Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

COMPLEXES OF SILVER PERCHLORATE WITH α,ω-DIOLEFINS

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(Received January 30th, 1967)

INTRODUCTION

In this paper we report the results of our study on coordination compounds obtained by addition of silver perchlorate to 1,5-hexadiene (C_6H_{10}), 1,7-octadiene (C_8H_{14}) and 1,9-decadiene ($C_{10}H_{18}$).

The nature of the bond between transition metal and olefin in compounds of this type was clarified by IR and NMR analyses[1–5], after the first fundamental hypothesis by Dewar[6], who suggested a direct interaction between Ag^+ and double bond in the particular case of silver derivatives. The olefinic character of the complexed hydrocarbon is not substantially modified, as clearly shown by IR spectra, characterized by simple shifts of the double bond frequencies.

The data concerning complexes of silver nitrate and silver perchlorate with linear olefins were especially obtained in solution[7–11]. So far, only $AgNO_3$–butene, $AgNO_3$–propene[12] and $AgNO_3$–ethylene[13], characterized by high dissociation pressures, have been isolated. On the other hand, more stable coordination compounds with a well defined composition were obtained from cyclic olefins[14,15] and, more recently, also from linear olefins and $AgBF_4$[4,5].

As far as we know complexes of silver salts and α,ω-diolefins have not been isolated and studied.

RESULTS AND DISCUSSION

Properties of the complexes

The crystalline products we obtained by addition of silver perchlorate to α,ω-diolefins in alcoholic solution exhibit a good thermal stability and melt without decomposition at temperatures higher than 100°. Stoichiometric ratios and melting points are reported in Table 1.

TABLE 1

COORDINATION COMPOUNDS $AgClO_4$–DIOLEFINS

Ligand	*Composition*	*M.p. (°C)*
1,5-Hexadiene	$2AgClO_4 \cdot 3C_6H_{10}$	104–106
1,7-Octadiene	$AgClO_4 \cdot C_8H_{14}$	126–130
1,9-Decadiene	$AgClO_4 \cdot C_{10}H_{18}$	119–121

In the case of hexadiene, we did not succeed in preparing the 1 : 1 complex, even by varying the ratios between reagents.

In view of the absence of free unsaturation, revealed by IR spectra, one Ag^+ ion must be coordinated to three double bonds for 2 $AgClO_4 \cdot 3\ C_6H_{10}$ and to two double bonds for $AgClO_4 \cdot C_8H_{14}$ and $AgClO_4 \cdot C_{10}H_{18}$.

The particular nature of hexadiene as ligand, with respect to the other two diolefins, is also proved by the higher value of the argentation equilibrium constant, calculated by Muhs and Weiss[16] by gas-chromatographic method ($K_1 = 28.8$; against 11.3 and 7.8 for octadiene and decadiene respectively). The association of an Ag^+ ion with three double bonds would satisfactorily account for the higher stability of the hexadiene complex.

An X-ray diffraction analysis is presently in progress in order to investigate the structure of the complexes. The first data obtained suggest the possibility for $AgClO_4 \cdot C_8H_{14}$ and $AgClO_4 \cdot C_{10}H_{18}$ of coordination of Ag^+ to two double bonds of different molecules with formation of macromolecular sequences, analogous to those previously established for $AgNO_3$–cyclooctatetraene[17]. On the contrary, for the complex of hexadiene, it is likely that coordination to three double bonds occurs according to the scheme indicated in Fig. 1.

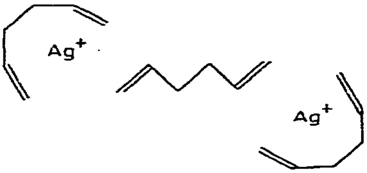


Fig. 1. Ag^+ coordination in the complex 2 $AgClO_4 \cdot 3\ C_6H_{10}$.

From the chemical point of view, the products examined do not differ from other complexes of silver nitrate and silver perchlorate already known.

Treatment with aqueous chloride ion precipitates silver as chloride and frees diolefin. The reaction occurs without isomerization, as ascertained by gas-chromatographic analysis of the final products.

Irradiation tests by γ-rays of the crystalline complexes did not reveal detectable polymerizations or isomerizations of the diolefin.

The easy formation of these complexes and the possibility of their crystallization without decomposition can provide a method for the separation of α,ω-diolefins from monoolefins, which can be isolated as complex from the solutions only with difficulty. An example of fractionation of a mixture of 1,7-octadiene and 1-octene is given in the experimental part.

Infrared spectra

IR spectra of crystalline complexes as nujol mulls and of pure 1,9-decadiene are reported in Fig. 2. The spectra of $AgClO_4 \cdot C_{10}H_{18}$ and $AgClO_4 \cdot C_8H_{14}$ are quite similar.

The almost total disappearance of the band at 1643–1645 cm^{-1} (C=C stretching of the free olefin) allows us to exclude the existence of uncomplexed double bonds. On the contrary the frequency of the C=C stretching is lowered by about 45–60 cm^{-1} (see Table 2) in agreement with the data reported for other complexes of silver[5,14].

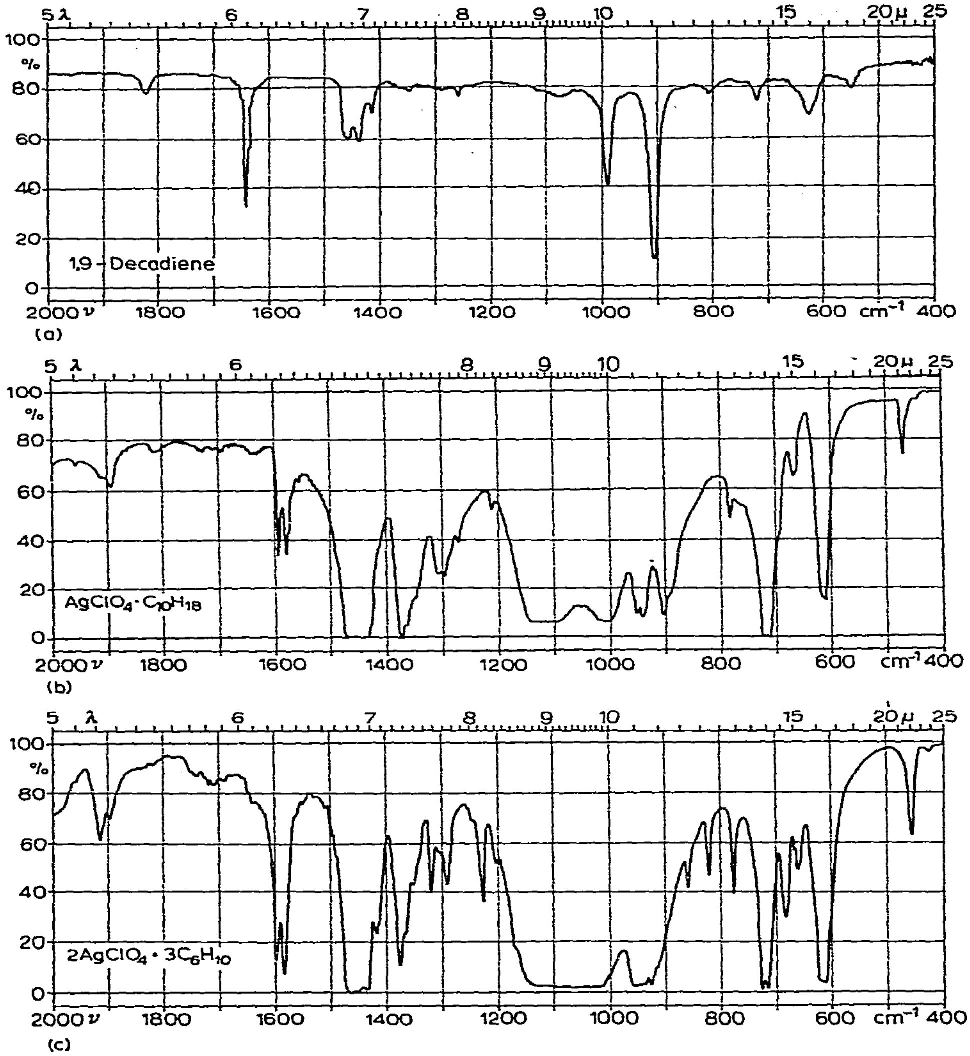


Fig. 2. Infrared spectra of (a) pure 1,9-decadiene and the nujol mulls of the solid complexes: (b) $AgClO_4 \cdot C_{10}H_{18}$; (c) $2\ AgClO_4 \cdot 3\ C_6H_{10}$.

TABLE 2

INFRARED FREQUENCY SHIFTS UPON FORMATION OF $AgClO_4$–DIOLEFINS COMPLEXES ($C=C$ STRETCHING, CM^{-1})

Compound	*ν(C=C)*	*Δν(C=C)*
1,5-Hexadiene	1643	45–57
$2AgClO_4 \cdot 3C_6H_{10}$	1598–1586	
1,7-Octadiene	1645	50–61
$AgClO_4 \cdot C_8H_{14}$	1595–1584	
1,9-Decadiene	1645	50–62
$AgClO_4 \cdot C_{10}H_{18}$	1595–1583	

Moreover, the corresponding band exhibits a splitting, which is peculiar of the solid state and disappears when the complexes are examined in solution. Thus for $AgClO_4$–octadiene dissolved in ethyl alcohol, only one absorption band can be observed at 1586 cm^{-1}, which is intermediate between the two bands in the crystalline complex.

The bands at 940–955 cm^{-1}, observed for all examined complexes and attributed, as for the silver coordination compounds described so far[5], to the out-of-plane deformation of vinyl CH_2, exhibit analogous splittings for solid $AgClO_4 \cdot C_8H_{14}$ and $AgClO_4 \cdot C_{10}H_{18}$.

Interactions between complexed hydrocarbon molecules, due to restrictions of the crystalline structure, can explain these splittings, as observed by Quinn *et al.*[5] for $AgBF_4$–monoolefins complexes.

With regard to the 900–1000 cm^{-1} region, of considerable interest for the double bond, we note that:

(*a*) The data concerning the known coordination compounds between silver salts and straight chain 1-olefins[5] confirm that upon complex formation the following shifts take place:

C–H out-of-plane deformation: nearly from 990 to 1030 cm^{-1}

CH_2 out-of-plane deformation: nearly from 910 to 950 cm^{-1}

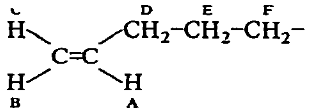
(*b*) An analogous situation seems possible for the complex of hexadiene, by taking into account that the band at 1030 cm^{-1} can be covered by a wide absorption beyond 1000 cm^{-1}.

(*c*) The spectra of $AgClO_4 \cdot C_8H_{14}$ and $AgClO_4 \cdot C_{10}H_{18}$ reveal a band at about 910 cm^{-1}, corresponding with the CH_2 out-of-plane deformation for the free olefin (912 cm^{-1}); this band cannot, however, be attributed to uncomplexed double bonds because it is too intense in comparison with the C=C stretching.

Moreover all the examined spectra show an intense absorption at 615 cm^{-1} of uneasy attribution.

TABLE 3

CHEMICAL SHIFTS[a] IN NMR SPECTRA OF DIOLEFINS AND THEIR COMPLEXES



Compound	H_A	ΔH_A	H_B	ΔH_B	H_C	ΔH_C	H_D	ΔH_D	H_E	ΔH_E	H_F	ΔH_F
1,5-Hexadiene	5.37	0.53	4.52	0.51	4.62	0.43	1.75	0.37				
$2AgClO_4 \cdot 3C_6H_{10}$	5.90		5.03		5.05		2.12					
1,7-Octadiene	5.40	0.35	4.55	0.2	4.63	0.15	1.70	0.15	1.05	0.13		
$AgClO_4 \cdot C_8H_{14}$	5.75		4.75		4.78		1.85		1.18			
1,9-Decadiene	5.45	0.55	4.61	0.35	4.68	0.30	1.75	0.28	1.03	0.19	1.03	0.19
$AgClO_4 \cdot C_{10}H_{18}$	6.00		4.96		4.98		2.03		1.22		1.22	

[a] Expressed in ppm from TMS external reference.

NMR spectra

A lowfield shift of all bands, especially of those attributed to vinyl hydrogens, is observed in the three complexes.

The values of the coupling constants differ very little from those of non complexed olefins. The chemical shifts directly obtained by multiple resonance experiments are reported in Table 3.

The change in chemical shift caused by the formation of the complex presents decreasing values in the order:

$$\Delta H_A > \Delta H_B > \Delta H_C > \Delta H_D$$

in agreement with previous remarks[5].

EXPERIMENTAL

Silver perchlorate used for the preparation of the complexes was a pure BDH reagent.

1,5-Hexadiene, a product of Janssen Pharmaceutica-Beerse (Belgium), after rectification was 98% pure.

1,7-Octadiene of Columbian Carbon Co., Princeton N.J., after rectification was 99% pure.

1,9-Decadiene was prepared from allyl bromide and Grignard compound of 1,4-dibromobutane in ethyl ether[18,19]. The product, obtained with low yield, was 94% pure. (Found: C, 87.20; H, 12.98. $C_{10}H_{18}$ calcd.: C, 86.87; H, 13.13%.) The IR spectrum is reported in Fig. 2.

$2AgClO_4 \cdot 3C_6H_{10}$ was obtained from silver perchlorate (5.6 g) dissolved in absolute ethanol (4.5 cc) and 1,5-hexadiene (2.2 g). The complex was precipitated by addition of anhydrous ethyl ether (4 cc) and washed with ether after filtration (3.8 g). It was subsequently crystallized from nitrobenzene (from which crystals suitable for X-ray analysis were obtained, being big enough and non-geminate), washed with ether and dried in vacuum at room temperature. The product melted at 104–106°. (Found: C, 32.36; H, 4.50; Ag, 32.69. $C_{18}H_{30}Ag_2Cl_2O_8$ calcd.: C, 32.70; H, 4.58; Ag, 32.64%.)

$AgClO_4 \cdot C_8H_{14}$ was obtained from silver perchlorate (3.6 g) dissolved in a mixture of absolute ethyl alcohol (2 cc) and anhydrous ethyl ether (2 cc), by addition of 1,7-octadiene (2 g). The product (3 g), crystallized from acetone, melted at 126–130°. (Found: C, 30.55; H, 4.66; Ag, 33.55. $C_8H_{14}AgClO_4$ calcd.: C, 30.26; H, 4.44; Ag, 33.97%.)

$AgClO_4 \cdot C_{10}H_{18}$ was obtained from silver perchlorate (1.55 g) dissolved in a mixture of anhydrous ethyl ether (1 cc) and absolute ethyl alcohol (1.5 cc), by addition of 1,9-decadiene (1.05 g). The product (1.9 g), crystallized from acetone, melted at 119–121°. (Found: C, 34.60; H, 5.27. $C_{10}H_{18}AgClO_4$ calcd.: C, 34.75; H, 5.25%.)

Separation of 1,7-*octadiene from* 1-*octene*

Silver perchlorate (2.1 g) was dissolved in a mixture of absolute ethyl alcohol (1.6 cc) and anhydrous ether (0.4 cc). A mixture of 1,7-octadiene (0.55 g) and 1-octene (0.45 g) was added.

The solid product (1 g), separated after some hour rest at −5°, was decomposed with an aqueous solution of KCl. The olefin, released from the complex, was extracted with ether. Gas-chromatographic analysis of the residue after ether evaporation revealed that the product consisted of 1,7-octadiene containing less than 3% of 1-octene.

IR spectra

IR spectra were obtained at room temperature by Perkin-Elmer mod. 125 grating spectrophotometer.

The complexes, as nujol mulls, were placed between polyethylene sheets in order to prevent the attack of KBr glasses.

NMR spectra

The spectra were run at room temperature from 3% solution in CD_3COCD_3, using tetramethylsilane as external reference. Operations were performed at 100 Mc/sec with a Varian HA 100 spectrometer equipped with Hewlett–Packard 5512 A frequentiometer.

ACKNOWLEDGEMENTS

We are indebted to Dr. FAGHERAZZI for helpful discussion on X-ray structural data.

SUMMARY

Preparation and properties of anhydrous complexes of silver perchlorate and α,ω-diolefins are described. The special nature of 1,5-hexadiene as ligand, in comparison with 1,7-octadiene and 1,9-decadiene, is pointed out. IR and NMR spectra of the complexes are recorded.

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