Journal of Thermal Analysis, Vol. 22 (1981) 33–40

THERMAL AND X-RAY DIFFRACTION INVESTIGATIONS OF VANADIUM(V) OXIDE-ALKALI PERSULFATE BINARY SYSTEMS

F. JASIM*, H. J. JAFFER and M. M. BARBOOTI

Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq

(Received October 23, 1980)

Thermoanalytical investigations of the V_2O_5—$K_2S_2O_8$ system have revealed that, in the presence of excess amounts of V_2O_5, the initial decomposition temperature is lowered compared to that of the pure salt. An explanation for this lowering is based on the interaction between V_2O_5 and the peroxo group of the persulfate ion. The reaction however, is, not unimolecular. The presence of an unknown potassium sulfate complex of V(V) with a catalytic character is indicated by XRD patterns obtained for samples heated up to 410°. It has been found that the formation of K_3VO_8, $KV(SO_4)_2$, $K_3V_5O_{14}$ and $K_4V_{10}O_{27}$ depends on whether V_2O_5 or K_2SO_4 is present in excess during thermal decomposition.

Sharp *d*-lines for unknown phases are identified. V_2O_5 is found to behave differently towards sodium and potassium persulfates.

Compounds such as α-$NaVO_3$, $NaVO_3$, NaV_3O_8 and NaV_6O_{15} are obtained on thermal analysis of various molar ratios of the V_2O_5—$Na_2S_2O_8$ system.

The action of metal oxides on the thermal transitions of sodium and potassium peroxodisulfates (persulfates) has been the subject of many investigations in this laboratory [1–4]. The oxides exert different effects on the reactions involved in the persulfate decomposition: some of them catalyze it, whereas others react with intermediates to form stable compounds. In this work the systems of vanadium (V) oxide + sodium or potassium persulfate are studied in the temperature range ambient to 1000°, using techniques such as DTA, TG, DTG and XRD.

Experimental

The V_2O_5 used throughout this work was analytical grade from Fluka. The analyzed molar ratios were 1 : 6, 1 : 3, 1 : 2, 1 : 1, 2 : 1, 3 : 1 and 6 : 1 (oxide: persulfate).

The preparation and analysis of samples were as described elsewhere [4].

---

* To whom correspondence should be addressed.

Results and discussion

$V_2O_5-K_2S_2O_8$ system

In the presence of V_2O_5, the thermal decomposition of $K_2S_2O_8$ into the pyrosulfate is as follows:

$$K_2S_2O_8 \rightarrow K_2S_2O_7 + 1/2\ O_2$$

which starts at lower temperatures as compared with the pure salt. The influence of the proportion of V_2O_5 on this process is shown in Fig. 1. Pure $K_2S_2O_3$ begins to lose oxygen slowly at 182°; the process suddenly accelerates above 190°, and it finishes at 200° [5]. The DTG curve of the reaction indicates a single-step decomposition with a well-defined peak in the temperature range involved. Starting from the lowest proportion of V_2O_5, the initial decomposition temperature is lowered down to 163°. The DTG curves in Fig. 1 show that the process proceeds in more than one step. For the 2 : 1 molar ratio, the reaction is indicated by a wide DTG valley, extending between 160° and 230°. On increase of the V_2O_5 content, the main part of the DTG peak is reduced at the expense of the first part observed in the early stages of the process. A possible explanation of this behaviour is the weak interaction between V_2O_5 and the oxygen of the peroxo group, which may cause the weakening of the S – O bonds of the anion. This affinity towards oxygen may be due to the oxygen deficiency of the oxide [6]. The loosely bonded oxygen is then likely to be lost at temperatures lower than that needed for the deoxygenation of the pure salt. However, for the 1 : 1 and 1 : 6 ratios, the DTG curves in Fig. 1, show that the largest quantity of O_2 is lost in a faster process, with a maximum rate at 200°. This indicates that the main fraction of the persulfate is not

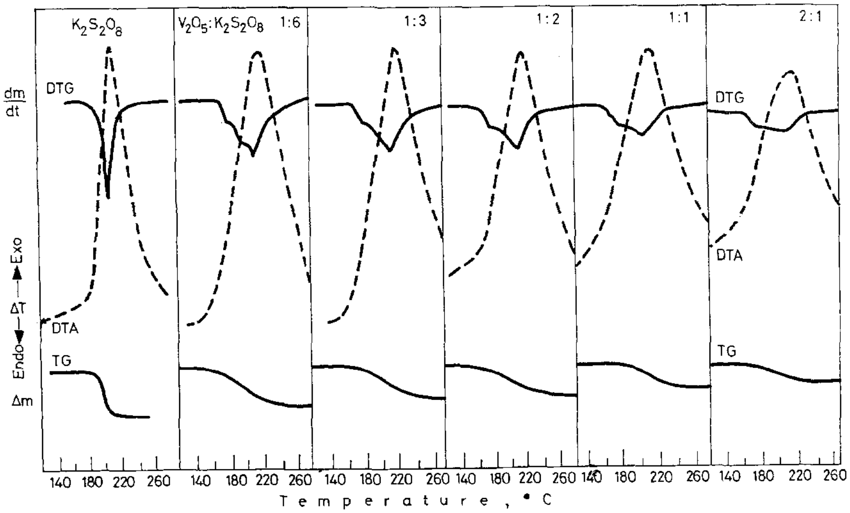

Fig. 1. TG, DTG and DTA curves of $K_2S_2O_8$: V_2O_5 mixtures

affected by the V_2O_5 and the interaction is not unimolecular with respect to V_2O_5.

The expansion of the reaction temperature interval may be attributed to the dilution effect of the excess of the oxide, because the persulfate decomposition is a second-order reaction [7].

In the temperature range 280–400°, $K_2S_2O_7$ is known to undergo two typical endothermic transitions. The first of these, at 330°, relates to the *B-a* phase transition [8], and the second, at 382°, to the fusion of potassium pyrosulfate [5]. Neither of these peaks appeared in the DTA curves at any of the molar ratios studied. Nevertheless, in a previous investigation with other oxides, the existence of one or both of these peaks was taken as evidence of the existence of $K_2S_2O_7$ at that temperature [9]. X-ray analysis of the 1 : 2 mixture heated up to 410° gave no indication of $K_2S_2O_7$ or V_2O_5. The XRD patterns of the known K-V-S-O compounds do not disclose any information. The *d*-spacing lines displayed by the sample are listed in Table 1. However, a mixture with a molar ratio close to 1 : 2 has recently been evaluated as a catalyst in the oxidation reaction $SO_2 \rightarrow SO_3$, at a temperature close to 410° [10]. The XRD pattern for this was produced in this laboratory (Table 1) and demonstrates the presence of a potassium salt of an unknown sulfato complex of V(V). Further, at room temperature vanadium is known to form a hydrated complex, of which the alkali metal salts are known [11]

On increase of the V_2O_5 content of the binary mixture, (Fig. 2.) the temperature at which the decomposition of the $K_2S_2O_7$ becomes appreciable is shifted to higher values. The pure pyrosulfate decomposes after melting, i.e. at 380° [5]. However, at the 1 : 2 and 2 : 1 ratios this temperature is pushed up to 417 and 557°, respectively. A wide endothermic peak is recorded for the molar ratios 1 : 1, 1 : 2, 1 : 3 and 1 : 6, with peak temperatures at 573, 600, 620 and 620°, respectively. This illustrates the fact that the melting of the V_2O_5 is affected by the presence of $K_2S_2O_7$. It is important to note that the 1 : 2.5 mixture melts at about 450° [10]. The melting could not be observed in the DTA curves (Fig. 1), because of the low V_2O_5 content of the mixture. When melting occurs, the decomposition of $K_2S_2O_7$ into K_2SO_4 and further into K_2O is enhanced. The weight loss process is attributed to the reaction of V_2O_5 with K_2SO_4 to form the vanadate. This reaction starts at 650°, and this means that the pyrosulfate decomposition into the sulfate may overlap the reaction of the latter with V_2O_5 above this temperature. This complicates the situation and the weight loss process takes place at various rates, as indicated by the irregular DTG curves over the temperature range involved. Samples heated to temperatures corresponding to the middle of the weight loss process were analyzed by XRD. In samples where the molar content of the sulfate is greater, the pattern corresponds to K_3VO_8, K_2SO_4, $KV(SO_4)_2$, and another phase which could not be identified (Table 1). On the other hand, with samples rich in V_2O_5, two compounds have been identified: $K_3V_5O_{14}$ and $K_4V_{10}O_{27}$. The former was produced in the anhydrous system $K_2O-V_2O_5$ by Kelmers [12] and its structure was reported by Byström and Evans [13].

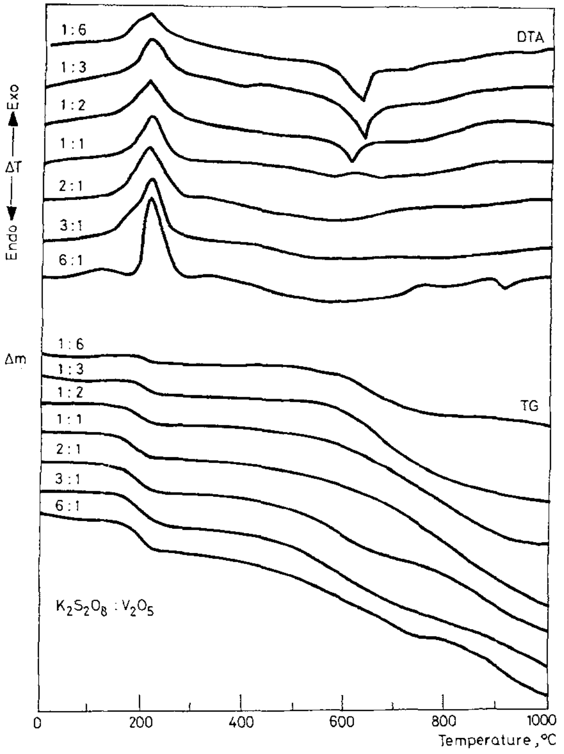

Fig. 2. TG and DTA curves of $K_2S_2O_8$: V_2O_5 mixtures

$V_2O_5-Na_2S_2O_8$ *system*

The thermal transition of sodium persulfate into the pyrosulfate is affected by the presence of V_2O_5, even at low proportions. The initial decomposition temperature is lowered to 160°, as compared to 185° for the pure salt [5]. The final decomposition temperature for most of the molar ratios studied is 238°. This change in the rate of decomposition and the characteristic temperature is not so significant as that found with the potassium system. Furthermore, the DTG peaks of the process are not complicated and become symmetrical as the V_2O_5 proportion is increased.

Unlike the behaviour of the $V_2O_5-K_2S_2O_8$ system, the melting endotherm of $Na_2S_2O_7$ appears at all molar ratios studied. However, it is shifted from its position because of the presence of V_2O_5. At the ratios 1 : 2 and 1 : 1, the reaction mixtures undergo 1.00 and 0.75% weight loss, at 360–400° and 350–372°, respectively. This process is slightly endothermic, as indicated by the small peak dividing the wide melting endotherm of $Na_2S_2O_7$. The weight loss is found to be proportional to the percentage of $Na_2S_2O_7$ present. However, for the remaining molar ratios the details of the DTA curves differ slightly due to the different composition; they are clearest at the above two ratios. The XRD patterns of these two ratios heated at 390–400° clearly reveal the presence of V_2O_5 in addition to an unknown phase (Table 1). Broadly speaking, the quantity of the unidentified phase is found to be greater in samples containing more sodium pyrosulfate, because brighter lines are formed. In this respect, Ti(IV) oxide exhibited a similar effect on $Na_2S_2O_7$, and the formation of some polymeric sulfate was suggested as product [2].

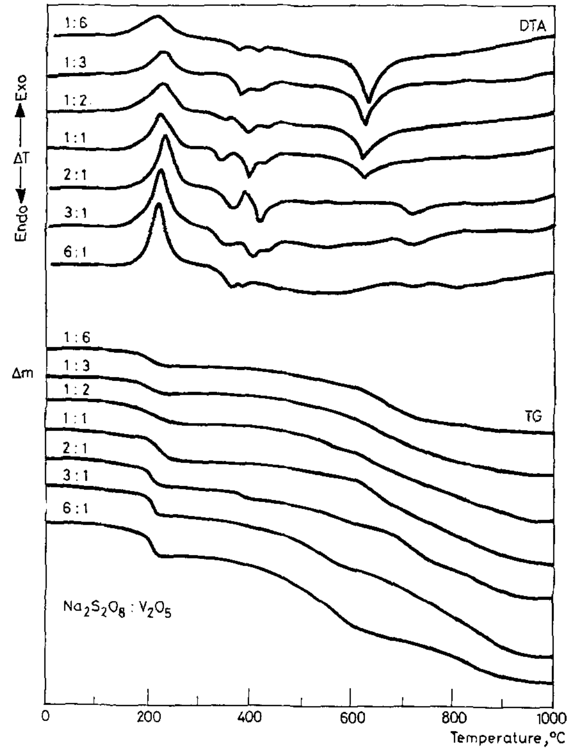

Fig. 3. TG and DTA curves of $Na_2S_2O_8$: V_2O_5 mixtures

Above 500°, the TG curves indicate a slow weight loss process. The rate of weight loss increased rapidly during and after the melting of the oxide, as indicated by the endothermic peak at 640°. The weight loss is of an extent matching the amount of SO_3 liberated on decomposition of the pyrosulfate. This suggests the reaction of the freshly formed Na_2SO_4 with V_2O_5, leading to the formation of sodium vanadates [14]. This reaction, however, is shown to be incomplete for the ratios 1 : 6 and 1 : 1, owing to the fact that the heating program ends at 1000°. It is worth recalling that Kolta et al. [14] studied the reaction between V_2O_5 and Na_2SO_4 at different ratios and were able to isolate some sodium vanadates whose

Table 1

The brightest XRD patterns recorded for the unidentified phases obtained for the systems $V_2O_5-Na_2S_2O_8$ and $V_2O_5-K_2S_2O_8$

$V_2O_5-Na_2S_2O_8$ (1 : 2), at 400°	*d*-spacing, Å	8.466	5.980	4.238	3.720	3.201	3.137	2.796	2.107
	I/I_0	40	40	80	90	50	50	100	50
$V_2O_5-K_2S_2O_8$ (1 : 2), at 410°	*d*-spacing, Å	5.604	5.555	3.544	2.930	2.908	2.362	2.220	—
	I/I_0	80	60	25	30	100	40	45	—
$V_2O_5-K_2S_2O_8$ (1 : 3), at 1000°	*d*-spacing, Å	8.036	7.893	4.148	3.492	3.195	3.127	2.203	1.76
	I/I_0	100	100	100	40	50	60	70	30

compositions depended on the molar ratios of the reactants and on the reaction temperature.

In the present system, samples at all molar ratios were heated up to 1000° and then subjected to XRD analysis. The data obtained are as follows:

Ratio	Compounds identified
1 : 3, 1 : 2 or 1 : 1	a-$NaVO_3$, $NaVO_3$, and Na_2SO_4
2 : 1	a-$NaVO_3$ and NaV_3O_8
3 : 1	NaV_3O_8 and a little NaV_6O_{15}
6 : 1	80% NaV_6O_{15} and 20% NaV_3O_8

It is clear that the type of vanadate formed is dependent on the molar proportion of the reactant and the temperature at which the sample is isolated. The formation of Na_2SO_4 from the 1 : 1 ratio is expected, and the reaction between the latter and the oxide proceeds slowly below 900°. At the 2 : 1 ratio the formation of NaV_3O_8 occurs via the formation of a-$NaVO_3$ and its subsequent reaction with excess V_2O_5. This is confirmed by the XRD pattern of the products at 900°.

The results for the 3 : 1 and 6 : 1 ratios are consistent with the stoichiometry of the mixed reactants. It is important to note that the formation of NaV_3O_8 is shifted to lower temperatures with increase of the amount of V_2O_5 in the ratio. The formation of NaV_6O_{15} proceeds via the reaction between NaV_3O_8 and excess V_2O_5.

References

1. Khalida R. Idan and F. Jasim, Thermochim. Acta, 39 (1980) 227.
2. idem, Thermochim. Acta, 23 (1978) 103.
3. M. M. Barbooti and F. Jasim, J. Thermal Anal., 13 (1978) 563.
4. R. M. Al-Shukry and F. Jasim, Thermochim. Acta, 37 (1980) 97.
5. M. M. Barbooti and F. Jasim, Thermochim. Acta, 16 (1976) 402.
6. T. Allersoma, R. Hakim, T. N. Kennedy and J. D. Mackenzie, J. Chem., Phys., 46 (1967) 154.
7. M. M. Barbooti and F. Jasim, Thermochim. Acta, 23 (1978) 103.
8. B. J. Meehan, S. A. Tariq and J. O. Hill, J. Thermal Anal., 12 (1977) 235.
9. Khalida R. Idan and F. Jasim, Thermal Analysis (Proc. 6th ICTA), Vol. 2, Birkhäuser Verlag, Basel, 1980 p. 211.
10. A. Tamura, R. R. Hudgins and P. L. Silveston, J. Catalysis, 42 (1976) 122.
11. R. J. H. Clark, in Comprehensive Inorganic Chemistry, (C. Bailer Ed.) Vol. 9, Pergamon Press, Oxford, 1973.
12. A. D. Kelmers, J. Inorg. Nucl. Chem., 23 (1961) 279.
13. A. M. Byström and H. T. Evans, Acta Chem. Scand., 13 (1959) 377.
14. G. A. Kolta, I. F. Hewaidy and N. S. Felix, Thermochim. Acta, 4 (1972) 151.

Résumé — L'étude thermoanalytique du système V_2O_5 — $K_2S_2O_8$ montre que la température initiale de la décomposition diminue en présence d'un excès de V_2O_5. Une explication de cette diminution repose sur l'interaction de V_2O_5 avec le groupe peroxo de l'ion persulfate. Cependant, la réaction n'est pas unimoléculaire. Les clichés XRD obtenus avec des échantillons chauffés à 410° indiquent la présence d'un complexe inconnu de sulfate de potassium avec V(V) de caractère catalytique. On a trouvé que la formation de K_3VO_8, $KV(SO_4)_2$, $K_3V_5O_{14}$ et $K_4V_{10}O_{27}$ dépend de la présence d'un excès de V_2O_5 ou K_2SO_4 pendant l'analyse thermique. On a identifié des raies *d* nettes pour les phases inconnues. On a trouvé que V_2O_5 se comporte de façon différente vis-à-vis de sulfates de potassium et de sodium. Des composés tels que: *a*-$NaVO_3$, $NaVO_3$, NaV_3O_8 et NaV_6O_{15} ont été obtenus lors de l'analyse thermique du système V_2O_5 — $Na_2S_2O_8$ avec divers rapports molaires.

Zusammenfassung — Thermoanalytische Untersuchungen des Systems V_2O_5 — $K_2S_2O_8$ zeigten, daß die Zersetzungstemperatur in Gegenwart überschüssiger Mengen von V_2O_5 im Vergleich zu dem reinen Salz herabgesetzt wird. Eine Erklärung für diese Verminderung beruht auf der Wechselwirkung zwischen V_2O_5 und der Peroxo-Gruppe des Persulfat-Ions. Die Reaktion ist jedoch nicht unimolekular. Die Gegenwart eines unbekannten Kaliumsulfatkomplexes von V(V) mit katalytischen Charakter wird durch die Röntgenbeugung bei bis zu 410° erhitzen Proben angedeutet. Es wurde festgestellt, daß die Bildung von K_3VO_8, $KV(SO_4)_2$, $K_3V_5O_{14}$ und $K_4V_{10}O_{27}$ davon abhängt, ob während der thermischen Zersetzung V_2O_5 oder K_2SO_4 im Überschuss vorhanden ist. Scharfe *d*-Linien wurden für die unbekannten Phasen identifiziert. Es wurde gefunden, daß sich V_2O_5 gegenüber den Persulfaten von Natrium und Kalium unterschiedlich verhält. Verbindungen wie *a*-$NaVO_3$, $NaVO_3$, NaV_3O_8 und NaV_6O_{15} werden bei der thermischen Analyse verschiedener Molverhältnisse des V_2O_5 — $Na_2S_2O_8$-Systems erhalten.

Резюме — Термоаналитические исследования систем V_2O_5—$K_2S_2O_8$ показали, что в присутствии значительного избытка V_2O_5 начальная температура их разложения понижается по сравнению с температурой для чистой индивидуальной соли. Понижение температуры разложения объяснено взаимодействием между V_2O_5 и пероксогруппой иона персульфата. Реакция не является мономолекулярной. В образцах нагретых до 410° установлено с помощью рентгено-диффракционного анализа наличие неизвестного калий сульфатного комплекса ванадиум(V), обладающего каталитическим действием. Найдено, что образование K_3VO_8, $KV(SO_4)_2$, $K_3V_5O_{14}$ и $K_4V_{10}O_{27}$ зависит от того, что V_2O_5 или K_2SO_4 находится в избытке во время термического разложения. Идентифицированы резкие *d*-линии неизвестных фаз. Установлено различное поведение пятиокиси ванадия в персульфатах натрия и калия. При термическом анализе системы V_2O_5—$Na_2S_2O_8$ с различным молярным соотношением компонентов получены такие соединения как α-$NaVO_3$, $NaVO_3$, NaV_3O_8 и NaV_6O_{15}.