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# Investigation of Possible Interactions between Palladium(II) and -(IV) and between Palladium(II) and Platinum(IV) in Hydrochloric Acid Solutions and in the Crystalline State<sup>1,2</sup>

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The properties of some strongly colored polynuclear complexes containing palladium and platinum in both the +2 and +4 oxidation states have been studied. The substance  $Pd(NH_3)_2Cl_2Pd(NH_3)_2Cl_4$  and the newly synthesized  $Pd(NH_3)_2Cl_2Pt(NH_3)_2Cl_4$  and the newly synthesized  $Pd(NH_3)_2Cl_2Pt(NH_3)_2Cl_4$  are dichroic and it is believed that these substances contain chains, --Pd-<sup>II</sup>Cl---M<sup>IV</sup>Cl---Pd-<sup>II</sup>-Cl---M<sup>IV</sup>-Cl---, (M = Pd or Pt) as discovered for an analogous platinum compound by Brosset.<sup>10</sup> Strong absorption occurs for light polarized with the electric vector parallel to the chain axis. The palladium compound is diamagnetic or very weakly paramagnetic, confirming the conclusion that it does not contain independent  $Pd^{III}$  ions. There is no non-additive absorption of light by hydrochloric acid solutions containing palladium(II) and palladium(IV) or platinum(IV), or by solutions of platinum(IV). platinum(II) and -(IV).

#### Introduction

It has long been known that the polynuclear complexes of either palladium or platinum containing the elements in both the +2 and +4 oxidation states display an abnormally intense coloration. Werner<sup>4</sup> felt there was an analogy between this deep color and that of quinhydrone. St. Claire-Deville and Debray,<sup>5</sup> in 1878, discovered the jet black " $Pd(NH_3)_2Cl_3$ " and assigned the correct empirical formula. Later Rosenheim and Maass<sup>6</sup> erroneously stated that this was a mixture, while others<sup>7a</sup> confused it with isomeric  $Pd(NH_3)_{4}$ -PdCl<sub>6</sub>. In 1932, Drew and co-workers<sup>8</sup> prepared this complex and postulated a Pd-Pd metal bond. In 1936, Mann and Purdie<sup>9</sup> came nearer to the true structure, representing the formula as (NH<sub>4</sub>)<sub>2</sub>Cl<sub>2</sub>Pd<sup>Cl</sup><sub>2</sub>Pd<sup>Cl</sup><sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>. In 1948, Brosset, <sup>10</sup> by

the determination of the crystal structure of Pt- $(NH_3)_2Br_2 \cdot Pt(NH_3)_2Br_4$ , clarified the situation in regard to polynuclear complexes of this type. The crystals of this substance are orthorhombic, and consist of the infinite chains, illustrated in Fig. 1, which are oriented along the c (needle) axis. Each chain contains alternate planes of trans- $Pt^{II}(NH_3)_2Br_2$  and octrahedra of trans- $Pt^{IV}(NH_8)_2$ -Br4. Platinum (II and -(IV) atoms are bonded together by bromine bridges, the bromine-platinum(IV) bonds being shorter. One would accordingly expect that the abnormally intense coloration of this crystal associated with the presence of

(1) Research supported in part by the O. N. R., under contract N6onr-244.

(2) For tables of the extinction coefficients of palladium(II) and -(IV) and platinum(II) and -(IV), plotted in Fig. 2, order Document 3044 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6  $\times$ 8 inches) readable without optical aid.

(3) (a) Atomic Energy Commission Postdoctoral Research Fellow in the Physical Sciences of the National Research Council, 1949-1950; (b) U. S. Naval Ordnance Test Station, China Lake, California.

(4) A. Werner, Z. anorg. Chem., 12, 53 (1896).

(5) H. St. Claire-Deville and H. Debray, Compt. rend., 87, 926 (1878).

(6) A. Rosenheim and T. A. Maass, Z. anorg. Chem., 18, 331 (1898). (7) M. M. J. Sutherland in J. N. Friend's "A Textbook of Inorganic Chemistry," Vol. X, "The Metal Ammines," Chas. Griffin and Co.,

Ltd., London, 1928, (a) p. 212, (b) p. 208. (8) H. D. K. Drew, F. W. Pinckard, G. H. Preston and W. Wardlaw, J. Chem. Soc., 1895 (1932). (9) F. G. Mann and D. Purdie, *ibid.*, 873 (1936).

(10) C. Brosset, Arkiv Kemi, Mineral. Geol., 25A, No. 19 (1948).

platinum in two oxidation states would be observed only for light polarized with its electric vector along the chain axis.



Fig. 1.—A portion of an infinite chain of the Pt(NH<sub>3</sub>)<sub>2</sub>Br<sub>2</sub>. Pt(NH<sub>3</sub>)<sub>2</sub>Br<sub>4</sub> structure (after Brosset<sup>10</sup>).

In order to better understand the color deepening in compounds of this type, the magnetic susceptibility and the optical properties of a similar polynuclear palladium compound,  $Pd(NH_3)_2Cl_2$ · Pd(NH\_3)\_2Cl\_4, have been studied. In view of the equality of the octahedral covalent radii of palladium and platinum,<sup>11</sup> and of the relative stabilities of dipositive palladium and tetrapositive platinum, one would expect that chains like those of Fig. 1 containing palladium(II) and platinum(IV) could exist and we report here the synthesis of  $(Pd(NH_3)_2$ - $Cl_2$ ·Pt $(NH_3)_2Cl_4$ .

The abnormal coloration of some solutions containing an element in two different oxidation states have been studied in this Laboratory,<sup>12</sup> and it was of interest to study the absorption spectra of solutions containing palladium(II) and -(IV), or platinum(II) and -(IV), or palladium(II) and platinum(IV).

## Experimental

Methods.—The petrographic microscope used for the optical examinations was a Winkle-Zeiss instrument with calcite polarizer and analyzer. Magnetic susceptibility measurements were made using a biflar suspension method similar to that first described by Theorell<sup>13</sup> and more recently by Howland and Calvin.<sup>14</sup> The sample tube used was calibrated with standard nickel(II) chloride solutions, water and air.

Absorption spectra of solutions were measured using a Beckman model DU quartz spectrophotometer. The absorption cells were the usual rectangular right prism cells with 1.0 cm. light path. Quartz spacers were employed to reduce the light path to 0.1, 0.03 and 0.01 cm. The optical density, D and molar extinction coefficient,  $\epsilon$ , are defined by  $\epsilon Cl = D = \log_{10} I_0/I$ , where C is the volume formal concentration of the absorbing species and l is the light path in cm.

**Preparations.**—Powdered C.P. grade  $PdCl_2 2H_2O$  and crystalline C.P. grade  $H_2PtCl_5 6H_2O$  were used as starting materials for the preparation of the various compounds and solutions. The palladium compound gave a negative thiocyanate test for iron.

(1)  $Pd(NH_3)_2Cl_2$  was prepared<sup>7b</sup> by dissolving  $PdCl_2$ . 2H<sub>2</sub>O in an ammoniacal solution, heating to volatilize the excess ammonia, and then adding a slight excess of concentrated hydrochloric acid to precipitate the bright yellow crystalline product.

(2) Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>·Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> was prepared in two ways both based on methods of Drew, et al.<sup>§</sup>: (a) By bubbling chlorine through an ice-cold suspension of slightly soluble Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (from 2.23 g. PdCl<sub>2</sub>·2H<sub>2</sub>O) until the black microcrystalline product precipitated and no solid starting material remained (absence of yellow material mixed with The product was washed with water and dried the black). by suction filtration and desiccation. (b) By bubbling chlorine through a 100-ml. aqueous suspension of the product from (a), the black microcrystalline material turned deep red due to the formation of unstable  $Pd(NH_3)_2Cl_4$ . This intermediate was allowed to stand in suspension for several days at room temperature in a desiccator under reduced pressure. Shiny jet black needles of the desired product about 0.005 to 0.08 mm. thick and from 0.5 to 2.0 mm. in length formed by this procedure. On continued standing the palladium(IV) compound completely changed into this macrocrystalline product. The crystals were washed with water and dried between layers of filter paper. This mate-rial cannot be recrystallized for on dissolution it is reduced rat cannot be recrystalized for on dissolution it is reduced completely to the starting material,  $Pd(NH_8)_2Cl_2$ . The yield of the crystalline material was 2.35 g., 92%, based on PdCl<sub>2</sub>·2H<sub>2</sub>O. *Anal.* Calcd. for  $Pd(NH_3)_2Cl_2$ ·Pd(NH<sub>3</sub>)<sub>2</sub>-Cl<sub>4</sub>: Pd, 43.2; Cl, 43.1; N, 11.3; H, 2.47. Found: Pd, 42.5 (by difference); Cl, 42.3; N, 12.1; H, 3.1. It is easier to obtain a pure preparation by (b) then by (a) alone alone.

(3) To synthesize  $Pd(NH_3)_2Cl_2 Pt(NH_3)_2Cl_4$ ,  $Pt(NH_3)_2-Cl_2$  was obtained by heating colorless  $Pt(NH_3)_4Cl_2$  (prepared as directed in "Inorganic Syntheses"<sup>156</sup>) at 150° until completely yellow in color and no loss in weight occurred on further heating. Care must be taken not to reduce to the metal by over-heating.  $Pt(NH_3)_2Cl_4$  was prepared by bubbling chlorine through a boiling aqueous solution of  $Pt(NH_3)_2Cl_2$ . The product crystallized out on cooling as lemon-yellow octahedra. The desired final product,  $Pd(NH_3)_2Cl_2 Pt(NH_3)_2Cl_4$ , was obtained by completely dissolving equivalent amounts of  $Pd(NH_3)_2Cl_2$  and  $Pt-(NH_3)_2Cl_4$  in separate minimal portions of boiling water, pouring these two solutions together and continuing to boil for ten minutes. On cooling, orange to orange-red needles of the product crystallized out. The crystals are from 0.005 to 0.1 mm. thick and from 0.5 to 3.0 mm. in length. The larger crystallized but there is some decomposition into the two starting materials. Anal. Calcd. for  $Pd(NH_3)_2Cl_2$ . Pt(NH\_3)\_2Cl\_4: Pt, 34.3; Cl, 36.5; N, 9.61; H, 2.08. Found: Pd, 17.4; Pt, 33.7; Cl, 37.8; N, 10.1; total metallic content, 51.1. Palladium was determined by the dimethyleyoxime method, platinum by difference.

total metallic content, 51.1. Faliadum was determined by the dimethylglyoxime method, platinum by difference. (4) To obtain platinum(II) chloride, pulverized platinum(IV) chloride (from  $H_2PtCl_8 \cdot 6H_2O^{16b}$ ) in a porcelain boat in a combustion tube was heated to  $450^{\circ}$  in a stream of chlorine for two hours. The product was removed from the hot combustion tube and cooled in a desiccator. The crude product was leached with water to remove any unreacted platinum(IV) chloride and dried.

(5) A 0.998 F hydrochloric acid solution was standardized by a gravimetric (AgCl) method. Sodium thiosulfate solutions were standardized against dried reagent grade potassium iodate.

Solutions containing the PdCl<sub>4</sub><sup>-</sup> ion were prepared by dissolution of PdCl<sub>2</sub>·2H<sub>2</sub>O in 0.998 F hydrochloric acid and were standardized by precipitation and weighing the palladium as the dimethylglyoxime compound. Solutions containing PdCl<sub>6</sub><sup>-</sup> were prepared either by chlorination of the PdCl<sub>4</sub><sup>-</sup> solutions or by dissolving K<sub>2</sub>PdCl<sub>6</sub> in hydrochloric acid. This solid was obtained by addition of excess potassium chloride to a chlorinated PdCl<sub>4</sub><sup>-</sup> solution. Solutions were analyzed for PdCl<sub>6</sub><sup>-</sup> plus chlorine iodo-

Solutions were analyzed for  $PdCl_6^-$  plus chlorine iodometrically, by addition of potassium iodide and thiosulfate titration. On addition of the potassium iodide, palladium-(II) iodide precipitated as a colloidal black solid that was removed by suction filtration through a sintered glass crucible. The starch end-point cannot be used unless this is done.

The PtCl<sub>4</sub><sup>-</sup> solution, prepared by dissolution of powdered platinum(II) chloride in concentrated hydrochloric acid and dilution was standardized by oxidation of the PtCl<sub>4</sub><sup>-</sup> to PtCl<sub>5</sub><sup>-</sup> with chlorine and precipitation of Cs<sub>2</sub>PtCl<sub>6</sub>. Formality of PtCl<sub>6</sub><sup>-</sup> in the solution as an impurity was determined by precipitation as Cs<sub>2</sub>PtCl<sub>6</sub> before oxidation. The PtCl<sub>6</sub><sup>-</sup> solutions were prepared by solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in 0.998 *F* hydrochloric acid.

### Results

Petrographic Examination.-Crystals of Pd- $(NH_3)_2Cl_2 \cdot Pd(NH_3)_2Cl_4$  were found to be dichroic. When the electric vector of the polarized light was vibrating parallel to the needle axis it was completely absorbed, even in the smallest crystals. The transmitted color was lemon-yellow when the electric vector of the plane polarized light was perpendicular to the needle axis. Because of their shape it was not possible to examine the crystals oriented with the needle axis along the microscope axis. There were a few larger crystals (ca. 0.08 mm. thick) and all of these exhibited an anomalous dichroism, with a light gray color transmitted when the vibration direction was parallel to the needle axis and complete absorption of the light when the vibration direction was perpendicular

(15) R. N. Keller, "Inorganic Syntheses," Vol. 2, McGraw-Hill Book Co., Inc., New York, 1946, (a) p. 250, (b) p. 253.

<sup>(11)</sup> L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 182.

<sup>(12)</sup> N. Davidson, et el., THIS JOURNAL, 72, 3168 (1950); 71, 3809 (1949).

<sup>(13)</sup> H. Theorell, Arkiv Kemi, Mineral. Geol., 16A, No. 1 (1943).

<sup>(14)</sup> J. J. Howland, Jr., and M. Calvin, J. Chem. Phys., 18, 239 (1950).

to this axis. The external symmetry of the crystal is that of a rectangular prism. The crystals all exhibit parallel extinction under crossed nicols. It was impossible to obtain interference figures due to the unusual absorption and small size of the crystals. The refractive indices appeared to be greater than 1.70 and thus not easily determinable by oil immersion methods.

Crystals of Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>·Pt(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> have the same external symmetry as those discussed above and exhibited parallel extinction under crossed nicols. Similar dichroism was observed and the color transmitted when the electric vector of the light was perpendicular to the needle axis was also lemon-yellow. The color transmitted when the electric vector was parallel to the needle axis varied from deep red to almost complete absorption in the thicker crystals. In unpolarized light, the material appeared bright orange to orange-red. Due to the larger size of these crystals compared to the analogous palladium complex, it was possible to obtain an acute bisectrix interference figure although it was quite diffuse. The 2V observed was quite small (ca.  $5^{\circ}$ ) and the crystal was found to be optically negative by use of the gypsum plate. These data indicated that the biaxial crystal is orthorhombic or monoclinic and that the gamma (high) refractive index is the one parallel to the needle axis.

Magnetic Susceptibility of Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>·Pd-(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>. A detailed description of the magnetic susceptibility apparatus and its operation will be given later by the group that designed it. We report here the observed susceptibilities per gram formula weight of samples of Pd(NH3)2Cl2 Pd- $(NH_3)_2Cl_4$ : (a) a powdered sample obtained by the procedure (2a) of the Preparations section, -650 $(=200) \times 10^{-6}$  c.g.s.; (b) two separate fillings of the susceptibility tube with a more macrocrystalline product obtained by oxidation of the (a) sample according to procedure (2b),  $105(\pm 30)$  and  $70-(\pm 30) \times 10^{-6}$  c.g.s. It is suspected that these variable results are not due principally to the instrumental error or to chemical impurities. They could be due to the differences in the degree of orientation of the crystals packed in the susceptimeter tube if the substance has a high magnetic anisotropy. The significant result is that the substance is not strongly paramagnetic and hence

does not contain any unpaired electrons. Spectrophotometric Investigations.—Figure 2 shows the absorption spectra of the PdCl<sub>4</sub><sup>-</sup> and PdCl<sub>6</sub><sup>-</sup> ions. A tabular presentation of the data is available.<sup>2</sup> The PdCl<sub>4</sub><sup>-</sup> data were obtained from solutions 0.118, 0.0118 and 0.00237 F in 0.998 F hydrochloric acid. A solution 9.08 ×  $10^{-3}$  F in K<sub>2</sub>PdCl<sub>6</sub>, 0.106 F in chlorine and 0.998 F in hydrochloric acid was compared to a similar chlorine, hydrochloric acid solution to obtain the PdCl<sub>6</sub><sup>-</sup> data.

As regards positions and intensities of absorption maxima, the results of the PdCl<sub>4</sub><sup>-</sup> solutions agree well with those of Samuel and Despande<sup>16</sup> for a solution of  $K_2$ PdCl<sub>4</sub> in potassium chloride of unspecified concentration. For  $K_2$ PdCl<sub>6</sub> in hydrochloric acid of unspecified concentration, these

(16) R. Samuel and A. R. R. Despande, Z. Physik, 80, 395 (1933).



Fig. 2.—Extinction coefficients ( $\epsilon = (1/lc) \log_{10}(I_0/I)$  liter/ mole cm.) of PdCl<sub>4</sub><sup>-</sup>, PdCl<sub>6</sub><sup>-</sup>, PtCl<sub>6</sub><sup>-</sup>, PtCl<sub>6</sub><sup>-</sup>.

authors report an absorption maximum at 280 m $\mu$  as well as those obtained in the present research. This was probably due to some PdCl<sub>4</sub>-formed according to the reaction

$$PdCl_{6}^{-} \rightarrow PdCl_{4}^{-} + Cl_{2} \tag{1}$$

The equilibrium data of Wellman<sup>17</sup> ( $K = 2.4 \times 10^{-4}$ ) give the ratio of (Pd<sup>II</sup>/Pd<sup>IV</sup>) as 2.5  $\times 10^{-3}$  for the solution used by us.

The following procedure was used to investigate the possibility of interaction absorption in mix-tures of PdCl<sub>4</sub><sup>-</sup> and PdCl<sub>6</sub><sup>-</sup>. A solution of palladium(II) chloride in 0.998 F hydrochloric acid was oxidized and saturated with chlorine. A blank of 0.998 F hydrochloric acid was found to be 0.106F in chlorine; and the oxidizing titer of the palladium solution minus that of the blank indicated  $(Pd^{Iv}) = 0.905$ . The spectrum of a sample of this solution was measured in the 540-620 m $\mu$  range using a 0.010 cm. cell length. The solution was then extracted four times with equal volumes of carbon tetrachloride, in order to remove chlorine and drive reaction (1) to the right. The composition was then 0.53 F palladium(IV) and 0.37F palladium(II) (calculated free chlorine, 3.5  $\times 10^{-4}$  F). The optical densities of this solution corresponded with 1% with those predicted, using Beer's law, from the light absorptions of the components. The extinction coefficients of palladium(IV) determined from the fully chlorinated solution described above agreed within 1% with those obtained from the 9.08  $\times$  10<sup>-3</sup> F PdCl<sub>6</sub>solution in 0.998 F hydrochloric acid using a 1.0 cm. cell. This is somewhat surprising, because the total amount of chloride in the concentrated

(17) H. B. Wellman, THIS JOURNAL, 52, 985 (1930).

solution allows for a  $(Cl^{-I}/Pd^{IV})$  ratio of only 5.1:1 whereas the dilute solutions contained presumably PdCl<sub>6</sub><sup>=</sup> ions.

A mixture of equal volumes of 1.47 F platinum (II) chloride (containing 0.058 F PtCl<sub>6</sub>) in ca. 6 F hydrochloric acid and 2.0 F H<sub>2</sub>PtCl<sub>6</sub> in 1.0 Fhydrochloric acid had the same optical density as the sum of one-half of the optical densities of the two component solutions in the wave length region 430-560 m $\mu$ . Similarly, Beer's law applied to a 1:1 mixture of 0.234 F palladium(II) chloride and 2.0 F H<sub>2</sub>PtCl<sub>6</sub>, each in 1.0 F hydrochloric acid. The absorption spectra of the platinum solutions are illustrated in Fig. 2.

### Discussion

The marked dichroism of the substance Pd- $(NH_3)_2Cl_2 \cdot M(NH_3)_2Cl_4$  (M = Pd or Pt) is consistent with the view that these have the same structure as that of  $Pt(NH_3)_2Br_2 \cdot Pt(NH_3)_2Br_4$ determined by Brosset, so that there is a chain  $-M^{II} - Cl - M^{IV} - Cl - M^{II} - Cl - M^{IV}$ , along the needle axis of the crystal. Anomalous and strong light absorption due to the oscillation of electrons between the atoms in the +2 and +4oxidation states under the influence of the electric vector of the light would occur only for light polarized with the electric vector along this axis. This should also be the axis of highest refractive index. It may be mentioned that crystal structure investigations of these substances in these laboratories to be published separately confirm this point of view. (For the larger crystals where the strong absorption was for light perpendicular to the needle axis, it is possible that the crystals have grown differently, and the c axis in this case is not the needle axis.) In view of the difference in the H-IV oxidation potentials for platinum and palladium (ca. -0.7 and -1.3 v.) one would expect, as observed, that the mixed platinum-palladium compound would be less colored than the palladium -palladium compound.

The magnetic studies, while not very precise, show that the palladium compound does not contain any unpaired electrons and hence no independent palladium(II) kernels. Syrkin and Belova<sup>18</sup> have reported that the substances PtCl<sub>3</sub>, Pt(H2NCH2CH2NH2)Cl3 and Pt(NH3)2Cl2(OH) are diamagnetic although they are formally compounds of tripositive platinum. The latter compound has been reported to be strongly dichroic.<sup>19</sup> Janes<sup>20</sup> reports that the compound of palladium(III), "[Pd(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>]<sub>2</sub>" is diamagnetic, and we suppose that this refers to Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>·Pd(NH<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub>.

The non-occurrence of interaction absorption in solution shows that similar strongly colored polymers or dimers do not form, even in solutions which contain rather high concentrations of palladium-(II) and palladium(IV) or platinum(IV). It might be supposed that in solutions containing excess free chloride ion, the planar PdCl4<sup>=</sup> ion would form two weaker bonds to chlorides in directions perpendicular to the plane, and that this effect would inhibit the formation of the chains illustrated above responsible for the strong coloration. However, this could not have been the case for the solutions studied which contained less chloride than that required for the formation of PdCl<sub>4</sub><sup>-</sup> and PdCl<sub>6</sub><sup>-</sup> ions.

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(18) Ya. K. Syrkin and V. I. Belova, Zhur. Fiz. Khim., 23, 664 (1949); C. A., 43, 7277 (1949).
(19) G. B. Bokil and G. I. Distler, Doklady Akad. Nauk S. S. S. R.,

56, 923 (1947); C. A., 43, 3683 (1949)

(20) R. B. Janes, This Journal, 57, 471 (1930).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

#### XXXII. The Solvolysis and Intramolecular Rearrangement Allylic Rearrangements. of $\alpha, \alpha$ -Dimethylallyl Chloride<sup>1</sup>

### By W. G. YOUNG, S. WINSTEIN AND HARLAN L. GOERING<sup>2</sup>

The acetolysis of  $\alpha, \alpha$ -dimethylallyl chloride (I) involves simultaneous solvolysis and intramolecular isomerization to primary chloride  $\gamma, \gamma$ -dimethylallyl chloride (II).

$$(CH_3)_2 CHClCH = CH_2 \xrightarrow{k_1} (CH_3)_2 C = CH - CH_2 Cl \xrightarrow{k_p} \text{ solvolysis products}$$

$$I \qquad II \qquad k_T$$

The kinetics have been treated so as to obtain the rate constants  $k_1$ ,  $k_T$  and  $k_p$ . The possibility of a common intermediate for solvolysis and rearrangement of I is suggested and discussed.

In connection with a general investigation of the kinetics and products of replacement reactions of allylic compounds, we have scrutinized the acetolysis of  $\alpha, \alpha$ -dimethylallyl chloride (I) and  $\gamma, \gamma$ dimethylallyl chloride (II). During this investigation it developed that a rearrangement of the

(1) Presented before the Organic Division of the American Chemical Society, Philadelphia, April, 1950.

$$\begin{array}{ccc} CH_3 & CH_3 \\ | \\ CH_3 - C - CH = CH_2 & CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - C = CH - CH_2C1 \\ | \\ CH_3 - CH_3 \\ | \\ C$$

tertiary chloride I to the primary isomer II proceeds concurrently with the solvolysis of the tertiary chloride and that it was possible to treat the kinetics of the simultaneous acetolysis and

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