

## QUALITATIVE AND QUANTITATIVE CHARACTERIZATION OF THE REACTION LEADING TO THE FORMATION OF $K_2[Pd_2(OAc)_6]$ IN A NON-AQUEOUS MEDIUM (MIXTURE OF GLACIAL ACETIC ACID AND ACETIC ANHYDRIDE)

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**Abstract:** The methods of the ultraviolet-visible (UV-VIS) spectroscopy were used to study the reaction between trimeric palladium acetate and potassium acetate in a mixture of glacial acetic acid and acetic anhydride. When the palladium acetate : potassium acetate mole ratio is higher than 1:150, the reaction leads to the formation of  $K_2[Pd_2(OAc)_6]$  ( $OAc^-$  stands for  $CH_3COO^-$ ). The spectrophotometric data were used to estimate the equilibrium constant  $K$  for the studied reaction. At a temperature of 297 K ( $\pm 1$  K) it was found that  $K = 1.663 \cdot 10^3 \text{ mol}^{-5} \cdot \text{dm}^{15}$ , the corresponding  $s$  value being  $0.376 \cdot 10^3 \text{ mol}^{-5} \cdot \text{dm}^{15}$ .

### Introduction

The reactions leading to the formation of complex palladium(II) compounds of the  $M_2[Pd_2(OAc)_6]$  type have already been followed in glacial acetic acid medium. In the above-mentioned reaction products  $M$  could be K or Na [1, 2], as well as Li [1] or ammonium [3]. Since, to the best of our knowledge, such reactions have not been carried out in any other solvent, we deemed it worthwhile to investigate the reaction between potassium acetate and palladium(II) acetate in a different medium. To facilitate comparisons with the known data (especially those contained in ref. 2), we decided to work in an equimolar mixture of glacial acetic acid and acetic anhydride. Such a mixture is expected to behave in a way similar to that of glacial acetic acid, but the presence of water would be completely excluded and some other properties (such

as the polarities of the two solvents) may also differ. The experimental conditions were practically identical with those described in our previous paper [2].

### Experimental

Three series of solutions of palladium(II) acetate in equimolar mixtures of glacial acetic acid and acetic anhydride were prepared. In each series the palladium(II) acetate concentration was kept constant ( $8.24 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ,  $1.09 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$  and  $1.21 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ) while the potassium acetate concentration was gradually changed so that the Pd : OAc mole ratio varied from 1 : 1 up to 1 : 500. The UV-VIS spectrum for each of the solutions was measured in the 190–500 nm region. The spectra were recorded immediately after the preparation of the solutions and then at one hour intervals up to twelve hours after the preparation of the solutions. In the following 30 days the measurements were repeated every 24 hours. The solutions were then checked once a week until the end of a three month period.

At selected wavelengths (350 and 365 nm) the absorbance values were determined for each solution and subsequently used during the calculation of the equilibrium constants. Solutions with a known palladium(II) acetate concentration ( $2.52 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ ,  $2.71 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ , and  $3.15 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$  respectively) were separately prepared. For each of these solutions the absorbance was measured at 350 and 365 nm and the values thus obtained were used to estimate the values for the absorption coefficients of palladium(II) acetate [denoted hereafter  $\epsilon_T$ , T standing for the trimer,  $\text{Pd}_3(\text{CH}_3\text{COO})_6$  or, for short,  $\text{Pd}_3(\text{OAc})_6$ ]. The corresponding values for the dimeric reaction product ( $\epsilon_D$ ) were determined in a similar manner, by measuring the absorbance values of the systems in which the palladium-to-acetate mole ratio was 1 : 200. These values were determined nine hours after the reactants were mixed.

All measurements were carried out at 297 K ( $\pm 1$  K) on a Perkin-Elmer 137 UV and Beckman DU 2 instruments.

### Results and discussion

#### 1. Qualitative characterization of the reaction

The UV-VIS spectrum of palladium(II) acetate dissolved in an equimolar mixture of glacial acetic acid and acetic anhydride is shown in Fig. 1. As can be seen, two bands are observed in the region studied. One of them is found at  $\approx 402$  nm whereas the exact position of the band at shorter wavelengths is difficult to determine since the cut-off region of acetic anhydride extends up to 287 nm. In any case, it does seem that it appears at wavelengths longer than 253 nm, this latter value being the one found [2] for the analogous band in the case of the glacial acetic acid solution where it was attributed to an

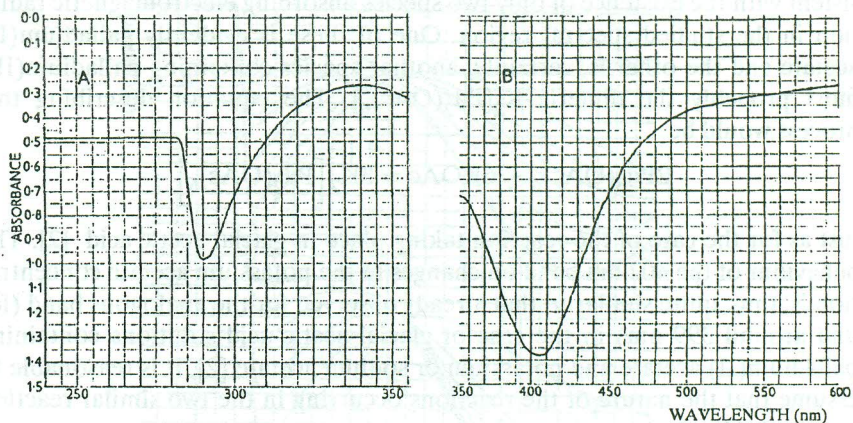


Fig. 1 – Ultraviolet (A) and visible (B) spectrum of palladium(II) acetate in an equimolar mixture of glacial acetic acid and acetic anhydride [ $c(\text{Pd}_3(\text{OAc})_6 = 2.35 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ )]

$L(\sigma) - M$  transition. Because of the uncertainties involved, the band at  $\leq 287$  nm will not be considered any further.

There are no appreciable changes in the appearance of the spectra on increasing the potassium acetate concentration up to a palladium : acetate mole ratio of 1 : 10. When this ratio is further increased, the 402 nm band starts to gain in intensity and to shift towards shorter wavelengths, its final position being  $\approx 365$  nm. This value is reached (in solutions with a palladium : acetate ratio of 1 : 150) after eight hours. As can be seen in Fig. 2, all spectral curves pass through an isobestic point located around 322 nm. Such a finding is con-

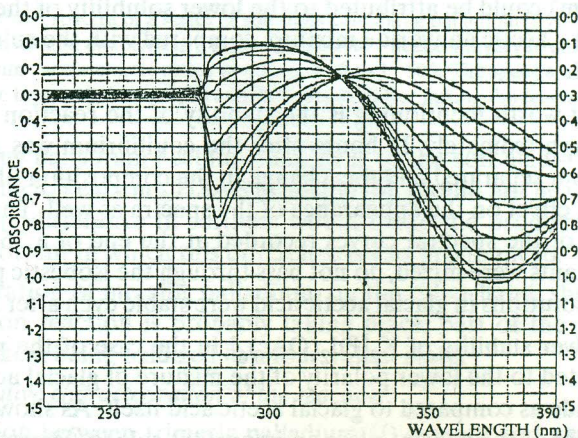


Fig. 2 – Ultraviolet spectra (recorded 8 hours after mixing the reactants) of a series of solutions containing palladium(II) acetate and potassium acetate dissolved in a mixture of glacial acetic acid – acetic anhydride. The palladium : acetate mole ratios vary from 1 : 0 to 1 : 500

sistent with the existence of only two species absorbing electromagnetic radiation in the studied spectral region. One of these is evidently palladium(II) acetate and the other is, certainly, another species containing palladium(II), most probably the dimeric  $K_2[Pd_2(OAc)_6]$ . The equation describing this process would be



just as for the case of the reaction taking place in glacial acetic acid [2]. The behaviour of the 402 nm band on changes in the potassium acetate concentration is, thus, quite similar to that already observed for the analogous band (found around 399 nm) in the case of glacial acetic acid solutions containing palladium(II) acetate and potassium or sodium acetate [2], it is reasonable to assume that the nature of the reactions occurring in the two similar reaction systems is identical.

It should be noted, however, that in the presently studied case the reaction seems to proceed more slowly and the final equilibrium is reached after eight hours (rather than after 30 minutes as was found when the reaction was carried out in glacial acetic acid [2]). As pointed out by Yatsimirskii and Ryabov [4] the breaking out of the acetate bridges present in the trimeric palladium acetate is a result of the combined action of acetate anions and acetic acid. Since the relative amount of acetic acid in the present case is approximately one half of that existing in the systems studied in [2], it is easy to understand the lower reaction rate between palladium(II) acetate and potassium acetate in a mixture of glacial acetic acid and acetic anhydride, as compared with the case of solutions in glacial acetic acid alone. Some other differences (e.g. a higher OAc : Pd ratio needed to start the reaction or to reach the equilibrium) could be attributed to the lower solubility of the reactants in the acetic acid – acetic anhydride mixture, compared with the solutions in glacial acetic acid.

A point worth mentioning is the stability of the reaction product. On standing for approximately 24 hours after the equilibrium was reached, colloidal palladium separated and the change in the composition of the reaction system had an effect on the appearance of the spectra as well. Thus, as seen in Fig. 3c, some of the spectral curves recorded at the end of a 36 hour period after the reactants were mixed, do not pass through the isobestic point. On the contrary, the solutions in glacial acetic acid were stable even after 3 months [2].

The lower stability of  $K_2[Pd_2(OAc)_6]$  in the case of the present study can be attributed to the lower polarity of the mixture of glacial acetic acid and acetic anhydride as compared to glacial acetic acid itself. As shown by Pearson [5], the polarity of the solvent plays an important role in determining the degree of softness (or hardness) of the acids and bases and it is possible that the present solvent increases the difference in the softness between palladium and

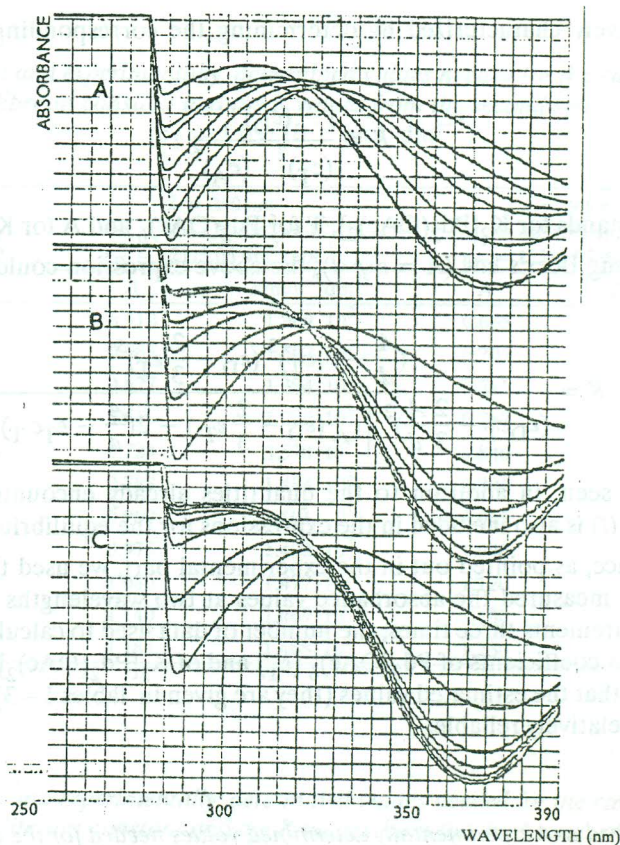


Fig. 3 – Ultraviolet spectra of a series of solutions containing palladium(II) acetate and potassium acetate dissolved in a glacial acetic acid – acetic anhydride mixture. The palladium : acetate mole ratios vary from 1 : 0 to 1 : 500. The spectra were recorded one hour (A), 8 hours (B) and 36 hours (C) after mixing the reactants.

acetates. Since any palladium acetate complex is of the soft acid – hard base type and, according to Pearson's HSAB principle [6], should not be very stable, an increase of the difference in softness would make the product even less stable than in a solvent in which this difference is less pronounced.

The separation of metallic palladium, on the other hand, shows that a disproportionation reaction is probably taking place, part of the palladium present in the system being oxidized to a four-valent state.

### 2. Quantitative characterization of the reaction

The reaction between trimeric palladium(II) acetate and an excess of acetate ions in a mixture of glacial acetic acid and acetic anhydride could be

quantitatively characterized by determining the corresponding equilibrium constant:

$$K = \frac{(c_D)^3}{(c_T)^2 \cdot (c_A)^6}$$

where D stands for  $K_2[Pd_2(OAc)_2]$ , T for  $Pd_3(OAc)_6$  and A for KOAc.

Using Beer's law ( $A = \epsilon \cdot c \cdot l$ ), the above expression could be rewritten as:

$$K = \frac{\left(\frac{A}{d} - \epsilon_T c_T\right)^3 \left(\epsilon_D - \frac{2}{3} \epsilon_T\right)^5}{\left(\epsilon_D c_T - \frac{2}{3} \frac{A}{d}\right)^2 \left[c_A \left(\epsilon_D - \frac{2}{3} \epsilon_T\right) - 2\left(\frac{A}{d} - \epsilon_T c_T\right)\right]^6}$$

As seen, in addition to the quantities already encountered, the cell thickness ( $l$ ) is also included in the expressions for the equilibrium constants.

Since, as pointed out in the experimental part, we used three series of solutions, measured the absorbance values at two wavelengths and repeated the measurements three times, the number of data used to calculate the molar absorption coefficients of  $Pd_3(OAc)_6$  ( $\epsilon_T$ ) and of  $K_2[Pd_2(OAc)_2]$  ( $\epsilon_D$ ) was sufficient, so that the estimated values (they are given in Tables 1–3) can be taken as being relatively reliable.

Table 1

Measured and experimentally determined values needed for the calculation of the equilibrium constant and the  $K$  values from the first series of solutions ( $c_T = 8.24 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ )

$c_A$ mol dm <sup>-3</sup>	$\lambda = 350 \text{ nm}$		$\lambda = 365 \text{ nm}$	
	$\epsilon_T = 3513.32 \text{ dm}^2 \text{ mol}^{-1}$		$\epsilon_T = 4695.25 \text{ dm}^2 \text{ mol}^{-1}$	
	$\epsilon_D = 12115.06 \text{ dm}^2 \text{ mol}^{-1}$		$\epsilon_D = 12361.92 \text{ dm}^2 \text{ mol}^{-1}$	
	$A$	$K/\text{mol}^{-3} \text{ dm}^{15}$	$A$	$K/\text{mol}^{-3} \text{ dm}^{15}$
0.033	0.412	$2.933 \cdot 10^3$	0.502	$2.883 \cdot 10^3$
0.037	0.420	$1.771 \cdot 10^3$	0.518	$2.170 \cdot 10^3$
0.041	0.451	$1.901 \cdot 10^3$	0.545	$2.143 \cdot 10^3$
0.045	0.480	$1.869 \cdot 10^3$	0.570	$2.143 \cdot 10^3$
0.049	0.523	$2.241 \cdot 10^3$	0.597	$1.899 \cdot 10^3$
0.058	0.575	$1.818 \cdot 10^3$	0.646	$1.770 \cdot 10^3$
0.066	0.630	$1.569 \cdot 10^3$	0.695	$1.531 \cdot 10^3$
0.074	0.693	$1.510 \cdot 10^3$	0.748	$1.435 \cdot 10^3$
0.082	0.735	$1.476 \cdot 10^3$	0.792	$1.419 \cdot 10^3$
0.091	0.805	$1.473 \cdot 10^3$	0.845	$1.368 \cdot 10^3$
0.099	0.858	$1.467 \cdot 10^3$	0.890	$1.356 \cdot 10^3$

Table 2

Measured and experimentally determined values needed for the calculation of the equilibrium constant and the  $K$  values from the second series of solutions ( $c_T = 1.09 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ )

$\frac{c_A}{\text{mol dm}^{-3}}$	$\lambda = 350 \text{ nm}$		$\lambda = 365 \text{ nm}$	
	$\varepsilon_T = 3513.32 \text{ dm}^2 \text{ mol}^{-1}$ $\varepsilon_D = 12115.06 \text{ dm}^2 \text{ mol}^{-1}$	$K/\text{mol}^{-5} \text{ dm}^{15}$	$\varepsilon_T = 4695.25 \text{ dm}^2 \text{ mol}^{-1}$ $\varepsilon_D = 12361.92 \text{ dm}^2 \text{ mol}^{-1}$	$K/\text{mol}^{-5} \text{ dm}^{15}$
0.033	0.512	$1.969 \cdot 10^3$	0.635	$2.039 \cdot 10^3$
0.044	0.585	$1.502 \cdot 10^3$	0.705	$1.565 \cdot 10^3$
0.049	0.627	$1.394 \cdot 10^3$	0.745	$1.450 \cdot 10^3$
0.054	0.666	$1.229 \cdot 10^3$	0.787	$1.360 \cdot 10^3$
0.060	0.724	$1.578 \cdot 10^3$	0.840	$1.429 \cdot 10^3$
0.065	0.788	$1.484 \cdot 10^3$	0.895	$1.492 \cdot 10^3$
0.076	0.900	$1.501 \cdot 10^3$	0.965	$1.414 \cdot 10^3$
0.087	0.975	$1.482 \cdot 10^3$	1.040	$1.408 \cdot 10^3$
0.098	1.080	$1.477 \cdot 10^3$	1.120	$1.402 \cdot 10^3$
0.109	1.140	$1.469 \cdot 10^3$	1.180	$1.394 \cdot 10^3$
0.120	1.185	$1.468 \cdot 10^3$	1.230	$1.139 \cdot 10^3$

Table 3

Measured and experimentally determined values needed for the calculation of the equilibrium constant and the  $K$  values from the third series of solutions ( $c_T = 1.21 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ )

$\frac{c_A}{\text{mol dm}^{-3}}$	$\lambda = 350 \text{ nm}$		$\lambda = 365 \text{ nm}$	
	$\varepsilon_T = 3513.32 \text{ dm}^2 \text{ mol}^{-1}$ $\varepsilon_D = 12115.06 \text{ dm}^2 \text{ mol}^{-1}$	$K/\text{mol}^{-5} \text{ dm}^{15}$	$\varepsilon_T = 4695.25 \text{ dm}^2 \text{ mol}^{-1}$ $\varepsilon_D = 12361.92 \text{ dm}^2 \text{ mol}^{-1}$	$K/\text{mol}^{-5} \text{ dm}^{15}$
0.036	0.678	$2.497 \cdot 10^3$	0.810	$2.645 \cdot 10^3$
0.048	0.779	$1.992 \cdot 10^3$	0.915	$2.241 \cdot 10^3$
0.054	0.830	$1.872 \cdot 10^3$	0.975	$1.976 \cdot 10^3$
0.060	0.885	$1.623 \cdot 10^3$	1.030	$1.821 \cdot 10^3$
0.066	0.949	$1.527 \cdot 10^3$	1.080	$1.691 \cdot 10^3$
0.073	1.015	$1.458 \cdot 10^3$	1.137	$1.660 \cdot 10^3$
0.085	1.180	$1.411 \cdot 10^3$	1.230	$1.511 \cdot 10^3$
0.097	1.269	$1.398 \cdot 10^3$	1.332	$1.398 \cdot 10^3$
0.109	1.325	$1.396 \cdot 10^3$	1.420	$1.386 \cdot 10^3$
0.121	1.370	$1.392 \cdot 10^3$	1.500	$1.372 \cdot 10^3$
0.133	1.422	$1.389 \cdot 10^3$	1.545	$1.345 \cdot 10^3$

Even more data were accumulated for the absorbances needed to calculate the equilibrium constants (66 absorbance values altogether). These values, as well as those for the calculated equilibrium constants, are also included in Tables 1-3.

A closer examination of these data makes it possible to conclude that the agreement between the calculated  $K$  values is certainly not perfect. In order to check whether these values are statistically reliable, the asymmetry (or scewness) of their distribution was calculated using the  $g_1$  statistics [6]. The calculated value for  $g_1$  (0.487) shows that there is indeed a positive asymmetry of the distribution but that for the accumulated number of data (66) it is tolerable [7] and the real distribution could be approximated by the normal one.

The hypotheses :

$$H_0 : \sigma_1^2 = \sigma_2^2 = \sigma_3^2 \quad \text{and} \quad H_a : \sigma_1^2 \neq \sigma_2^2 \neq \sigma_3^2$$

was tested by using the  $F$  statistical test [7] applicable for data obtained in several series of measurements. The test showed that at a significance level of 5% and for 63 degrees of freedom, the individual values for the equilibrium constants belong to the same population. Consequently, a common average value could be derived from all individual ones. The confidence intervals for different probabilities were also calculated. The results are given in Table 4.

Table 4

*The confidence intervals for  $K/\text{mol}^{-5} \text{dm}^{15}$  for various probabilities*

$p$	90 %	95 %	99 %
$\frac{K \cdot 10^3}{\text{mol}^{-5} \text{dm}^{15}}$	$1.663 \pm 0.343$	$1.663 \pm 0.410$	$1.663 \cdot 0.545$

According to the general practice, the value obtained for a 95% probability is considered as optimal. At a temperature of 297 K ( $\pm 1$  K), the value for the equilibrium constant thus obtained was  $1.663 \cdot 10^3 \text{ mol}^{-5} \cdot \text{dm}^{15}$ , the standard deviation being  $s = 0.376 \cdot 10^3 \text{ mol}^{-5} \cdot \text{dm}^{15}$ .



## REFERENCES

- [1] R. N. Pandey and P. M. Henry, *Can. J. Chem.*, **52** (1974) 1241.  
 [2] L. Šoptrajanova and I. Spirevska, *Bull. Chem. Technol. Macedonia*, **11** (1992), 11–17.  
 [3] Л. Шоптрајанова и Т. Тодоровски, *Год. Зборник Хем. Фак. Унив. Скопје*, **31** (1981) 43.  
 [4] А. К. Яцимирский, А. Д. Рябов, *Ж. Неорг. Хим.*, **22** (1977) 1863.  
 [5] R. G. Pearson, *J. Chem. Educ.*, **45** (1968) 581.  
 [6] R. Caulcut and R. Boddy, *Statistics for Analytical Chemists*, Chapman and Hall, New York, 1983.  
 [7] А. И. Герасимович, *Математическая статистика*, 2-е изд., Высшая школа, Минск, 1983.

## Резиме

**КВАЛИТАТИВНА И КВАНТИТАТИВНА КАРАКТЕРИЗАЦИЈА НА РЕАКЦИЈАТА ШТО ВОДИ КОН ОБРАЗУВАЊЕ НА  $K_2[Pd_2(OAc)_6]$  ВО НЕВОДНА СРЕДИНА (СМЕСА ОД ГЛАЦИЈАЛНА ОЦЕТНА КИСЕЛИНА И АНХИДРИД НА ОЦЕТНА КИСЕЛИНА)**

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Методите на ултравиолетовата (UV) и видливата (VIS) спектроскопија се употребени при изучувањето на реакцијата меу тримерниот паладиум ацетат и калиум ацетат во смеса од оцетна киселина и анхидрид на оцетна киселина.

Кога молскиот однос меѓу калиум ацетат и паладиум ацетат е поголем од 150 : 1, реакцијата доведува до образување на  $K_2[Pd_2(OAc)_6]$  (тука  $OAc^-$  означува  $CH_3COO^-$ ).

Спектрофотометриските податоци се ползувани за да се процени вредноста за константата на рамнотежа  $K$  на изучуваната реакција. Најдено е дека на температура од 297 K ( $\pm 1$  K) константата на рамнотежата изнесува  $K = 1.663 \cdot 10^3 \text{ mol}^{-3} \cdot \text{dm}^3$ , со вредност за стандардната девијација  $s = 0.376 \cdot 10^3 \text{ mol}^{-3} \cdot \text{dm}^3$ .