STUDY OF SOLID-PHASE REACTION BETWEEN $CsNO_3$ AND V_2O_5 IN THE MOLAR RATIO 6 : 5

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Using DTA, DTG and TG methods, the solid-phase reaction between $CsNO_3$ and V_2O_5 in the molar ratio 6 : 5 has been studied in oxygen and air streams in the temperature range 20—550°. The reaction proceeds stepwise and CsV_3O_8 has been identified as an intermediate. A mixture of $CsVO_3$ and $Cs_2V_4O_{11}$ is formed as final product of the reaction at 520°. The composition of this mixture does not change up to 1000°.

The solid-phase reactions in V_2O_5 — alkaline metal salt systems have been investigated and various phase diagrams have been constructed in many papers. The essential results of these papers are summarized in the monograph of Fotiev and Ivakin [1].

It is possible to use solid-phase reactions under defined conditions even for preparation of certain polyvanadates, e.g. pentavanadates. $K_3V_5O_{14}$ was prepared by the reaction of KNO_3 and V_2O_5 in the appropriate ratio at 500° [2], and identified in the $KVO_3-V_2O_5$ system [3]. Similarly, $Rb_3V_5O_{14}$ was identified in the $RbVO_3-V_2O_5$ system [4]. The above pentavanadates may be obtained by the reactions of V_2O_5 with the corresponding metal nitrates or carbonates, respectively in the appropriate stoichiometric ratio [1]. Thus, $Tl_3V_5O_{14}$ was obtained from the solid-phase reaction of $TlNO_3$ and V_2O_5 at 550° [5]. Caesium pentavanadate has not been unambiguously proved to exist; its existence was not indicated by the phase diagram of $Cs_2CO_3(Cs_2O)-V_2O_5$ [1, 6, 7]. On the other hand, the possibility of its preparation by the dehydration of $Cs_6V_{10}O_{28} \cdot xH_2O$ has been mentioned [8].

The solid-phase reaction between $CsNO_3$ and V_2O_5 in the molar ratio corresponding to pentavanadate was studied so as to ascertain the possibility of caesium pentavanadate preparation.

Experimental

V_2O_5 was prepared by the thermal decomposition of NH_4VO_3 in an oxygen stream. $CsNO_3$ was recrystallized three times. The substances were dried at 120° before reaction and sieved through a sieve with 4900 mesh/cm². The mixture of $CsNO_3 + V_2O_5$ in the molar ratio 6 : 5 was prepared just before the reaction. Measurements were made in a Pt crucible or on Pt-plates in an air or an oxygen stream, with a derivatograph (MOM, Hungary). The weighed amounts of mixtures

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were 600 mg on Pt plates and 300 mg in a Pt crucible, respectively. The temperature ranges varied (max. 20—1000°). Sensitivities: DTA 1/5, DTG 1/10, TG 100 mg; heating-rate 5°/min.

The products obtained at various temperature were left to cool to 20° in a suitable stream and identified by X-ray phase-analysis Phillips X-ray diffractometer, PW 1058 goniometer, $Cu_{K\alpha}$ radiation, by I.R. spectroscopy (Perkin Elmer 567 instrument) using the nujol technique, and by chemical analysis. Caesium was determined by flame-photometry (Flame-photometer III, C. Zeiss, Jena), vanadium(V) was determined volumetrically, and vanadium (IV) was detected by E.P.R. (E.P.R. spectrometer ER-9, C. Zeiss, Jena).

Results and discussion

Thermal synthesis

The thermal curves of the reaction between $CsNO_3$ and V_2O_5 in the molar ratio 6 : 5 in an air stream are shown in Figs 1 and 2.

The endothermic process with maximum at 152° (Fig. 1) is connected with the structural transformation of $CsNO_3$; this was also found in the DTA curve of $CsNO_3$. The weight loss starts at 235°. The further courses of the DTA, DTG and TG curves indicate the gradual character of the reaction. The course of the reaction was studied on Pt plates in order to obtain a better differentiation of the individual
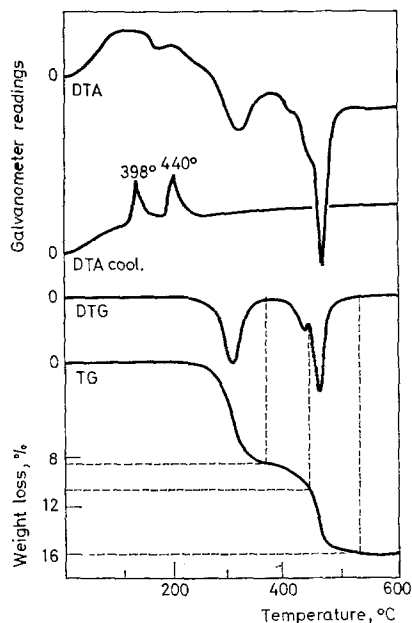

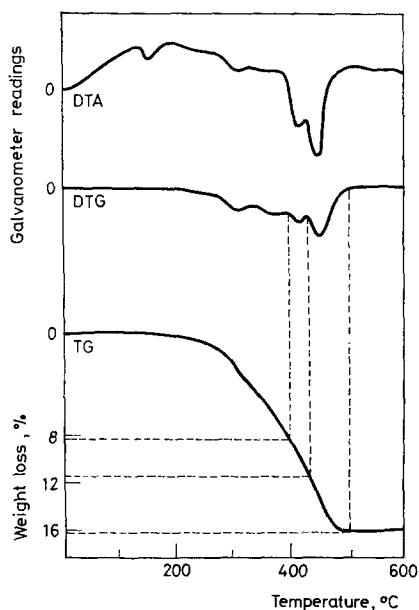Fig. 1. TG, DTG and DTA curves of the reaction performed in a Pt crucible

Fig. 2. TG, DTG and DTA curves of the reaction performed on Pt plates

reaction steps (Fig. 2). From the DTA and DTG curves the beginning of five reaction steps follow immediately after the structural transformation of the $CsNO_3$. The gradual character of the TG-curve is not as expressive as in a Pt crucible. On the other hand, there is a good agreement of the weight losses at the same temperatures in the both cases.

Vanadium (IV) was not detected in the products obtained by interrupting the reaction at 390°, nor in the final ones at 520°, in neither an air nor an oxygen stream. The weight losses and the overall courses of the reactions were similar, too. Accordingly, the thermal curves obtained in an oxygen stream are not presented in this paper; the reaction was studied in greater detail only in air.

Analysis of reaction products

I.R. spectroscopy and X-ray phase-analysis proved the intermediates obtained at 330, 390 and 420°, respectively, as well as the final product, to be mixtures.

An intermediate of the reaction interrupted at 330° (Fig. 3a, Table 1) is a mixture of CsV_3O_8 with unreacted starting compounds. An intermediate at 390° unambiguously contains CsV_3O_8 and $CsNO_3$. According to the stoichiometric reaction (weight loss approx. 8.0%), the intermediate should contain V_2O_5, too. However, it is not possible to prove this unambiguously from the X-ray pattern (Table 1). Its presence is only suggested by the I.R. spectra (Fig. 3b). The quantity of V_2O_5 is evidently less than the resolution limits of the both methods. In the two reaction steps exactly a half the mass of $CsNO_3$ reacts. A mixture of CsV_3O_8 and $CsNO_3$ is

also obtained at 420°, as follows from the X-ray phase-analysis. A new compound (denoted as phase X) starts to form at this temperature. It constitutes a substantial part of the final product of the reaction. CsV$_3$O$_8$ participates in its formation (Table 1). Another components, not identified as yet, occurs in a negligible amount
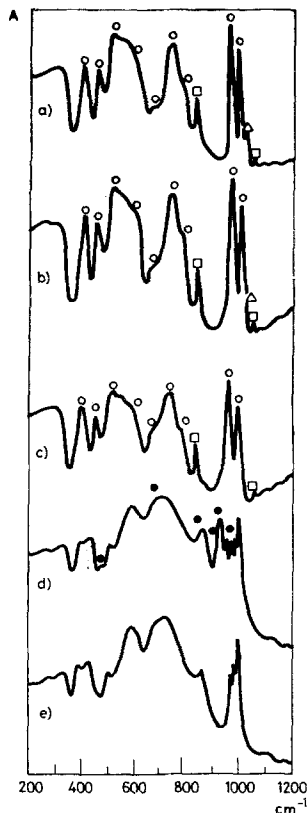

Fig. 3. I. R. spectra of the reaction products obtained at various temperatures: a: 330°, b: 390°, c: 420°, d: 520°, e: Cs$_2$V$_4$O$_{11}$, o absorption bands of CsV$_3$O$_8$, □ absorption bands of CsNO$_3$, △ absorption bands of V$_2$O$_5$, ● absorption bands of CsVO$_3$

at all temperatures investigated. Its content decreases with increasing temperature. It can be stated that this is none of the known caesium vanadates.

The weight loss stops at about 520°. Its value (16%) is in good agreement with the theoretical one (15.6%) and corresponds to the reaction of the total amount of CsNO$_3$. The product of the reaction is a two-component mixture of CsVO$_3$ with phase X (Fig. 3d, Table 1). There are two exothermic maxima in the DTA cooling curve of the mixture, namely at 398 and 440° (Fig. 1). The first one corresponds to the structural transformation of CsVO$_3$ [7]. The exothermic process

at 440° is connected neither with the structural transformation nor with the melting point of any known caesium vanadate. This value is close to the temperature of the structural transformation of Cs_3VO_4 [7]. However, the diffraction pattern excludes the presence of caesium orthovanadate in the mixture.

The final product is yellow coloured. It is possible to isolate phase X (yellow, too) as $CsVO_3$ is well soluble in water; this involves repeatedly washing the mixture with water and multiple decantation. Chemical analysis showed that phase X contains 41.10% Cs and 31.88% V(V). These values correspond to the general formula $Cs_2V_4O_{11}$ (Cs_c = 41.17%, $V(V)_c$ = 31.57%). It is evident from the I.R. spectrum (Fig. 3e) that the substance is a polymer. This is proved by the occurrence of the pronounced maxima in the region $400-700$ cm^{-1} (bridging vibrations of $V-O-V$). The diffraction pattern of $Cs_2V_4O_{11}$ may be seen in Table 1.

$Cs_2O \cdot 2 V_2O_5(Cs_2V_4O_{11})$ was found to exist in the narrow temperature range $380-446°$ [6]. This fact follows from the phase diagram of the $Cs_2CO_3(Cs_2O)-V_2O_5$ system. A thermooptical study of the $CsVO_3-V_2O_5$ system has demonstrated the presence of $Cs_2V_5O_{13.3}$ at higher temperature; $Cs_2V_4O_{11}$ does not occur [1]. However, the composition of $Cs_2V_5O_{13.3}$ requires the presence of V(IV). The results of the analysis of our compound do not agree with the prepared formula of the vanadium bronze. Neither the X-ray pattern nor the I.R. spectrum of this salt have been published. On the other hand, the I.R. spectrum of $K_2V_5O_{13.3}$ is known, but it differs substantially from the I.R. spectrum of our compound.

The X-ray patterns of two modifications of $Cs_2V_4O_{11}$ are published in paper [9]. With the expection of 0.354 nm, the interplanar distances of the orthorhombic modification have been observed in the X-ray pattern of the compound isolated from the mixture obtained at 520°. This diffraction appears only the X-ray patterns of the mixtures obtained at 700 and 1000°, respectively. In the X-ray pattern of our compound there are a greater number of weak diffractions mainly in the range of higher angles of Θ. This fact can be explained as a consequences of the different experimental conditions.

The compound obtained at 500° by the isothermal reaction of a mixture of $CsNO_3$ and V_2O_5 in the molar ratio 1 : 1 in an oxygen stream has the same composition and X-ray pattern as the compound isolated from the final product (at 520°). On the basis of these results, we propose that the product obtained at 520° from the reaction of $CsNO_3$ and V_2O_5 in the molar ratio 6 : 5 is a mixture of $CsVO_3$ and $Cs_2V_4O_{11}$.

According to [6], $Cs_2V_4O_{11}$ is stable in only a narrow temperature range ($380-446°$). The mixture of $CsVO_3$ and $Cs_2V_4O_{11}$ was therefore heated to 1000°. We assumed that under these conditions its components could react giving caesium pentavanadate. The heating was performed on a derivatograph and isothermically at 700 and 1000°, both in an oxygen and in an air stream. It was found that $CsVO_3$ and $Cs_2V_4O_{11}$ did not react. For completion, we have to add that in the case of isothermal heating traces of V(IV) were found in the mixture. However, the amount of V(IV) was so slight that it influenced neither the diffraction pattern nor the I.R. spectrum of $Cs_2V_4O_{11}$ isolated from this mixture.

Table 1

Interplanar distances, nm

330°a	390°a	420°a	520°a	$Cs_2V_4O_{11}$	V_2O_5 [1]	$CsNO_3^b$	$CsVO_3^b$	$CsV_3O_8^b$
0.804 w.	0.804 w.	0.442 m.	0.539 w.	0.495 w.	0.581 m.	0.443 s.	0.537 w.	0.811 v.w.
0.579 w.	0.584 w.	0.424 w.	0.490 w.	0.425 w.	0.438 v.s.	0.313 v.s.	0.490 v.s.	0.584 v.w.
0.573 w.	0.495 w.	0.404 w.	0.421 w.	0.357 v.s.	0.411 m.	0.256 v.s.	0.420 w.	0.494 v.w.
0.489 w.	0.444 m.	0.391 w.	0.405 m.	0.286 m.	0.341 s.	0.222 w.	0.404 m.	0.441 v.w.
0.470 w.	0.426 w.	0.376 w.	0.376 m.	0.282 v.s.	0.288 s.	0.199 s.	0.375 m.	0.425 v.w.
0.447 w.	0.405 m.	0.365 m.	0.354 v.s.	0.260 m.	0.279 m.	0.182 v.s.	0.332 v.s.	0.405 w.
0.441 m.	0.392 w.	0.353 w.	0.331 v.s.	0.251 v.w.	0.271 w.	0.157 m.	0.326 w.	0.393 v.w.
0.432 w.	0.376 m.	0.329 w.	0.325 m.	0.247 w.	0.261 m.		0.306 m.	0.376 v.w.
0.423 m.	0.365 v.s.	0.322 s.	0.307 m.	0.243 v.w.	0.218 w.		0.289 m.	0.366 m.
0.416 w.	0.330 m.	0.313 v.s.	0.290 m.	0.229 w.	0.217 m.		0.284 w.	0.330 w.
0.404 m.	0.323 v.s.	0.308 m.	0.284 s.	0.223 w.	0.192 w.		0.270 s.	0.323 v.s.
0.390 w.	0.314 v.s.	0.300 w.	0.280 v.s.	0.220 w.	0.189 w.		0.266 m.	0.308 w.
0.375 m.	0.308 s.	0.293 m.	0.271 m.	0.191 m.	0.177 m.		0.255 v.w.	0.301 w.
0.365 v.s.	0.300 m.	0.283 v.w.	0.267 w.	0.178 v.w.	0.176 m.		0.239 m.	0.294 w.
0.338 w.	0.293 s.	0.279 v.w.	0.260 v.s.	0.176 w.	0.165 m.		0.225 w.	0.271 v.w.
0.329 m.	0.271 v.w.	0.271 v.w.	0.256 w.	0.174 w.	0.156 m.		0.216 w.	0.268 v.w.
0.321 v.s.	0.268 w.	0.268 v.w.	0.250 v.w.	0.173 w.	0.151 m.		0.210 w.	0.258 v.w.
0.313 v.s.	0.256 m.	0.256 w.	0.247 w.	0.164 w.	0.149 m.		0.208 v.w.	0.248 w.
0.307 m.	0.248 w.	0.248 w.	0.244 w.	0.163 w.	0.144 m.		0.196 w.	0.246 w.
0.299 m.	0.246 m.	0.245 w.	0.240 w.				0.191 w.	0.238 v.w.
0.293 m.	0.238 w.	0.238 v.w.	0.230 m.				0.178 v.w.	0.221 v.w.
0.291 w.	0.235 v.w.	0.222 w.	0.226 v.w.				0.174 w.	0.215 w.
0.275 v.w.	0.222 m.	0.214 w.	0.220 m.				0.170 v.w.	0.206 v.w.
0.270 v.w.	0.215 m.	0.213 v.w.	0.219 w.				0.166 v.w.	0.203 v.w.

Table 1

Interplanar distances, nm

330°a	390°a	420°a	520°a	$Cs_2V_4O_{11}$	V_2O_5 [1]	$CsNO_3^b$	$CsVO_3^b$	$CsV_3O_8^b$
0.267 v.w.	0.206 w.	0.206 v.w.	0.211 w.					0.196 v.w.
0.256 m.	0.203 w.	0.203 v.w.	0.208 v.w.					0.190 v.w.
0.247 w.	0.199 m.	0.199 w.	0.195 v.w.					0.183 v.w.
0.245 m.	0.196 w.	0.195 v.w.	0.191 m.					0.178 v.w.
0.238 w.	0.190 w.	0.190 v.w.	0.178 v.w.					0.174 v.w.
0.222 w.	0.184 w.	0.187 v.w.	0.174 w.				0.164 v.w.	0.165 v.w.
0.214 w.	0.182 w.	0.183 v.w.	0.173 w.				0.160 w.	0.162 v.w.
0.206 w.	0.178 v.w.	0.181 w.	0.172 m.				0.156 v.w.	0.159 v.w.
0.203 w.	0.175 v.w.	0.178 v.w.	0.170 v.w.					0.157 v.w.
0.198 w.	0.174 w.	0.174 v.w.	0.166 v.w.					0.154 v.w.
0.195 v.w.	0.166 w.	0.165 v.w.	0.163 m.					
0.190 w.	0.162 v.w.	0.162 v.w.	0.161 v.w.					
0.183 v.w.	0.159 v.w.	0.157 v.w.	0.160 v.w.					
0.181 w.	0.157 w.	0.154 v.w.	0.155 v.w.					
0.178 v.w.	0.154 v.w.							
0.174 v.w.								
0.173 v.w.								
0.156 w.								
0.162 v.w.								
0.159 v.w.								
0.157 v.w.								
0.154 v.w.								

a = products were obtained by interruption of the reaction 6 $CsNO_3$ + 5 V_2O_5, at the indicated temperatures.

b = diffraction patterns were obtained in our Department.

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RÉSUMÉ — On a étudié par ATD, TGD et TG, la réaction en phase solide entre CsNO₃ et V₂O₅ avec le rapport molaire de 6 : 5, dans un courant d'oxygène et d'air, dans l'intervalle de températures compris entre 20 et 550°. La réaction s'effectue par étapes et on a identifié CsV₃O₈ comme produit intermédiaire. Lors de la réaction à 520°, un mélange de CsVO₃ et Cs₂V₄O₁₁ se forme comme produit final. La composition de ce mélange ne varie pas jusqu'à 1000°.

ZUSAMMENFASSUNG — Unter Anwendung der Methoden DTA, DTG und TG wurde die Festphasenreaktion von CsNO₃ und V₂O₅ im Molverhältnis von 6 : 5 im Sauerstoff- und Luftstrom im Temperaturbereich von 20 bis 550° untersucht. Die Reaktion verläuft stufenweise und CsV₃O₈ wurde als Zwischenprodukt identifiziert. Als Endprodukt der Reaktion bei 520° bildete sich ein Gemisch von CsVO₃ und Cs₂V₄O₁₁. Die Zusammensetzung dieses Gemisches ändert sich bis 1000° nicht.

Резюме — Используя методы ДТА, ДТГ и ТГ, была изучена реакция в твердой фазе соединений CsNO₃ и V₂O₅ при их молярном соотношении 6 : 5 и проведенная в токе кислорода и воздуха в области температур 20—550°. Реакция протекает ступенчато и в качестве промежуточного продукта реакции было идентифицировано соединение CsV₃O₈. Конечным продуктом реакции при 520° была смесь CsVO₃ и Cs₂V₄O₁₁, состав которых не изменяется до 1000°.