

# The Structure of Platinum Oxides

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TABLE I. Reaction of methyl radical with hydrogen isotopes.

Reaction	$P_1/P_2^{\frac{1}{2}} \times 10^3$	$E_1 - \frac{1}{2}E_2$ kcal
$\text{CH}_3 + \text{H}_2$	0.7	9.2
$\text{CH}_3 + \text{D}_2$	3.5	11.7
$\text{CD}_3 + \text{H}_2$	2.5	10.2
$\text{CD}_3 + \text{D}_2$	2.0	10.9

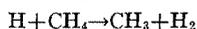
it is thus possible to arrive at the value of the activation energy difference  $E_1 - \frac{1}{2}E_2$ . Since  $E_2$  is almost certainly  $\approx 0$ , this is equivalent to the direct evaluation of  $E_1$ . Similarly, a value is obtained for the ratio of the steric factors  $P_1/P_2^{\frac{1}{2}}$ , and since  $P_2$  is now known with reasonable certainty,  $P_1$  can be evaluated approximately. In this way the values in Table I have been obtained. The values of the activation energies in Table I are reliable to within about 0.3 to 0.4 kcal. The results indicate that the substitution of deuterium for hydrogen causes an increase in activation energy of the order of magnitude of the zero-point energy difference. The substitution of  $\text{CD}_3$  for  $\text{CH}_3$  makes relatively little difference.

In view of the compensating errors in  $E$  and  $P$ , somewhat more reliable conclusions regarding the isotope effect can be drawn from a consideration of velocity constant ratios,  $k_1/k_2^{\frac{1}{2}}$  at a given temperature. Thus at  $210^\circ\text{C}$ , in the middle of the temperature range used, we have for these ratios

$$\left. \begin{aligned} \frac{\text{CH}_3 + \text{H}_2}{\text{CH}_3 + \text{D}_2} &= 3.3 \\ \frac{\text{CD}_3 + \text{H}_2}{\text{CD}_3 + \text{D}_2} &= 3.5 \end{aligned} \right\} \text{Average 3.4,}$$

$$\left. \begin{aligned} \frac{\text{CH}_3 + \text{H}_2}{\text{CD}_3 + \text{H}_2} &= 0.71 \\ \frac{\text{CH}_3 + \text{D}_2}{\text{CD}_3 + \text{D}_2} &= 0.74 \end{aligned} \right\} \text{Average 0.7.}$$

From the value of the activation energy of the reaction of  $\text{CH}_3$  with  $\text{H}_2$ , and the bond dissociation energies  $D(\text{CH}_3-\text{H})$  and  $D(\text{H}-\text{H})$ , the activation energy of the reverse reaction



is calculated to be  $7.0 \pm 1.3$  kcal. It seems impossible to stretch the limits of error sufficiently to reconcile this with the known slowness of the reaction of H-atoms with methane unless the steric factor for this reaction is of the order of  $10^{-3}$  or less.

Full details, together with the results of experiments on the reaction of methyl radicals with HD will appear later.

\* National Research Council Postdoctorate Fellow, 1950-51.

### The Crystal Structure of Formic Acid\*

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OSCILLATION and precession diagrams of single crystals of formic acid have been obtained at  $-45^\circ\text{C}$  using filtered Cu and Mo radiation. The low temperature x-ray camera and techniques used in investigation have been described elsewhere.<sup>1</sup>

The diagrams were indexed on the basis of an orthorhombic unit cell with  $a_0 = 10.22\text{A}$ ,  $b_0 = 3.62\text{A}$ , and  $c_0 = 5.34\text{A}$ , all dimensions  $\pm 0.03\text{A}$ . The volume of the unit cell is  $198\text{A}^3$ . The assumption that there are four molecules per unit cell leads to an x-ray density of 1.54. This is in reasonable good agreement with the density computed by extrapolating from the known density of the liquid at room temperature (1.24) to that of the solid at  $-45^\circ\text{C}$ .

Reflections of the following types were systematically absent: (*hol*) with  $h$  odd and (*okl*) with  $k$  plus  $l$  odd. The most probable

space groups are therefore Pna and Pnam. The latter can be ruled out on steric grounds.

The arrangements of molecules in the unit cell consistent with space group Pna appear to preclude the possibility that the molecules are associated as dimers in the crystal. Preliminary calculations indicate that the molecules are arranged in the crystal in the form of infinite chains, each molecule being linked to two neighbors by hydrogen bonds. It is interesting to note that the results of a recent study of the dielectric polarization of solid formic acid have been interpreted as being incompatible with a structure having dimeric molecules as the only units.<sup>2</sup>

A detailed account of the complete structure determination will be published in the near future.

\* This work supported by the ONR.

<sup>1</sup> Post, Schwartz, and Fankuchen, Rev. Sci. Instr. **22**, 218 (1951).

<sup>2</sup> J. F. Johnson and R. H. Cole, J. Am. Chem. Soc. **73**, 4536 (1951).

### The Structure of Platinum Oxides

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(Received July 26, 1951)

RECENTLY, J. Waser and McClanahan<sup>1</sup> have given the structure of a platinum compound prepared by the method of Jørgensen.<sup>2</sup> They put forward the formula  $\text{Pt}_3\text{O}_4\text{Na}$  for this compound. We have studied the product obtained by Jørgensen's method since 1941, trying to check the formula  $\text{Pt}_3\text{O}_4$  given by Galloni and Roffo<sup>3</sup> to an oxide found on a Pt wire. The two substances proved to be different. Our x-ray patterns of Jørgensen's oxide are identical with that reported by Waser and McClanahan. As a matter of fact, we have been unable to find a reasonable structure for this compound, the chemical composition of which has not been conclusively established.

In spite of the fact that the structural evidence favoring the formula  $\text{Pt}_3\text{O}_4\text{Na}$  is very satisfying, we think this formula is not possible because the compound *does not contain sodium*.

We have made a spectroscopic examination of the compound, using Hilger's spectrograph E 1, checking the spectrum obtained with that resulting from a solution containing 0.0025 mg percent sodium acetate. The persistent doublets 3302.3-3303 and 5889-5890 were selected for comparison. In the sodium acetate solution they appear very intense, but they are absent in the arc spectrum of the compound. Consequently, it is possible to state that Jørgensen's oxide does not contain appreciable amounts of sodium to fit the formula  $\text{Pt}_3\text{O}_4\text{Na}$ , which would require some 3 percent sodium.

In a footnote (p. 455), Waser and McClanahan express the opinion that the pattern reported by R. H. Busch<sup>4</sup> as being characteristic for  $\text{PtO}_2$  may belong to  $\text{PtO}$ , basing their argument on a paper by Moore and Pauling.<sup>5</sup> They also state that the oxide studied by Galloni and Roffo<sup>3</sup> was not  $\text{Pt}_3\text{O}_4$  but  $\text{PtO}_2$ . These two statements are, however, untenable, for the following reasons:

(1)  $\text{PtO}_2$  is a well-known substance, extensively used in organic synthesis, easy to prepare, not very difficult to analyze, and impossible to confuse with any other oxide. The analysis of  $\text{PtO}_2$  including determination of Pt, oxygen, and water gives results consistent with the formula  $\text{PtO}_2$  within a few per thousands. The x-ray pattern of this substance, prepared by the method of Vorhees and Adams,<sup>6</sup> washing out the Pt with aqua regia and washing thoroughly with water and drying, belongs to an hexagonal structure,  $c = 4.19\text{A}$ ,  $a = 3.08\text{A}$ ,  $c/a = 1.36$  (Busch, Cairo, Galloni, and Raskovan).<sup>7</sup> We may add that this is a fact, not an opinion. The same pattern has been observed by Finch, Murison, Stuart, and Thomson<sup>8</sup> by means of electron diffraction. The white tetrahydrate of  $\text{PtO}_2$ , added into fused  $\text{NaNO}_3$ , gives the same pattern. The dioxide dihydrate obtained by anodic oxidation by Altmann and Busch,<sup>9</sup> heated for a long time at  $350^\circ\text{C}$ , gives the same pattern, as does the oxide obtained by the method of Pigeon.<sup>10</sup> If  $\text{PtO}_2$  is prepared at low temperatures, it gives no pattern. The

properties and the x-ray pattern of PtO<sub>2</sub> are both dependent on the heat treatment.

(2) *The substance studied by Moore and Pauling<sup>6</sup> was probably not PtO.* They write: "PdO was prepared by the method of Shriner and Adams<sup>11</sup> involving fusing palladous chloride and potassium nitrate; and PtO by a similar method." . . . "The data are not sufficient to permit a rigorous structure determination to be made for PtO, but the similarity to the PdO photographs makes it highly probable that platinumous oxide has the PdO structure . . ."

The existence of PtO is questioned in Gmelin's handbook.<sup>12</sup> Wöhler and Frey<sup>13</sup> discuss the preparation of this compound and its easy oxidability. We think the method of Shriner and Adams<sup>11</sup> applied to H<sub>2</sub>PtCl<sub>4</sub> (because PtCl<sub>2</sub> is insoluble) would give PtO<sub>2</sub>, because of the oxidizing properties of fused KNO<sub>3</sub>. Moore and Pauling have not analyzed the compound obtained, so it is difficult to find out what they have actually studied.

In conclusion, the structure given for PtO is not supported by sufficient experimental evidence. It is doubtful if the authors prepared PtO or not.

(3) *It is possible to prepare the hydrate of PtO by the method of Wöhler and Frey.<sup>13</sup>* The dehydration of this compound gives an oxide whose composition fits well the formula PtO. The x-ray pattern is platinum-like. The only difference is that the parameters of PtO are slightly enlarged with respect to Pt. Chemically, the oxide cannot be confused with platinum because it is insoluble in aqua regia, and its density is very much lower (lying between 11.5 and 14 g/cm<sup>3</sup>). In the course of a great number of preparations of this substance, we have never found the lines reported by Moore and Pauling.

(4) *On some occasions, we have prepared the platinum oxide studied by Galloni and Roffo and have found the formula Pt<sub>3</sub>O<sub>4</sub> together with the x-ray pattern reported by them.* It has been obtained by thermal decomposition of hydrated PtO<sub>2</sub>, but it has not been possible to find a reproducible method of preparation, in spite of very numerous experiments. In two instances the right oxide has appeared, but the conditions upon which its preparation depend are not clear to us.

In conclusion, for the reasons given, we think that the compound studied by Waser and McClanahan is not Pt<sub>3</sub>O<sub>4</sub>Na, that the hexagonal pattern reported by Busch is caused by PtO<sub>2</sub>, that the pattern reported by Galloni and Roffo is caused by Pt<sub>3</sub>O<sub>4</sub>, and finally, that the structure given to PtO by Moore and Pauling is open to discussion. Even the existence of anhydrous PtO is open to discussion.

We are indebted to Dr. J. Winkel for obtaining the spectrograms.

<sup>1</sup> J. Waser and E. McClanahan, *J. Chem. Phys.* **19**, 413 (1951).

<sup>2</sup> S. M. Jørgensen, *J. prakt. Ch.* **16**, 344 (1877).

<sup>3</sup> E. E. Galloni and A. E. Roffo, *J. Chem. Phys.* **9**, 875 (1941).

<sup>4</sup> R. H. Busch, *Z. Naturforschung* **5a**, 130 (1950).

<sup>5</sup> W. J. Moore and L. Pauling, *J. Am. Chem. Soc.* **63**, 1392 (1941).

<sup>6</sup> R. Vorhees and R. Adams, *J. Am. Chem. Soc.* **44**, 1397 (1922).

<sup>7</sup> Busch, Cairo, Galloni, and Raskovan, 14a. Reunión de la Asociación Física Argentina, La Plata (1949).

<sup>8</sup> Finch, Murison, Stuart, and Thomson, *Proc. Roy. Soc. (London)* **A 141**, 414 (1933).

<sup>9</sup> S. Altman and R. H. Busch, *Trans. Faraday Soc.* **45**, 720 (1949).

<sup>10</sup> L. Pigeon, *Ann. chim. et phys.* (7), **2**, 480 (1894).

<sup>11</sup> Shriner and R. Adams, *J. Am. Chem. Soc.* **46**, 1684 (1924).

<sup>12</sup> Gmelin, *Handbuch der anorganischen Chemie*, eighth edition (1938), Vol. 68, part C.

<sup>13</sup> L. Wöhler and W. Frey, *Z. Elektrochem.* **15**, 133 (1909).

The presence of sodium in our compound was inferred from the following facts. An electron density projection showed the presence of a concentration of scattering matter of approximately the correct magnitude for one Na-atom per each four O-atoms. This peak could not have been caused by breaking-off errors since the Pt-contributions had been subtracted from the observed *F*'s. Thus our projection contained neither Pt peaks nor the subsidiary features which ordinarily accompany large peaks and are caused by termination of the Fourier series. The analogous breaking-off features of the oxygen peaks are correspondingly smaller and have a negligible effect on the sodium peak. The inclusion of a scattering contribution from Na at the positions 2a of O<sub>h</sub><sup>3</sup> significantly improved the agreement between calculated and observed intensities. The presence of Na further explains the ionic conductivity observed by us and the sodium content Wöhler reported for his preparations.<sup>3</sup>

However, as indicated in our paper, the compound NaPt<sub>3</sub>O<sub>4</sub> need not be of stoichiometric nature as far as sodium is concerned. The Na-atoms (or ions) are situated in holes formed by cubes of O-atoms, and the number of holes filled in various preparations may vary. The further possibility of filling the holes with other suitable cations exists.

Our findings may thus be reconciled with those of Galloni and Busch<sup>1</sup> by assuming the existence of a whole series of compounds of the formula Na<sub>x</sub>Pt<sub>3</sub>O<sub>4</sub>, 0 ≤ x ≤ 1, all having the same framework of Pt and O-atoms described in our paper.<sup>3</sup> A more detailed investigation is, however, required to clear up completely this question of solubility of Na and possibly other cations in Pt<sub>3</sub>O<sub>4</sub>.

We have now had the opportunity to analyze for sodium our original very small sample of Na<sub>x</sub>Pt<sub>3</sub>O<sub>4</sub> which had been used in the x-ray experiments. The sample was treated with strong HCl containing KI followed by boiling with aqua regia. Only a portion of the sample went into solution, the exact amount dissolved being unknown. Analysis with a Beckman flame spectrophotometer showed that the original sample contained 1.3 percent Na or more. As reported previously our preparation had been extracted several times with hot aqua regia to remove traces of Pt. The Na is therefore presumed to be part of the compound.

We wish to thank Dr. R. V. Talmage for the use of the flame spectrophotometer.

<sup>1</sup> E. E. Galloni and R. H. Busch, *J. Chem. Phys.* **19**, 198 (1951).

<sup>2</sup> J. Waser and E. D. McClanahan, Jr., *J. Chem. Phys.* **19**, 413 (1951).

<sup>3</sup> L. Wöhler, *Z. anorg. u. allgem. Chem.* **40**, 450 (1904).

## Carrier-Free Radioisotopes from Cyclotron Targets. XXIV. Preparation and Isolation of Ir<sup>188, 190, 192</sup> from Osmium\*

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**B**OMBARDMENT of osmium with 19-Mev deuterons produces, by (*d*, 2*n*) and (*d*, *n*) reactions, several relatively long-lived, known, radioactive isotopes of iridium:<sup>1,2</sup> *viz.*, Ir<sup>187</sup>, Ir<sup>188</sup>, two isomers of Ir<sup>190</sup>, and Ir<sup>192</sup>. Radioisotopes of rhenium and osmium are also produced concurrently in relatively low yield by (*n*, *p*) and (*d*, *p*) reactions. This paper reports a method for isolation of iridium activities from irradiated osmium without the addition of stable iridium carrier.

The target was osmium metal powder (*ca.* 0.5g) in which no iridium (less than 0.01 percent) was detected by spectrographic analysis. The osmium powder was held on a grooved, water-cooled target plate by a 0.25-mil platinum foil during bombardment in the 60-inch Crocker Laboratory cyclotron.

After bombardment the osmium powder was dissolved, with heating, in a minimal amount of aqua regia. Excess nitric acid was added and the solution was heated to dryness to distill off the osmium tetroxide. Two milliliters of nitric acid were added and

## The Structure of Na<sub>2</sub>Pt<sub>3</sub>O<sub>4</sub>

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**I**N the preceding note Galloni and Busch<sup>1</sup> report the results of a spectroscopic analysis of a platinum oxide similar to the compound recently investigated by us.<sup>2</sup> While their compound apparently did not contain significant amounts of sodium, we had assigned the formula NaPt<sub>3</sub>O<sub>4</sub> to our preparation.