STUDY OF SOLID-PHASE REACTION OF $RbNO_3$ WITH V_2O_5

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Using DTA, TG and DTG methods, the reaction between $RbNO_3$ and V_2O_5 in the molar ratio 6 : 5 in air atmosphere was studied. The reaction proceeds stepwise. In individual steps of the reaction the formation of RbV_3O_8, $RbVO_3$ and $Rb_3V_5O_{14}$ was observed. Rubidium pentavanadate is thermally unstable. At 1000°, $RbVO_3$ and $Rb_2V_4O_{11}$ were identified as products of its thermal decomposition. Rubidium tetravanadate was also prepared by the isothermal reaction of $RbNO_3$ with V_2O_5 in the molar ratio 1 : 1.

Under defined conditions, the solid-phase reactions of V_2O_5 with suitable salts are often used in the preparation of anhydrous vanadates of different compositions. In this way, potassium and thallium pentavanadates were prepared [1, 2]. As starting compounds, the corresponding nitrates were employed. A study of the $V_2O_5-RbVO_3$ phase diagram by thermooptical method led to the identification of $Rb_3V_5O_{14}$, which melts and decomposes at 390° [3].

Our aim was to find out whether it is possible to prepare rubidium pentavanadate by solid-phase reaction, and to identify the products of its thermal decomposition. Because of the relatively low melting point of $Rb_3V_5O_{14}$, the $RbNO_3-V_2O_5$ system was studied at the molar ratio corresponding to that needed for formation of the pentavanadate.

Experimental

V_2O_5 was prepared by thermal decomposition of NH_4VO_3. $RbNO_3$ was recrystallized three times. Both substances were dried at 120° before reaction, and were sifted through a sieve with 4900 mesh/cm². The mixtures of $RbNO_3$ and V_2O_5 with the molar ratios 6 : 5 and 1 : 1 were prepared just prior to the reactions.

The reactions were performed in an air stream, using Pt crucibles, on a derivatograph (MOM, Budapest). The weighed amounts of mixture were 300 mg and the temperature ranges varied (max. 20—1000°). Sensitivities: TG 100 mg, heating rate 5°/min. Isothermal reactions were studied in a crucible furnace.

The products obtained at individual temperatures were left to cool to 20° and then identified by X-ray phase analysis (Phillips X-ray diffractometer with PW 1058 goniometer, $Cu_{K\alpha}$ radiation), by IR spectroscopy (Perkin Elmer 567) using

the nujol technique, and by chemical analysis. Rubidium was determined by flame photometry (Flame photometer III, C. Zeiss, Jena and metal interference filter 799 nm were used).

Vanadium(V) was determined volumetrically ($0.1 N$ $FeSO_4$, diphenylamine). Vanadium(IV) was detected by EPR (EPR spectrometer ER-9, C. Zeiss, Jena).

Results and discussion

Thermal curves of the reaction between $RbNO_3$ and V_2O_5 in the molar ratio 6 : 5 are shown in Fig. 1.

The endothermic processes with maxima at 175 and 240° are connected with structural transformations of $RbNO_3$, which were observed even in the DTA curve of $RbNO_3$. The reaction proceeds in three steps, each characterized by endothermic processes, with maxima at 318, 438 and 465°, respectively. The reaction rate is the highest in the first step, which is significantly separated from the following two. The weight loss stops at 565°.

The observed total weight loss (18.3 %) is in agreement with the theoretical value (18.0 %) corresponding to the reaction of the total amount of $RbNO_3$. It follows from the weight losses in the individual steps that half of the total amount of $RbNO_3$ reacts in the first step, one-sixth in the second, and one-third in the third.

Analysis of reaction products

In order to identify the products of the individual reaction steps, the reaction was interrupted at 355, 455 and 505°, respectively. We also analyzed the substances formed at 600 and 1000°, although no weight loss occurred at these temperatures.

The presence of small amounts of vanadium(IV) was detected in all products obtained, even in the products of reaction in an oxygen stream. This is why the reaction was studied in more details only in an air stream.

It follows from the results shown in Table 1 that mixtures were obtained at each temperature. In the first reaction step, at 355°, RbV_3O_8 was formed; in the second one, at 455°, the formation of $RbVO_3$ was observed; and in the third endothermic

Table 1

Compositions of mixtures obtained at individual temperatures on the basis of X-ray phase analysis and IR spectra

T, °	Compositions of mixtures
355	RbV_3O_8 + $RbNO_3$ + traces of an unidentified compound
455	RbV_3O_8 + $RbVO_3$ + $RbNO_3$ + traces of an unidentified compound
505	$Rb_3V_5O_{14}$ + traces of $RbVO_3$ + traces of phase X
600	$Rb_3V_5O_{14}$ + $RbVO_3$ + phase X
1000	$RbVO_3$ + phase X
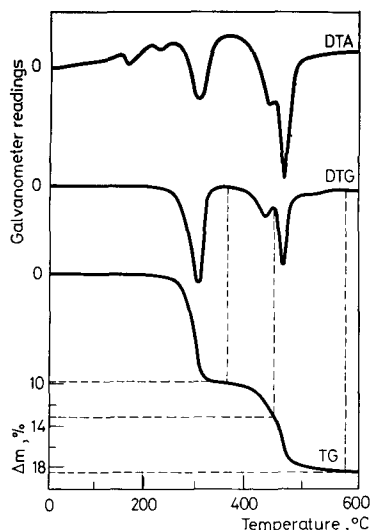
Fig. 1. Thermal curves of the reaction $RbNO_3 - V_2O_5$ with the molar ratio 6 : 5

process, at 505°, $Rb_3V_5O_{14}$ was identified as reaction product. A new compound (denoted phase X) was formed at 505, 600 and 1000°, respectively.

In an effort to prepare pure $Rb_3V_5O_{14}$ by the solid-phase reaction of $RbNO_3$ and V_2O_5, we performed a series of syntheses in the temperature range $480-600°$ (in steps of 5°), for the greatest amount of $Rb_3V_5O_{14}$ was found in the mixture obtained at 505° (Table 1). In each case, we obtained mixtures containing $Rb_3V_5O_{14}$ as the main constituent with unreacted portions of RbV_3O_8 and $RbVO_3$. At temperatures higher than 500°, $RbVO_3$ and phase X were identified as contaminants.

It follows from these results that the temperature at which the reaction of $RbNO_3$ and V_2O_5 was finished (weight loss stopped) is much too high for the formation of $Rb_3V_5O_{14}$ because of its thermal lability. Due to the solubility of $RbVO_3$ and phase X in water, it is possible to isolate $Rb_3V_5O_{14}$ from the mixture obtained at 505° after its thorough washing with water and subsequent decantation.

Pure $Rb_3V_5O_{14}$ could not be prepared even by the isothermal reaction in the crucible furnace in the temperature range $300-500°$. It was found experimentally that under these conditions the total amount of $RbNO_3$ reacts. The results of the isothermal study and those obtained by the study of the reaction using the dynamic method are identical.

The study of the thermal stability of $Rb_3V_5O_{14}$ (prepared from solution) showed that rubidium pentavanadate melts at 412° under the applied reaction conditions. As final products of its thermal decomposition, $RbVO_3$ and phase X were formed [4].

The identification of phase X was based on the presumption that the stoichiometry of thermal decomposition of $Rb_3V_5O_{14}$ requires phase X to be formulated as $Rb_2V_4O_{11}$:

$$Rb_3V_5O_{14} \xrightarrow{heat} RbVO_3 + Rb_2V_4O_{11} \qquad\qquad (A)$$
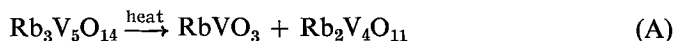
Our presumption was supported by the similarity of the IR-spectra and diffraction patterns of $CsVO_3 - Cs_2V_4O_{11}$ [5] and $RbVO_3$ − phase X mixtures, respectively.

In the case of cesium, $Cs_2V_4O_{11}$ was isolated from the mixture after dissolution of $CsVO_3$ by water. This was not possible in the case of rubidium, for the phase is also soluble in water.

For the preparation of $Rb_2V_4O_{11}$ a solid-phase reaction was used with the stoichiometry:

$$2\,RbNO_3 + 2\,V_2O_5 \xrightarrow{heat} Rb_2V_4O_{11} + 2\,NO_2 + 1/2\,O_2 \qquad\qquad (B)$$
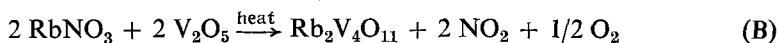
It was found that the isolation of $Rb_2V_4O_{11}$ is essentially influenced by the way in which it was cooled. $Rb_2V_4O_{11}$ was prepared after heating the reactants to $1000°$, then their gradual cooling in the furnace to $650°$, followed by rapid cooling in an air stream to $20°$.

The results of chemical analysis give the stoichiometric formula $Rb_2V_4O_{11}$ ($Rb_{exp} = 31.1\%$, $V_{exp} = 36.9\%$; $Rb_{theor} = 31.0\%$, $V_{theor} = 37.0\%$.

$Rb_2V_4O_{11}$ is yellow-brown compound. The IR spectrum (Fig. 2) indicates the polymeric nature of the compound, which is evidenced by the presence of absorp-
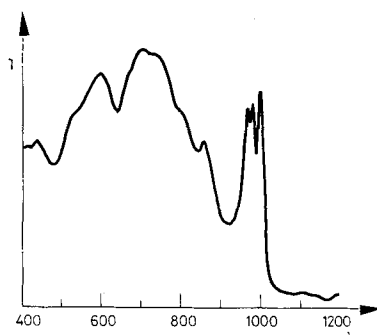

Fig. 2. The IR-spectrum of $Rb_2V_4O_{11}$

tion maxima in the range $500 - 800$ cm^{-1}, corresponding to the valence vibrations of the $V-O$ bonds in bridged $V-O-V$ groups.

The structural similarity of $Rb_2V_4O_{11}$ and $Cs_2V_4O_{11}$ follows from their diffraction patterns (Table 2) [5].

The published phase diagrams of $Rb_2O - V_2O_5$ show that $Rb_2V_4O_{11}$ has not been identified up till now. Only brief notes on its preparation from Rb_2SO_4 and V_2O_4 were found in the literature [6, 7].

Table 2

Interplanar distances of $Rb_2V_4O_{11}$

d, nm	0.493	0.347	0.345	0.283	0.278	0.247	0.243
I	s.	v. s.	v. s.	s.	v. s.	v. s.	w.
d, nm	0.220	0.218	0.215	0.186	0.185	0.173	0.171
I	m.	m.	w.	w.	m.	w.	w.
d, nm	0.170	0.163	0.160	0.157			
I	w.	w.	v. w.	m.			

v. s. — very strong, s. — strong, m. — medium, w. — weak, v. w. — very weak.

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RÉSUMÉ — On a étudié par ATD, TG et TGD dans l'air, la réaction $RbNO_3 - V_2O_5$ (rapport molaire 6 : 5). La réaction s'effectue par étapes, avec formation de RbV_3O_8, $RbVO_3$ et $Rb_3V_5O_{14}$. Le pentavanadate de rubidium est thermiquement instable. A 1000°, $RbVO_3$ et $Rb_2V_4O_{11}$ ont été identifiés comme produits de la décomposition thermique. Le tétravanadate de rubidium a également été préparé par voie isotherme en faisant réagir $RbNO_3 - V_2O_5$ (rapport molaire 1 : 1).

ZUSAMMENFASSUNG — Unter Anwendung der DTA-, TG- und DTG-Methoden wurde die Reaktion $RbNO_3 - V_2O_5$ bei dem Molverhältnis von 6 : 5 in Luft untersucht. Die Reaktion verläuft stufenweise. Bei den einzelnen Stufen der Reaktion wurde die Bildung von RbV_3O_8, $RbVO_3$ und $Rb_3V_5O_{14}$ beobachtet. Rubidiumpentavanadat ist thermisch instabil. Bei 1000° wurden $RbVO_3$ und $Rb_2V_4O_{11}$ als Produkte seiner thermischen Zersetzung beobachtet. Rubidiumtetravanadat wurde auch durch die isotherme Reaktion von $RbNO_3 - V_2O_5$ bei dem Molverhältnis von 1 : 1 hergestellt.

Резюме — Используя методы ДТА, ТГ и ДТГ, была изучена в атмосфере воздуха реакция $RbNO_3 - V_2O_5$ молярным соотношением реагентов 6 : 5. Реакция протекает ступенчато. На отдельных стадиях реакции наблюдали образование RbV_3O_8, $RbVO_3$ и $Rb_3V_5O_{14}$. Последнее соединение термически нестабильно и при 1000° были идентифицированы $RbVO_3$ и $Rb_2V_4O_{11}$, как продукты его термического разложения. Тетраванадат рубидия был также получен изотермической реакцией $RbVO_3 - V_2O_5$ при молярном соотношении реагентов 1:1.