[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

Effect of Silver Ion Coördination upon the Raman Spectra of Some Unsaturated Compounds[1]

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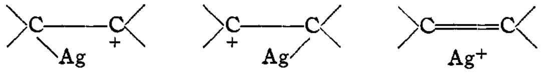
The assignment of configuration to metal–olefin complexes with platinum and silver has lately been the center of renewed interest.[3] Winstein and Lucas,[4] as a result of their work on complexes of olefins with silver ion, proposed a resonance hybrid with the three contributing forms



This structure requires no activated intermediate and was chosen to account for the rapid, reversible formation of the complex and for the absence of olefinic rearrangement.

Anderson[5] found that ultraviolet absorption methods were not helpful in determining the structure of platinum complexes. Since Raman spectroscopy affords another convenient means for studying unsaturation in organic molecules, it was felt that this method of attack should yield additional evidence on the structure of such complexes. For example, it should show distinctly whether the complex is formed through the disappearance[6] or only through the decrease of double-bond character.

Complexes of olefins with silver ion were chosen for examination as these are obtained in colorless water solution. It was observed that a number of monosubstituted acetylenes also form complex compounds soluble in concentrated aqueous silver nitrate, and coördinates of this type were included in the investigation. Spectra are reported for the complexes of four olefins and four acetylenes in silver nitrate solution and for benzene in concentrated silver perchlorate solution.

Experimental

The silver nitrate and silver perchlorate were of C. P. grade. The nitrate solution was 50% by weight and the perchlorate solution approximately 60% by weight. Both solutions were made sufficiently pure optically by repeated filtration, hardened filter paper being used for silver nitrate and glass wool for silver perchlorate.

The *cis*-2-butene and *trans*-2-butene were synthesized from carefully purified samples of *meso*-2,3-butanediol and *dl*-2,3-diacetoxybutane, respectively, according to the method of Wilson and Lucas.[7] The cyclopentene was kindly furnished by Dr. Saul Winstein. Redistillation yielded a product boiling at 43.8–44.1°. The hexene-1 was prepared by the action of allyl bromide on an excess of propylmagnesium bromide in dibutyl ether. The product, boiling at 63.3–64.0°, was distilled directly from the reaction mixture. The cyclohexene was an Eastman Kodak Co. product purified by refluxing over sodium and by subsequent distillation; b. p. 83°. The benzene was thiophene-free grade, redistilled. The ethylacetylene was prepared according to the method of Vaughn, Hennion, Vogt and Nieuwland[8] and yielded a product boiling at 18–20°. The propylacetylene (b. p. 41–43°) and amylacetylene (b. p. 98.6°) were prepared analogously. The phenylacetylene (b. p. 142°) was prepared by the method in "Organic Syntheses."[9] Commercial Prest-O-Lite acetylene was purified by bubbling twice through concentrated sulfuric acid and passing through a ten-inch tower of calcium chloride and a ten-inch tower of soda lime.

The spectrographic apparatus and method have been described elsewhere.[10] As the butenes are gases at room temperature, these complexes were prepared at −10°, the tube sealed, and the spectrum of the aqueous layer obtained at room temperature. Saturated solutions of the hydrocarbons were employed in every case. All were stable to Hg 4358 Å. with the exception of the phenylacetylene solution, the spectrum of which was obtained by changing the material frequently during the exposure. In general, the excitation time for the solutions was from seven to ten hours. Notable exceptions are the three-hour exposure required for the cyclopentene complex and the two-hour exposure for the phenylacetylene complex.

Method and Results

The olefins dissolved practically instantaneously when added dropwise (with shaking) to the concentrated silver nitrate solution. On the other hand, when phenylacetylene or amylacetylene was added to the silver nitrate solution a white precipitate was immediately formed, which, however, redissolved upon being shaken. When gaseous ethylacetylene and propylacetylene were bubbled through the silver nitrate solution, coördination was so rapid that no precipitate appeared until the solution neared satura-

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(2) This paper represents a part of a thesis presented by Harvey J. Taufen to the Faculty of the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.

(3) Keller, *Chem. Rev.*, **28**, 229 (1941).

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

(5) Anderson, *J. Chem. Soc.*, 1042 (1936).

(6) Kharasch and Ashford, THIS JOURNAL, **58**, 1733 (1936), postulated the opening of the double bond in the complex of ethylene with platinous chloride.

(7) Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936).

(8) Vaughn, Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **2**, 1 (1938).

(9) "Organic Syntheses," Coll. Vol. I, 1932, p. 428.

(10) Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **8**, 153 (1940).

tion. Dilution of the complex acetylene solutions with water caused an immediate precipitation; apparently this solid was the same as the intermediate obtained during complex formation. Likewise, when acetylene was bubbled through the silver nitrate solution, a white precipitate formed, which redissolved when shaken. This complex proved unstable, however, as clear, well-formed crystals soon precipitated. These, when washed with water, yielded (apparently) the original, white, flocculent intermediate.

No coördination could be observed with the dialkylacetylenes, diamylacetylene, ethylbutylacetylene and diethylacetylene.

That the acetylide linkage persists in the complex solution is indicated by *p*H values obtained for the silver nitrate solution and for solutions containing the phenylacetylene and amylacetylene complexes The *p*H of the concentrated solution of the silver nitrate used in this investigation was 3.4, that of the phenylacetylene complex was 0.25, and that of the amylacetylene complex was 0.45. The *p*H measurements were carried out qualitatively to determine whether the hydrogen ion concentration had been changed, and these values should not be interpreted as indicating the solubilities of the acetylenes.[11]

Although benzene did not dissolve appreciably even in saturated silver nitrate solution, it did dissolve in 60% silver perchlorate solution to the extent of about 10% by volume at room temperature. The estimated solubilities of the olefins and acetylenes in concentrated silver nitrate solution are listed in Table I.

TABLE I

ESTIMATED SOLUBILITIES OF SOME OLEFINS AND ACETYLENES IN CONCENTRATED AQUEOUS SILVER NITRATE AT ROOM TEMPERATURE

Olefin	Volume, %	Acetylene	Volume, %
cis-2-Butene[a]	15	Ethylacetylene	15
trans-2-Butene[a]	10	Propylacetylene	10
Cyclopentene	30	Amylacetylene	6
Hexene-1	5	Phenylacetylene	8
Cyclohexene	15	Dialkylacetylenes	0

[a] In a sealed tube under own vapor pressure.

The Raman data for the pure olefins and their complexes are tabulated in Table II. Table III shows the effect of silver ion coördination upon the triple-bond frequency of some monosubstituted acetylenes. The few other measurable lines in the acetylenic complexes showed rather insignificant frequency shifts and are not included in the table. The ordinary intensity scale does not retain its significance when applied to the complexes, as in general only the most intense lines appear on these plates. For this reason the intensities of the lines for the complexes are reported merely as strong (s), medium (m) or weak (w). The one exception is the cyclopentene complex, the spectrum of which was quite complete.

Discussion

Examination of the Raman spectra data of the olefinic complexes confirms the conclusion of Pfeiffer and Hoyer[12] that the complex formation in some way involves the double bond. In every case examined, the greatest frequency shift is in the line attributed to the olefinic double-bond frequency (1600–1700 cm.$^{-1}$), which is lowered from sixty to seventy wave numbers. Smaller frequency shifts are noted in some of the carbon–hydrogen vibrations (near 3000 cm.$^{-1}$), while the other frequencies of the original compound appear in the complex essentially unaltered. The carbon–hydrogen frequencies which are most altered appear to be those assigned to the hydrogen atoms attached to olefinic carbon atoms. Such an effect is to be anticipated, as any change in double-bond character will alter the nature of the neighboring bonds. Steric interactions could also be postulated to explain the change in these frequencies.

A reasonable interpretation of the data for the olefinic complexes is afforded by acceptance of the resonance formulation proposed by Winstein and Lucas.[4] That the double bond has not been broken, but merely weakened because of resonance lowering of the double-bond character, is evidenced by the presence of a line, still in the double-bond region but of definitely smaller displacement than in the pure compound. No new lines corresponding to a metal–carbon linkage could be discerned, nor could any trace of the original olefinic frequency be found in the complex. This latter fact also indicates that the concentration of any free olefin must be quite small.

Winstein and Lucas reported that the steric location of the double bond in the olefin determines its solubility to a large degree. This effect was also observed in the present work; the *cis*-olefin is more soluble than the *trans*-analog. Solubility is apparently favored by cyclic structures, but this effect is not to be expected from the argentation constants of Winstein and Lucas. These constants, obtained with one normal silver nitrate solution, indicate that hexene-1 is roughly ten times more soluble than cyclohexene. The reversal of relative solubility, noted in the concentrated solution, may be attributed to the large difference in the activity of the silver ion in dilute and concentrated solutions. Here there are two

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(11) A Coleman *p*H meter was equipped with a potassium nitrate bridge for these measurements.

(12) Pfeiffer and Hoyer, *Z. anorg. allgem. Chem.*, **211**, 241 (1933).

TABLE II

EFFECT OF SILVER ION COÖRDINATION ON THE RAMAN FREQUENCIES[a] OF SOME OLEFINS AND BENZENE

Cyclohexene		Cyclopentene		*cis*-2-Butene		*trans*-2-Butene		Benzene	
Pure[b]	Complex	Pure[b]	Complex	Pure[c]	Complex	Pure[c]	Complex	Pure	Complex
176(2b)									
284(2b)				290(0b)					
396(4)	[417(m)]	385(4b)	434(8b)	392(5b)	434(mb)				
453(2)									
491(2)						501(6)			
646(1)								606(3)	602(m)
720(1)		695(0)				740(3b)			
825(10)	820(s)							847(1)	
875(1)		895(8)	899(8)	870(10)	876(w)	864(5)			
902(3)		933(1)							
968(2)		965(7)	962(7)	1008(4)				993(10)	980(s)
1037(2)		1026(2b)		1031(1)		1035(1)			
1068(4b)		1083(0)							
1138(0)		1108(9)	1108(10)			1145(1b)			
1222(7)	1221(m)	1205(3b)	1215(3b)					1178(4)	1175(m)
1244(2)				1253(8)	1256(mb)				
1267(4)	1262(w)	1293(4)	1293(5)			1304(7)	1290(m)		
1347(1b)				1380(5)	[1382(w)]	1383(4)			
1434(7)		1442(7)	1440(10)	1422(1)		1449(6)	1450(m)	1586(3)	1568(m)
1455(1)		1467(4)	1465(6)	1454(4b)				1606(2)	1589(w)
1653(10)	1584(s)	1613(10)	1539(10)	1660(10)	1598(s)	1677(8)	1612(s)		
2836(9)	2839(w)	2847(10)	2847(10)	2860(5b)	2861(m)	2734(2)			
2863(6)						2860(5)	2864(wb)		
2883(4)		2893(10b)	2893(10vb)			2885(2)		2947(1)	
2911(10)				2921(10vb)	2920(sb)	2917(10)	2918(sb)	3044(5)	
2940(10)	2943(mb)	2953(10b)	2964(10vb)	2970(1b)	2962(m)	2948(5)		3061(10)	3065(svb)
3021(10)	3015(w)	3056(10)	3039(6)	3023(9)	3007(m)	3003(4)			

[a] Frequencies are given in cm.$^{-1}$. Estimated intensities are inclosed in parentheses. Brackets inclose data concerning which there is some uncertainty. [b] The values for the frequencies of these pure hydrocarbons are in good agreement with those listed by M. Magat, "Tables annuelles des constantes et données numériques," Vol. XII, Hermann et Cie., Paris, 1937. [c] The values for the frequencies of the pure butenes, as reported by Gershinowitz and Wilson [*J. Chem. Phys.*, **6**, 247 (1938)], are consistently higher than those found in the present investigation.

TABLE III

EFFECT OF SILVER ION COÖRDINATION ON THE TRIPLE-BOND FREQUENCY OF SOME MONOSUBSTITUTED ACETYLENES

	Pure	Complex		
Ethylacetylene	2114(10)	1990(sb)	1963(w)	
Propylacetylene	2117(10)	1997(sb)	1963(w)	
Amylacetylene	2118(10)	2000(w)	1978(w)	1954(w)
Phenylacetylene	2113(10)	1997(sb)	1979(sb)	1947(w)

opposing effects: *viz.*, the tendency of the olefin to coördinate, and the salt effect of the electrolyte. The relative importance of the effects varies with the concentration of electrolyte and the olefin under examination. In this regard it is interesting to note that the distribution ratio between carbon tetrachloride and one normal potassium nitrate indicates that cyclohexene is twice as soluble in the potassium nitrate solution as is hexene-1.[4]

The data for the complex of benzene in aqueous silver perchlorate show two vibrations to be greatly affected, and these are the only two Raman-active carbon–carbon stretching vibrations of the hydrocarbon.[13] One is the totally symmetrical vibration at 993, and the other is the 1586, 1606 doublet. This latter vibration appears as two lines because of Fermi resonance interaction. There might be some question as to whether both lines of the doublet are shifted in the complex by an approximately equal amount, or whether the 1586 component has remained practically constant while the 1606 component has been lowered to 1568. From consideration of the intensities of these lines, it seems more probable that the doublet has been shifted as a unit. This is possible because the combination of 602 and 980 in the complex could still cause Fermi resonance interaction with the fundamental near 1580.

The 606 vibration of benzene seems to be shifted a very slight amount, although 4 wave numbers *is* near the experimental error involved in the comparison of different spectra. The vibration con-

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[13] Langseth and Lord, *Kgl. Danske Vid. Sels. Math. Fys. Medd.*, **16**, No. 6 (1938).

cerned here is a carbon–carbon deformation, which should not be so greatly affected by a lowering of the force constant through the coördination of silver ion as a stretching vibration would be.

The postulation of Winstein and Lucas,[4] that the silver ion is on the six-fold symmetry axis of the ring, seems to be a reasonable one, first, because a smaller frequency shift than that observed for ordinary olefins indicates that the influence of the coördinated ion in benzene is directed toward more than one "double" bond; second, because the lowering, by 13 wave numbers, of the totally symmetrical vibration noted in the spectrum of the complex seems too small to account for the attachment of appreciable mass anywhere else than on the six-fold symmetry axis.

A consideration of the data for the acetylenic complexes indicates that the triple-bond frequency has not only been greatly lowered, but is also split into two or three lines. While this shows that the triple bond is involved in the coördination, it does not throw much light on the specific nature of the complex. Although this splitting might easily arise from Fermi resonance, the postulation of a multiplicity of distinct compounds is an alternate interpretation. In either case the phenomenon can probably be regarded as of the same general nature as that for the olefins, but one must recognize that the complex really involves an acetylide rather than an acetylene, as indicated by the *p*H values.

It is difficult to understand why dialkylacetylenes do not coördinate. It may well be that the absence of one alkyl linkage, rather than the presence of the C–Ag linkage, is the necessary condition for complex formation.

Winstein and Lucas found that coördination of olefins was decreased by conjugation. In phenylacetylene the triple bond is conjugated with the benzene ring, and a lowered coördinating tendency might therefore have been expected. However, phenylacetylene was distinctly more soluble than amylacetylene. An explanation of this phenomenon is afforded by the observation that the 1601 cm.$^{-1}$ line, characteristic of the monosubstituted phenyl group, appears at 1591 cm.$^{-1}$ in the complex. This is thought to be the same effect noted in the complex of benzene with silver perchlorate, and it is felt that here the silver ion coördinated both with the triple bond and with the benzene ring, causing the unexpectedly large solubility.

Acknowledgment.—The authors wish to thank Dr. Saul Winstein for his many helpful suggestions and also for making available the cyclopentene and *dl*-2,3-diacetoxybutane employed in this investigation.

Summary

By means of the Raman effect, a study has been made of the coördination complexes of silver ion with (a) *cis*-2-butene, *trans*-2-butene, cyclopentene, cyclohexene, ethylacetylene, propylacetylene, amylacetylene and phenylacetylene, employing concentrated silver nitrate solution; and (b) benzene, employing concentrated silver perchlorate solution.

Olefinic complexes show a general lowering of approximately 65 wave numbers for the strong double-bond frequency. Monosubstituted acetylenes form complex compounds (containing the acetylide linkage), in which the triple-bond frequency is approximately 100 cm.$^{-1}$ lower than that of the pure hydrocarbons. The vibrations of benzene which are affected significantly by coordination are those involving the stretching of carbon–carbon bonds.

The formulation of Winstein and Lucas for silver ion–olefin complexes and for the silver ion–benzene complex is consistent with the results of the present study.

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