Redetermined Lattice Constants of PtP$_2$, PtAs$_2$, PtSb$_2$, and α-PtBi$_2$

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A number of compounds have earlier been prepared and investigated in the binary systems between platinum and elements of group V in the periodic table. Compounds with composition metal : metalloid = 1 : 2 are found in all systems, except the platinum-nitrogen system, where no intermediate compounds are known at present. The compounds PtP$_2$, PtAs$_2$, PtSb$_2$, and α-PtBi$_2$ have been studied by means of X-ray methods and all of them have structures of the pyrite ($C2$) type.

Platinum diphosphide was first prepared by Davey [1]. The structure was established by Thomassen [2] and later confirmed by Biltz *et al.* [3] and Rundqvist [4].

Platinum diarsenide was first synthesized by Gehlen [5]. It occurs in nature as the mineral sperrylite. The structural identity of sperrylite and artificial PtAs$_2$ was established by Ramsdell [6] and De Jong [7] by means of X-rays. The structure of PtAs$_2$ has later been investigated by Aminoff and Parsons [8] and Thomassen [2].

Platinum diantimonide was first obtained by Roessler [9]. The structure, *i.e.*, its lattice constant and atomic parameter, was determined by Thomassen [10].

Platinum dibismuthide was also first prepared by Roessler [9]. The crystal structure was established by Wallbaum [11] and its correctness later confirmed by Zhuravlev and Kertes [12]. By thermal, metallographic and X-ray studies these authors found the existence of one more PtBi$_2$ phase, β-PtBi$_2$, which was found to be hexagonal.

The *alloys* were prepared by heating accurately weighed quantities of platinum and phosphorus, arsenic, antimony or bismuth, respectively, in evacuated and sealed silica tubes. In each system alloys with 25.00, 33.33 and 40.00 atomic % platinum were made. All samples were heated at 650°C for 30 days and cooled slowly to room temperature over a period of another 30 days.

All samples were crushed and X-ray powder photographs taken in cameras with 114.6 mm effective diameter and asym-

Table 1. Lattice constants of PtP$_2$, PtAs$_2$, PtSb$_2$, and α-PtBi$_2$.

Sample	a (Å)	Reference
PtP$_2$	5.6956 ± 0.0005	Present
	5.694 ± 0.004	Thomassen [2]
	5.694	Rundqvist [4]
PtAs$_2$	5.9665 ± 0.0004	Present
	5.97	Ramsdell [6]
	5.95 (sperrylite)	Ramsdell [6]
	5.93 (sperrylite)	De Jong [7]
	6.01 (sperrylite)	Aminoff and Parsons [8]
	5.969 ± 0.003	Thomassen [2]
PtSb$_2$	6.4400 ± 0.0004	Present
	6.441 ± 0.003	Thomassen [10]
α-PtBi$_2$	6.7022 ± 0.0006	Present
	6.696 ± 0.005	Wallbaum [11]

metric film mounting. The lattice constants, which were found by extrapolation according to the method of Nelson and Riley [13], are expressed in Ångström units on the basis of λ Cu$K\alpha_1$ = 1.54050 Å. Results from earlier investigations expressed in kX-units have been transformed to Å by multiplication by the factor 1.00202.

The lattice constants of the samples with composition PtX$_2$ are found in Table 1 together with the previous lattice constant values. The lattice constants of the different compounds are found to be independent of the composition of the alloys within the experimental error, indicated by the limits in Table 1. Thus, the homogeneity ranges of the phases are supposedly rather narrow. The earlier data agree well within their limited accuracy except for α-PtBi$_2$.

The redetermination of the atomic parameters in these compounds will be discussed in a forth-coming paper.

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5. Gehlen, A. F. *Journal f. Chem. u. Phys.* **20** (1817) 353.
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7. De Jong, W. F. *Physica* **5** (1925) 292.
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9. Roessler, F. *Z. anorg. Chem.* **9** (1895) 31.
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12. Zhuravlev, N. N. and Kertes, L. *Zhur. Eksp. i Teoret. Fiz.* **32** (1957) 1313; *Soviet Physics JEPT* **5** (1957) 1073.
13. Nelson, J. B. and Riley, D. P. *Proc. Phys. Soc. (London)* **57** (1945) 160.

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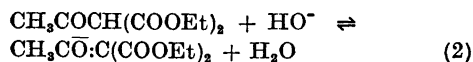# The Alkaline Hydrolysis of Diethyl Acetomalonate

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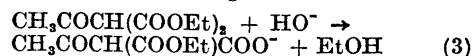*Chemical Laboratory, Royal Veterinary and Agricultural College, Copenhagen, Denmark*

When diethyl acetomalonate is dissolved in an aqueous solution of a strong base it will react with 3 hydroxyl ions according to the scheme

$$CH_3COCH(COOEt)_2 + 3 HO^- \rightarrow CH_2(COO^-)_2 + CH_3COO^- + 2 EtOH \quad (1)$$
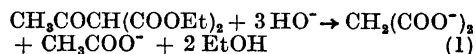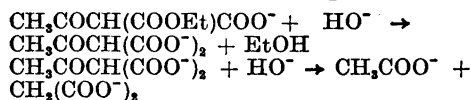
One hydroxyl ion disappears immediately, while the other two are consumed at a measurable rate which is proportional to the ester concentration but independent of the hydroxyl ion concentration. This experimental result is explained as follows. The keto-form of the diethyl ester is rapidly and nearly completely transformed into enolate ion by the balanced reaction

$$CH_3COCH(COOEt)_2 + HO^- \rightleftharpoons CH_3C\bar{O}:C(COOEt)_2 + H_2O \quad (2)$$

The rate-determining reaction is

$$CH_3COCH(COOEt)_2 + HO^- \rightarrow CH_3COCH(COOEt)COO^- + EtOH \quad (3)$$

It is followed by the two rapid reactions

$$CH_3COCH(COOEt)COO^- + HO^- \rightarrow CH_3COCH(COO^-)_2 + EtOH$$
$$CH_3COCH(COO^-)_2 + HO^- \rightarrow CH_3COO^- + CH_2(COO^-)_2$$

The rate of reaction 3 will be proportional to the product of the hydroxyl ion concentration and the concentration of the keto-form of the diethyl ester, but since the latter, according to scheme 2, is inversely proportional to the hydroxyl ion concentration, the rate will be independent of the hydroxyl ion concentration and of first order with respect to the total concentration of diethyl acetomalonate (keto-form and enolate ion).

Diethyl acetomalonate was prepared according to Lund [1] and was distilled twice under reduced pressure in an all-glass apparatus fitted with a Widmer stillhead. The fraction used in the experiments distilled within less than 1°C. It was found that the ester could be titrated as a monobasic acid when thymolphthalein was used as indicator and a rather strongly blue colour was chosen as end-point. The average of several titrations was that 99.7 % of the calculated amount of base was used. When the ester is dissolved in an excess of strong base, it will therefore be rapidly and nearly completely transformed into enolate ion by reaction 2.

To 60 ml of 0.2 N barium hydroxide in a glass-stoppered flask was added 0.8 g of the ester. The clear solution was left at room temperature. After half an hour the first crystals were noticed, and the next day a large crystalline precipitate had been formed. The crystals were isolated by suction, washed with ice-cold water, and air-dried to constant weight. It was shown that they did not contain carbonate, from which it is concluded that no decarboxylation takes place in the reaction. In order to show that the crystals consisted of barium malonate this substance was prepared by mixing solutions of malonic acid and barium acetate. The crystals obtained here were isolated and dried in the same way as before. Weighed amounts of the two preparations were transformed into carbonate by ignition in a platinum crucible, and the residues were weighed. On the assumption that one molecule of both substances gives one molecule of barium carbonate, it was found that the molecular weight of the substance prepared from diethyl acetomalonate was 254.5 while that of the salt prepared from malonic acid was 255.0 (calc.