TABLE I

INFRARED TRANSMISSION MINIMA FOR BUTADIENE–METALLIC SALT COMPLEXES[a]

K_2-$(Pt_2Cl_6C_4H_6)$	$(PdCl_2$-$C_4H_6)_2$	$(PtCl_2C_4H_6)_2$	$Cu_2Cl_2C_4H_6$	$Cu_2Br_2C_4H_6$
2.34 w	2.35 w	2.34 vw	...	...
2.38 w	...	2.46 vw	...	...
3.71 vw	...	2.92 m	...	...
4.43 w	7.64 m	6.22 w	6.66 sh	6.62 sh
8.10 w	7.94 m	8.54 band	...	7.90 w
8.34 vw	8.14 w	9.36 band	...	...
8.58 vw	8.62 w	9.66 m	...	...
8.66 vw	9.23 w	9.82 m	9.91 w	9.91 w
9.65 s	10.15 w	10.00 m	10.51 w	10.49 vw
9.94 s	10.50 m	10.27 m	10.96 m	11.10 m
10.36 s	11.20 vw	10.38 m	...	...
11.80 s	11.32 w	11.78 band	...	...
12.39 w	11.56 w	12.34 w	...	...
	14.86 m	13.47 w	13.01 w	...

[a] w, weak; vw, very weak; s, strong; m, medium; sh, shoulder.

The complex compounds $Cu_2X_2C_4H_6$ are not very stable even though infrared data indicate the possibility of a butadiene bridge or a butadiene chelate ring in line with a coördination number of four for Cu(I) ion. However, this decrease in stability might also be due to the decreased coördinating tendency of the copper(I) ion toward olefins.[12]

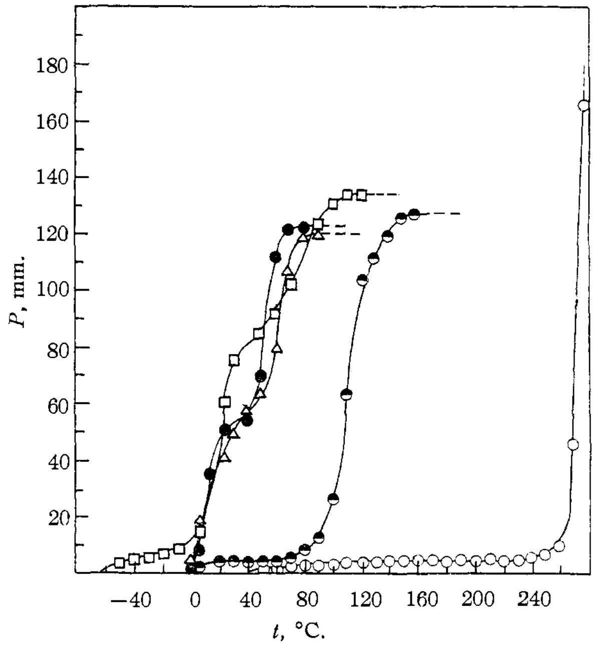

Fig. 1.—Thermal decomposition of butadiene complexes: ○, $K_2[Pt_2Cl_6C_4H_6]$; ◒, $(PdCl_2C_4H_6)_2$; △, $Cu_2Cl_2C_4H_6$; ●, $Cu_2Br_2C_4H_6$; □, $(PtCl_2C_4H_6)_2$.

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NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TULANE UNIVERSITY]

Olefin Coördination Compounds. IV. Platinum(II) Complexes with *cis*- and *trans*-2-Butene

BY HANS B. JONASSEN AND WARREN B. KIRSCH[1]

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1,3-Bis-(*cis*-2-butene)-2,4-dichloro-μ-dichlorodiplatinum(II) $(C_4H_8PtCl_2)_2$, (hereafter referred to as *cis*-2-butene platinous chloride), and 1,3-bis-(*trans*-2-butene)-2,4-dichloro-μ-dichlorodiplatinum(II) $(C_4H_8PtCl_2)_2$, (abbreviated to *trans*-2-butene platinous chloride) were prepared by the displacement of ethylene from 1,3-bis-(ethylene)-2,4-dichloro-μ-dichlorodiplatinum(II), (hereafter referred to as ethylene platinous chloride) $(C_2H_4PtCl_2)_2$. The infrared spectra of the two solids show that isomerization of the olefin does not occur. When the olefins are displaced from the complexes the corresponding *cis* and *trans* isomers are recovered with no rearrangement.

Introduction

The preparation of crystalline platinum–olefin complexes using both *cis* and *trans* isomers of a particular olefin, as the ligand has been questioned.[2,3] Usually one isomer gives a crystalline complex, and the other a tar. Anderson[3a] obtained a crystalline product using *trans*-2-pentene as the ligand, but Oppegard[3b] reported that a tar resulted. He was successful using *cis*-2-pentene and the infrared spectra of the tar and the crystalline complex differed. Oppegard assumed that this was evidence for the preservation of the rigid structure about the double bond.

A similar conclusion was reached by Winstein and Lucas,[4] using aqueous solutions of silver, in which the olefin was dissolved. Within experimental error, they found that no rearrangement of *cis* or *trans* isomers resulted.

In this study, crystalline coördination compounds of platinous chloride with *cis*-2-butene and with *trans*-2-butene have been prepared. Their infrared spectra show them to be different compounds. Decomposition of these two compounds with sodium cyanide yields the respective isomeric olefin without rearrangement.

Experimental

A. Materials.—Hydrocarbons; Phillips High Grade *cis*-2-butene and *trans*-2-butene (99 mole % minimum). Other chemicals were C.P. grade reagents.

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(1) Abstracted in part from the M.S. Thesis of Warren B. Kirsch, Tulane University, 1955.

(2) M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1733 (1936).

(3) (a) J. S. Anderson, *J. Chem. Soc.*, 971 (1934); (b) A. L. Oppegard and J. C. Bailar, private communications.

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

B. **Preparations.** (1) **Ethylene Platinous Chloride** $(C_2H_4PtCl_2)_2$.—This complex compound was prepared by refluxing anhydrous sodium chloroplatinate with absolute ethanol, according to Jorgensen.[5] After three days, the solution was filtered to remove sodium chloride and some colloidal platinum. The alcohol was then removed under reduced pressure. The product was a yellow-orange powder.

Anal. Calcd. for $(C_2H_4PtCl_2)_2$: Pt, 66.4. Found: Pt, 65.6.

This complex decomposed without melting at 160-165°, as determined on a Fisher–Johns melting point apparatus.

(2) ***trans*-2-Butene Platinous Chloride** $(C_4H_8PtCl_2)_2$.—Approximately 5 ml. of *trans*-2-butene was condensed in a test-tube cooled with a Dry Ice-bath and 0.5 g. of ethylene platinous chloride was added. The liquid was then allowed to warm to room temperature. As the butene evaporated, the solid material turned first to bright yellow in color, then to a salmon pink on reaching room temperature. The transformation of the ethylene complex to the corresponding butene complex apparently was not quite quantitative, since the olefin, when displaced by cyanide, contained a very small amount of ethylene.

Anal. Calcd. for $(C_4H_8PtCl_2)_2$: Pt, 60.6. Found: Pt, 61.0.

This compound melted in the range 110–115°, and decomposed between 125–135°.

(3) ***cis*-2-Butene Platinous Chloride** $(C_4H_8PtCl_2)_2$.—This complex was prepared by the displacement method described above, using ethylene platinous chloride and *cis*-2-butene.

Anal. Calcd. for $(C_4H_8PtCl_2)_2$: Pt, 60.6. Found: Pt, 59.9.

This compound decomposed without melting between 165-175°.

C. **Infrared Studies.**—The spectra of both complexes were determined by the potassium bromide wafer technique. The instrument used was a Perkin–Elmer Model 21 spectrophotometer. Table I gives the important transmission minima.

Decomposition Studies.—Samples of the complexes were decomposed *in vacuo* with 0.2 *N* sodium cyanide. After the water had been removed by fractionation the vapor pressures of the residual gases were measured at the temperature of a Dry Ice-bath (−77°). Olefin from the *trans*-2-butene complex gave a value of 6.1 mm. whereas that from the *cis*-2-butene complex had a vapor pressure of 8.0 mm. The infrared spectra of both gas samples were taken.

Discussion of Results

A. $(C_4H_8PtCl_2)_2$.—Sanderson[6] lists a value of 6.2 mm. for the vapor pressure of *cis*-2-butene at Dry Ice sublimation temperature.

This seems to prove that the olefin evolved on decomposition of *cis*-2-butene platinous chloride retained its *cis* configuration.

The infrared spectrum of the gas also showed it to be *cis*-2-butene as compared to a spectrum taken on a known sample, and to the values listed in the literature. Since none of the characteristic bands of *trans*-2-butene were present this seems to prove that no isomerization of the olefin occurred. The gas evolved on decomposing *trans*-2-butene platinous chloride had a vapor pressure of 8.0 mm. at Dry Ice temperature, the repeated value being 8.1 mm. This would indicate that the product was *trans*-2-butene. Its infrared spectrum contains all the absorption bands of *trans*-2-butene, and none of the characteristic bands of *cis*-2-butene. Again no isomerization seems to have occurred.

TABLE I[a]

INFRARED FREQUENCIES IN CM.$^{-1}$ OF PLATINUM–OLEFIN COÖRDINATION COMPOUNDS CONTAINING 2-BUTENE AS THE LIGAND

(*cis*-2-Butene $PtCl_2)_2$	(*trans*-2-Butene $PtCl_2)_2$
3435 w	3425 m
3010 w	2975 w
2940 w	2940 m
2905 w	2900 w
1625 w	2840 w
1615 w	1620 w
1505 m	1525 w
1450 m	1520 w
1430 m	1460 s
1400 m	1445 m
1375 vs	1435 m
1355 vw	1420 m
1150 w	1375 m
1050 m	1365 vs
1035 s	1310 vw
1015 w	1075 vw
992 vw	1045 m
961 vs	1040 m
877 w	1020 w
869 w	999 vs
862 w	979 vs
830 vs	889 vw
	882 w
	850 m
	730 vw

[a] Abbreviations: s = strong; m = medium; w = weak; v = very.

The infrared spectra of the gases obtained by the cyanide displacement of both complexes showed indication of slight amounts of ethylene present. This was noticeable only in the 10–11 μ region where ethylene shows heavy, characteristic absorption, particularly the peak at 10.52 μ. This peak was present in both spectra, superimposed over the absorptions of *cis*-2-butene and *trans*-2-butene both of which also absorb in this region.

The spectra of both displaced gas samples also showed a sharp absorption band at 14.02 μ, which is not characteristic of either *cis*- or *trans*-2-butene. It is suggested that this was due to a very small amount of HCN gas present. Choi and Barker[7] have investigated the infrared spectrum of HCN gas, and reported a band at 712 cm.$^{-1}$ (14.04μ) which was so intense that the transmission minima could only be measured at very low pressures. They found at this wave length at a pressure of 1 mm. the transmission of HCN gas to be 45%, using cells 2.5 cm. in length. In a scale of relative intensities assigned by Choi and Barker, the band at 712 cm.$^{-1}$ is approximately 100 to 10,000 times as strong as the other absorption bands. This high intensity would explain why other absorption bands due to HCN are absent in the spectra of the butenes taken in this investigation. The intensity of the band at 14.02 was in the range of 50–60% transmission, in cells 10 cm. in length. This would suggest that the pressure of any HCN gas present was much less than 1 mm. Since the total pres-

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[5] S. M. Jorgensen, *Anorg. Chem.*, **24**, 153 (1900).

[6] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 126.

[7] K. N. Choi and E. F. Barker, *Phys. Rev.*, **42**, 777 (1932).

sure of the gas samples was between 30 to 34 mm. this small amount would not affect the vapor pressure measurements.

Acknowledgment.—The assistance of Mr. J. Baudian of the Perkin–Elmer Corp., and Mrs. Elsie Dupre and Mr. R. J. O'Connor of the Southern Utilization Research Branch, Agricultural Research Service, U.S.D.A., in obtaining the infrared spectra is gratefully acknowledged.

NEW ORLEANS 18, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

Absorption in the Ultraviolet and Visible Regions of Chloroaquochromium(III) Ions in Acid Media

BY PHILIP J. ELVING AND BERNARD ZEMEL

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The absorption spectra of the hexaaquo-, chloropentaaquo- and dichlorotetraaquochromium(III) ions were observed in the presence of high hydrogen ion concentration to minimize the contribution of basic and polymeric chromium species. In solutions of high perchloric acid concentration the positions of the band maxima for the three ions shifted toward the red in a regular manner with increase in the number of complexed chloride ions. In the presence of 12 *M* hydrochloric acid, the absorption spectra obtained fitted this pattern in a way consistent with the formation of a new species in solution: trichlorotriaquochromium(III); the latter does not occur to any extent in concentrations of hydrochloric acid much below 12 *M*. Since this species was not formed in saturated (5 *M*) calcium chloride solution, its formation is apparently highly hydrogen-ion dependent; a mechanism for formation of the $[Cr(H_2O)_3Cl_3]$ species is suggested. The structure of its spectrum indicates $[Cr(H_2O)_4Cl_2]^+$ to be the *cis* form.

The absorption bands of complexes of the transition metals in the visible and ultraviolet are generally of two kinds: those due to electron transfer processes between metal and ligand, and those arising from transitions within the d-shell of the ion.[1] The relatively intense bands in the ultraviolet having molar absorptivities of 10^3 or greater are considered to be electron transfer bands; bands having molar absorptivities below *ca.* 10^2 are treated as transition spectra. It is these relatively weak transition bands which are of particular interest in the chromium(III) complexes and which account for the characteristic colors of chromium(III) solutions, *e.g.*, the violet of the hexaaquo ion, the light green of the chloropentaaquo ion and the dark green of the dichlorotetraaquo ion. The chromium(III) ion lies within a negative field due to its coördinated ligands. In the presence of this field, the degeneracy of the ground state is removed, and the d-orbital set is split into two multiplet levels. The two absorption bands in the visible correspond to the two allowed transitions between these levels.

Following the isolation and identification of the chloroaquochromium(III) complexes, several investigators[2] reported absorption spectra for them; this work was qualitative in nature and served merely to confirm the existence of absorption bands. Bjerrum[3] in a very carefully performed set of experiments, reported molar absorptivity values for the wave length region from 450 to 700 $m\mu$; however, this region includes only one of the two transition bands. Later, Sueda[4] published absorption curves for the 250 to 470 $m\mu$ region; unfortunately, he had difficulty with impurities in solution, and some, if not all, of his results seem questionable. Since the hexaaquochromium(III) ion is a starting material for the substituted ammino and thiocyanato complexes, its spectrum has been reported in connection with investigations on these systems.[5]

The objective of the present investigation was to examine and correlate the absorption spectra of the chloroaquochromium(III) ions in aqueous solution under such circumstances that the state of the chromium(III) species would be well-defined. Consequently, the absorption spectra of the hexaaquo-, the chloropentaaquo- and the dichlorotetraaquochromium(III) ions were investigated in solutions of high perchloric acid and high hydrochloric acid concentration; under such conditions, the contributions of basic and condensed chromium species are negligible, and the only ligands available in solution for complexing chromium are the chloride ion and the solvent water.

Absorption Spectra of the Chloroaquochromium(III) Complexes

Perchloric Acid Solution.—Absorption spectra of $[Cr(H_2O)_6]^{+3}$ ion in perchloric acid solution in the region from 200 to 800 $m\mu$ show the expected broad bands (Figs. 1 and 2). In addition to maxima at 407 $m\mu$ ($a_M = 16.1$) and 575 $m\mu$ ($a_M = 13.9$), there is a shoulder at 670 $m\mu$ and a steep cutoff in the far ultraviolet with a shoulder at 260 $m\mu$. Above 350 $m\mu$, the spectrum is independent of perchloric acid concentration up to 6 *M* and follows Beer's law for concentrations below 0.08 *M* in chromium. The spectrum in the far ultraviolet is a function of both perchloric acid and chromium concentrations.

The absorption bands in the spectra of $[Cr(H_2O)_5Cl]^{++}$ and $[Cr(H_2O)_4Cl_2]^+$ ions, obtained under similar conditions, show the expected bathochromic effect (Figs. 1 and 2); the band shapes are, however, different. The $[Cr(H_2O)_5Cl]^{++}$ ion shows

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[1] E. Rabinowitch, *Revs. Modern Phys.*, **14**, 112 (1942); H. Hartmann and H. L. Schlafer, *Angew. Chem.*, **66**, 768 (1954).

[2] A. Byk and H. Jaffe, *Z. physik. Chem.*, **68**, 323 (1909); H. C. Jones and W. W. Strong, *Physik. Z.*, **10**, 499 (1909); H. C. Jones and J. A. Anderson, "The Absorption Spectra of Solutions," Carnegie Publication 89, Washington, 1923.

[3] N. Bjerrum, *Z. anorg. Chem*., **63**, 140 (1909).

[4] H. Sueda, *Bull. Chem. Soc. Japan*, **12**, 480, 524 (1937).

[5] (a) R. I. Coleman and F. W. Schwartz, THIS JOURNAL, **54**, 3206 (1932); (b) E. L. King and E. B. Dismukes, *ibid.*, **74**, 1674 (1952); (c) J. Bjerrum and A. Lamm, *Acta Chem. Scand.*, **9**, 216 (1955).