− 3.5	57.4	BC
23.3	57.4	AB			
25	57.5	AB	−26	61.7	BE
			−26	61.3	BE
36	56.5	AB			
40	55.6	AB	−23	59.5	ED
		(metastable)	−13.5	57.6	ED
			−13	57.6	ED
			−13	57.8	ED*

an abundance of silver nitrate crystals does not induce crystallization along the metastable equilibrium CD and below. The components of the solid solution may be $AgNO_3 \cdot C_3H_6$ and $AgNO_3 \cdot 2C_3H_6$, though there is no quantitative evidence for either.

The series of solid solutions is cut off at both ends by the equilibria AB and ACD, which prevents observation of freezing point or composition of either propylate.

A liquid of 61.7 mole % propylene (saturated with liquid propylene at −26°) freezes without any cloudiness in the liquid phase due to droplets or bubbles of propylene. (If there were no subcooling, crystals of composition E would separate together with some liquid propylene, causing cloudiness. Actually there is subcooling to F, giving the appearance of congruent freezing.) The crystals remelt sharply over a range of less than 0.3°, but give a very cloudy liquid phase. This can be cleared by shaking and standing at constant or falling temperature. The liquid complex in equilibrium with propylene always clouds on warming, even by the heat of a finger.

In a system of two liquid layers the upper propylene layer remains clear with temperature changes in both directions even at Dry Ice temperature. A tube thus cooled was opened, and the upper layer was decanted into a cooled test-tube and evaporated gradually, leaving no residue. This shows complete insolubility of silver nitrate and of complex in the propylene layer.

Ternary miscibility relations at 0° are illustrated in Fig. 2, in which the third component is any liquid, *e.g.*, propane, miscible with propylene and inert to and not a solvent for silver nitrate. C is the liquid complex in equilibrium with silver nitrate and containing 25% propylene; D is the complex saturated with pure propylene and containing 26.5% total propylene; and H is the hydrocarbon mixture of minimum propylene content to form the complex, 75% (at 0°). It is in equilibrium with both C and silver nitrate crystals. The small arrows beside D and H indicate the movements of these points with rising temperature. H reaches the propylene corner at 36°, but D moves only about 1.5% to the left, reaching C at the same temperature. In a conventional diagram of this type neither C nor H would be quite on the side lines. It is only because of the insolubility of propane in the complex and of silver nitrate in the hydrocarbon phase that the points are on the side lines within the accuracy of the diagrams.

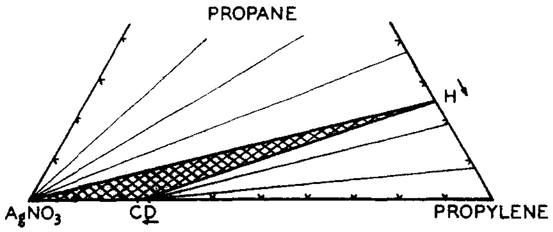

Fig. 2.—Ternary relations of silver nitrate with propylene and propane at 0° (weight per cent.).

Typical tie lines are shown across the two two-phase areas, paraffinic hydrocarbon liquid with silver nitrate crystals, and olefinic hydrocarbon liquid with liquid complex, respectively. The latter phase is not of uniform composition, but varies about 2% in propylene content with the purity of the propylene as well as with the temperature. The thin cross-hatched triangle covers compositions separating into three phases, a solid and two liquids, At room temperature this area is much thinner and lower. The graph makes it clear why the addition of a small amount, 10% or even less, of propane, of *n*-heptane, or of ethylene, which mixes with propylene but is not soluble in the complex, destroys it suddenly and completely. Such an addendum changes the composition across the three-phase area into the upper area in which no complex is possible. Isobutene likewise prevents the formation of the complex if too much is present.

Figure 3 indicates the ternary relations of silver nitrate, propylene, and water at 25°. S is a saturated solution of silver nitrate in water, 71% silver nitrate by weight, C is the anhydrous liquid phase containing 24.5% propylene, and D is that complex saturated with propylene, 25% total propylene. The curve, water–D, shows the solubility of propylene in aqueous solutions of silver nitrate.[6] An experiment described below extends this curve to a system containing still less water than in a saturated solution, and also indicates an increase in solubility of the salt in presence of propylene (line S–C). Actual tie lines cross the large area, propylene–aqueous solution, and typical ones cross the corner area, silver nitrate—aqueous propylene solution. The uncrossed area represents a single liquid phase. At 0° S is higher on the graph (only 55% $AgNO_3$), and D is more to the right (26.5% propylene), but the position of C is almost unchanged.

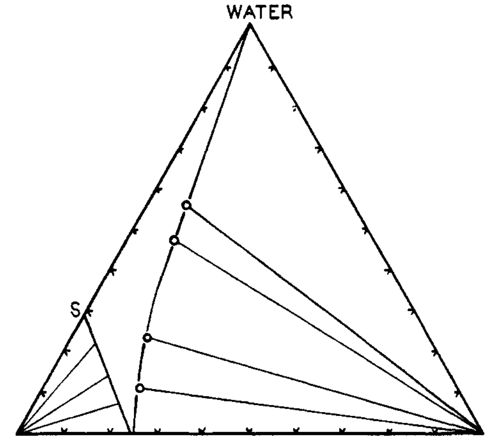

Fig. 3.—Ternary relations of silver nitrate, water and propylene at 25° (weight per cent.).

Since propane and other saturated hydrocarbons are insoluble in the liquid phase, formation of this liquid complex provides a method for purifying propylene of 70 to 99% purity.[10] (The complex is not formed at all from a hydrocarbon liquid containing less than about 70% propylene.) After the complex is formed, (near 0°, unless the propylene is already nearly pure), the undissolved hydrocarbon is separated under pressure. The propylene is evolved from the complex *completely* either by *slight* reduction of pressure or by warming. In this way pure propylene is obtained, under pressure if desired. By this means a mixture of 86% propylene and 14% propane was separated into one containing 99.3% propylene and one containing 59% propylene.

The dissociation pressure in atmospheres of the liquid complex in equilibrium with solid silver nitrate (AC of Fig. 1) is indicated approximately by the equation $\log P = 5.24 - 1257/T$, on the assumption of a linear equation of this form from the values at 0 and 36°. The pressure at 36° is equal to the vapor pressure of pure propylene at that temperature, 15.1 atm., since ternary equilibrium exists under these conditions. The pressure at 0° is equal to the partial pressure of propylene from a mixture of about 75 mole % propylene and 25 mole % propane at the same temperature since 0° is about the highest temperature for stable existence of the complex in contact with this mixture. Since these two hydrocarbons form nearly ideal mixtures, the propylene partial pressure is assumed to be 75% of the pressure of pure propylene at 0° (5.81 atm.) or 4.36 atm. Figure 4 is a plot of this equation together with that for the vapor pressure of propylene,[11] $\log P = 4.357 - 983/T$, and similar relations for 1-butene. The data for the lines for the latter olefin are presented below.

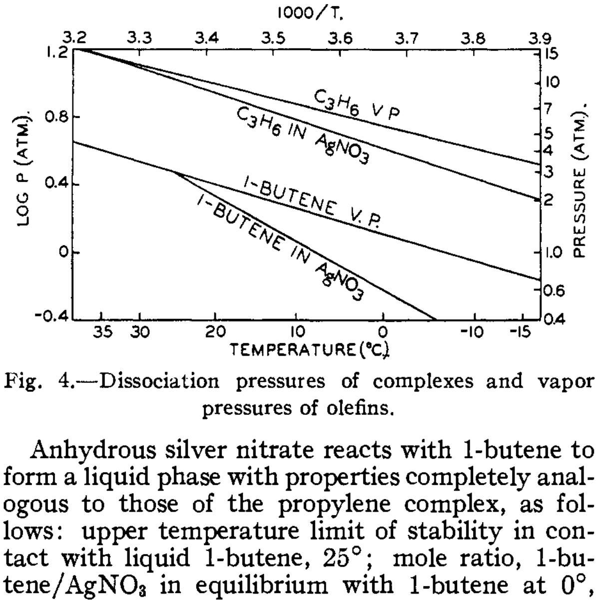

Fig. 4.—Dissociation pressures of complexes and vapor pressures of olefins.

Anhydrous silver nitrate reacts with 1-butene to form a liquid phase with properties completely analogous to those of the propylene complex, as follows: upper temperature limit of stability in contact with liquid 1-butene, 25°; mole ratio, 1-butene/$AgNO_3$ in equilibrium with 1-butene at 0°, 1.54; in equilibrium with silver nitrate, 1.35 (at 0 and 25°); freezing points corresponding to points B and C of Fig. 1, $-45°$ and $> -35°$ (but the liquid usually forms a glass at low temperature); dissociation pressure at 25°, 2.98 atm. (vapor pressure of 1-butene).

Ethylene, 2-butene, isobutene and mixed pentenes have not been found to form similar complexes. The reason may be that their dissociation pressures exceed the vapor pressures of the olefins at all temperatures. Complexes do exist in aqueous solution, however, since all lower olefins are soluble in water solutions of silver nitrate (to the exclusion of paraffins), the molar solubility of ethylene being even greater than that of propylene.[6] For olefins other than propylene and 1-butene, line SC of Fig. 3 probably intersects line water–D so that no binary composition C–D exists.

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[10] A. W. Francis, U. S. Patent 2,498,204 (1950).

[11] A. W. Francis and G. W. Robbins, THIS JOURNAL, **55**, 4342 (1933).

Detailed Experiments[12]

Two typical experiments in glass tubes with silver nitrate and pure propylene are summarized in Table II, with observations at two temperatures with each tube. Actually at least thirty such fillings were made with varying sizes and shapes of tubes and proportions of reagents (and several observations with each filling). The usual apparatus consisted of a thick-walled Pyrex tube about 30 cm. long, including 5 cm. of narrow neck. Each tube was calibrated by weighing on a balance accurate to centigrams while filled to various measured depths with pure benzene. Benzene is preferable to water as a calibrating liquid because it drains down more readily.

A tube was weighed, charged with silver nitrate crystals which had been ground in a glass mortar to facilitate reaction, and weighed again. It was cooled in a bath of Dry Ice and acetone and charged with pure propylene from a lecture bottle by condensation through a capillary tube. The apparatus was sealed while still in the cold bath, and then warmed to room temperature and weighed with the tip of glass which had been pulled off in sealing it, to measure the weight of propylene charged. The tube was cooled in ice water and shaken vigorously with intermittent readings of the levels of the interface and meniscus. The progress of the reaction was measured by the rise of the former and the fall of the latter until all of the crystals had liquefied, whereupon both levels remained constant at constant temperature (after settling), regardless of long continued shaking. At room temperature dissolution of the crystals requires about four times as much time as at 0°. This may be due to a higher solubility of propylene in the complex at 0° (*cf.* Fig. 1).

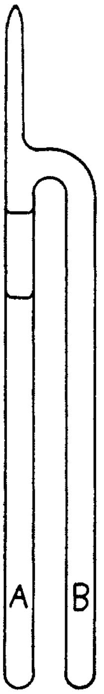

Fig. 5.—Apparatus for estimation of compositions of complexes and their equilibria.

An apparent density of 0.74 was calculated for the combined propylene from the density of the lower layer and that of silver nitrate crystals, 4.35. This value is much higher than the density of liquid propylene at 25°, 0.505.

The dissociation of the complex with moderate reduction of pressure was noted repeatedly whenever the tube was partly immersed in ice water or a Dry Ice-bath. A film of liquid complex on the uncooled portion of the tube, resulting from a previous shaking, changed quickly to a film of solid crystals (silver nitrate) as soon as the pressure was reduced. It was quickly reconverted to liquid by flooding it with the propylene layer.

The study of this dissociation was made more nearly quantitative in the apparatus of Fig. 5, a tube of two legs which could be immersed together in a cold bath, or immersed in separate baths at different temperatures. Each leg was calibrated as to volume against depth by weighing with varying amounts of pure benzene. Leg A of the tube was charged with silver nitrate and propylene care being taken to sweep out all of the air in the tube by decanting some of the propylene into leg B and evaporating it before sealing.

The liquid layer was formed as usual by tipping and gentle shaking, and then decanted as completely as possible into leg A. Part of the excess propylene was decanted back into leg B and the rest distilled over by cooling leg B in a Dry Ice-bath. Distillation was continued until crystals of silver nitrate appeared at the meniscus in leg A. The new depths in both legs were observed, and then some of the crystals were sunk by tapping the tube to make certain that the entire liquid was saturated with silver nitrate. The amount of propylene condensed in leg B (calculated from the volume and density at −78°, 0.648) and that in the vapor phase, subtracted from the charge, gave that still combined, which equalled 1.32 moles per mole of silver nitrate or 57 mole % when leg A was at 19.4°. The complex under these conditions had a density of 1.95.

TABLE II

COMPLEX OF SILVER NITRATE WITH PROPYLENE

Capacity of tube,[a] ml.		15.97		19.20	
Internal cross section,[a] mm.^{2}		66.5		52	
Silver nitrate,[b] g.		14.42		10.28	
Silver nitrate, mmoles		84.8		60.4	
Propylene,[b] g.		6.55		5.33	
Propylene, mmoles		156		127	
Time for dissolution of crystals		56 min. at 25°		16 min. at 0°	
Temperature, °C.		0	−18	24	0
Meniscus,[c] mm.		200	194	207	201
Interface,[c] mm.		165	170	143	146
Volume[d] ml.	Gas[e]	3	3.4	8.62	9.0
	Upper layer	2.33	1.59	3.39	2.85
	Lower layer	10.64	10.97	7.19	7.35
Weight, g.	Gas[f]	0.03	0.02	0.18	0.10
	Upper layer[f]	1.28	0.91	1.71	1.54
	Lower layer[e]	19.66	20.04	13.72	13.97
Density of lower layer		1.85	1.83	1.91	1.90
Propylene, mmoles	Free[g]	30	22	45	39
	Combined and dissolved[e]	126	134	82	88
Mole ratio in lower liquid phase $C_3H_6/AgNO_3$		1.49	1.58	1.36	1.46

[a] From previous calibration by weighing with benzene. [b] By weighing. [c] Height as measured with a vertical scale, including about 5 mm. allowance for thickness and curvature of bottom. [d] From depth and calibration. [e] By difference. [f] From volume and density of propylene at observed temperature. Density of liquid propylene 0.5067, 0.5450, 0.5705 at 24, 0, and −18°. Density of propylene vapor 0.0211, 0.0109, 0.0061 at same temperatures. [g] Gas plus upper layer.

Nearly the same ratio, 1.37, resulted when the experiment was repeated on the same filling but with leg A at 0°. These data give a steep line for equilibrium AC in Fig. 1. The amount of propylene removable without crystallization, as represented by the thickness of the area ABC, was greater at the lower temperature. On the other hand, that amount of propylene was observed by additional distillations on the same filling to be much less at −10, −13 and −19°.

In three of the above experiments, distillation from the liquid complex was continued until all of it had disappeared with formation of crystals. At 19.4 and at 0° the amount of propylene collected in leg B agreed within 0.5% (experimental uncertainty) with the total propylene charged by weight. The silver nitrate was left as a solid sponge throughout leg A. During the distillation the crystals deposited dry to form this sponge above the meniscus, so that the amount of residual liquid complex at any time could be estimated from the volume as measured by the depth. Sixteen intermediate readings in each case were made of this volume and, simultaneously, readings were made of the volume of propylene condensed. A linear relation between these two volumes indicated that no solid complex was crystallizing out, since propylene was not removed from the liquid phase in steps. That is, half of the complex had disappeared when half of the propylene was evolved. At −13°, however, the liquid complex had crystallized completely when the composition in leg A was reduced only to 57.8 mole % propylene. On warming to 0° without agitation all of these crystals melted, showing that no free silver nitrate had deposited.

In another experiment the complex was made as in Table II, frozen in a Dry Ice-bath, and the tube was opened. The excess propylene was decanted out, and replaced with 5 ml. of *n*-heptane. The tube was sealed and warmed to room temperature in a vertical position in a water-bath. A heavy crust of crystals appeared at the interface. On vigorous

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[12] In working with silver solutions it is difficult to avoid occasional contact of them with the skin or clothing, causing black stains not removable by washing with soap. These stains can be eradicated by application of a concentrated aqueous solution of a thiocyanate.

shaking each layer leaked through the crust into the other, causing apparently complete precipitation of the silver nitrate. There was no noticeable temperature change. This was to be expected from the steepness of the equilibrium line AC in Fig. 1. In an experiment with about equal weights of propylene and isobutene the silver nitrate remained unaffected even at low temperature, indicating that the latter olefin inhibits complex formation almost as much as do propane and *n*-heptane.

The miscibility of the complex with water was shown by an experiment in a tube with 12.51 g. of silver nitrate, 2.07 g. of water (which dissolved less than half of the salt) and 5.68 g. of propylene. At 0° all of the silver nitrate and 4.29 g. of propylene dissolved in the lower colorless layer rather more quickly than usual because the water helped to disintegrate the crystals. These quantities corresponded to 1.39 moles of propylene per mole of silver nitrate. At 25° the amount of propylene dissolved was 3.98 g., or 21.4% of the solution. On subcooling to −78° and shaking, almost all of the propylene dissolved before the liquid froze (mole ratio 1.80). Since this last composition is closer to the expected ratio of two moles to one, it may be an indication of the ultimate composition of the solid complex. Crystallization was partly inhibited by the water present. Several attempts to repeat this high degree of subcooling failed, however, because the subcooled complex is very viscous, and the vigorous shaking required to saturate it with propylene before it warmed up invariably induced crystallization. The other three points shown on Fig. 3 are 8.7, 10.9 and 15.8% propylene, and 35.6, 42.2 and 59.8% silver nitrate, respectively.

In contrast with the propylene complex, that of 1-butene is stable at atmospheric pressure at low temperature. In fact it was formed by stirring silver nitrate crystals in liquid 1-butene in an open tube at about −15°. The "boiling point," or temperature at which the dissociation pressure is one atmosphere, was observed by stirring the liquid complex with a thermometer while the tube was in a bath at a slightly higher temperature. After crystals of silver nitrate had begun to form, the temperature remained constant at 7.2° until the liquid had solidified, and the weight indicated that evolution of 1-butene was complete. The barometer reading was 760 mm. From this observation and the dissociation temperature, 25°, under the saturation pressure of 2.98 atm., it was computed that the dissociation equilibrium follows the equation, $\log P = 7.85 - 2200/T$. This may be compared with the equation for the vapor pressure of 1-butene, $\log P = 4.50 - 1200/T$, calculated for the range 500 to 1500 mm. from values selected by the Bureau of Standards.[13] These equations are plotted in Fig. 4.

Other Olefins.—Experiments with ethylene were made in a visual autoclave[14] in order to accommodate the much higher pressures. No liquid complex of silver nitrate crystals was formed with ethylene under 700 pounds pressure at 10 to 25°, nor in the presence of liquid ethylene at 0 to 10° (the critical temperature of ethylene); and none was formed with liquid ethylene in small tubes down to −190°. In another experiment the propylene complex was formed in the visual autoclave with silver nitrate and pure propylene. Ethylene pressure was then applied, giving instantly a heavy network of long crystals and eliminating the liquid complex. On cooling the autoclave to 5°, which is below the critical temperature, liquid ethylene appeared, but there was no effect upon the crystals.

Other Salts.—Several other silver salts were tested similarly with liquid propylene, but no formation of a new liquid phase nor of any solid complex was observed. This is contrary to a suggestion of Soday.[4] These salts included the chloride, sulfate, acetate, phosphate and carbonate. The distinction between these and the nitrate may be related to the much higher solubility of the nitrate in water. It was considered inadvisable, however, to try the other highly soluble silver salt, the perchlorate, because of risk of explosion. Each salt tested was kept in contact for about 17 hours with liquid propylene at room temperature, and agitated with it for several minutes at about 0°. The tube was then cooled below −47°, the boiling point of propylene, opened and warmed to about −42° to evaporate off the uncombined olefin. The tube was then connected to a gas receiver and warmed to 100° to dissociate any complex formed. In no case was more than a trivial amount of gas (25 ml.) collected. This gas probably results from desorption of absorbed propylene and expansion of the vapor phase. Other monovalent metal salts tested similarly with the same result were mercurous chloride, mercurous sulfate, and cuprous sulfate (*cf.* citation 4).

Mercuric Salts.—Propylene forms a liquid complex with anhydrous mercuric acetate, which resembles the one with silver nitrate in appearance, rate of formation, insolubility in hydrocarbons, and miscibility with water. It differs from it in several important respects. One mole of propylene combines with one mole of mercuric acetate *irreversibly*, so that the complex remains as a stable liquid on release of pressure and even on evacuation and heating up to 70°. Higher heating causes extensive irreversible decomposition to a heavy gray sludge. Addition of hydrochloric acid to the liquid complex evolves the combined propylene with formation of mercuric chloride and acetic acid. The liquid complex dissolves additional but limited amounts of propylene reversibly but not selectively, since propane, butane, etc., also are dissolved. On standing for weeks the liquid complex gradually decomposes with deposition of sludge.

Mercuric acetate forms similar liquid equimolar complexes with 1- and 2-butenes. Mercuric nitrate also seemed to form a liquid complex with propylene; but since on standing the tube was destroyed by a chemical explosion, the reaction was not investigated further.

Discussion

The literature contains numerous discussions in regard to the molecular structures of olefin–metal salt complexes.[1,2,3,15,16,17] The mercuric acetate–propylene complex here described must be the one which Whitmore[15] (p. 115) stated had not been isolated.

Winstein and Lucas[17] presented evidence for complexes of one silver ion with one-half, one, and two olefin molecules, respectively, in dilute aqueous solution. In the present investigation a mixture of at least two such complexes seems to have been isolated in both liquid and solid form, but no one of them seems capable of individual isolation.

As in the case of aqueous solutions of silver nitrate,[6] the anhydrous liquid silver nitrate complex behaves in some respects like a physical solution and in others like a chemical compound. It resembles the former in being rapidly and repeatedly reversible with pressure and temperature changes; in allowing rapid extraction of the olefin by any non-reacting solvent miscible with the latter, and with negligible heat effect; and in lacking integral molar proportions. On the other hand, the liquid complex resembles a chemical compound in having no solubility in excess olefin; and in being perfectly selective for propylene with respect to paraffins. That is, propane is insoluble in it. No physical solvent approaches this selectivity. Moreover, it is unreasonable to consider the physical solubility of silver nitrate to be 76% in propylene at 35° and zero in propylene above 36°, or in propane and in other saturated hydrocarbons at all temperatures.

PAULSBORO, N. J.

RECEIVED OCTOBER 19, 1950

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(13) Am. Petroleum Inst. Project 44, Table 8k (1944).

(14) W. F. Caldwell, *Ind. Eng. Chem.*, **38**, 572 (1946).

(15) F. C. Whitmore, "Organic Compounds of Mercury," A. C. S. Monograph, Chem. Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1921, pp. 107-117.

(16) R. Adams, F. L. Roman and W. N. Sperry, THIS JOURNAL, **44**, 1781 (1922).

(17) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).