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ON THE THERMAL DECOMPOSITION MECHANISM OF URANYL AND URANIUM(IV) ACETATES

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ABSTRACT

The methods of isothermal kinetics, X-ray spectrography, mass spectrometry and IR spectroscopy were used to study the thermal decomposition of uranyl acetate, $UO_2(CH_3COO)_2$, and uranium(IV) acetate, $U(CH_3COO)_4$. The data obtained were supported by the results of the chemical analysis of products formed in decomposition processes and in model reactions. The compounds studied are assumed to be decomposed by a single mechanism including the following elementary stages: (1) breaking the carbon–oxygen bond of the carboxyl group, (2) forming a new carbon–oxygen bond with the appearance of an intermediate compound (co-ordinated to uranium atoms) with the structure of acetic anhydride, (3) breaking the uranium–oxygen bond with a subsequent rotation of the acetyl group, (4) transferring a hydrogen atom from a methyl radical of one acetate group to the oxygen of another and evolving a molecule of acetic acid which is the primary product of metal acetate decomposition. Arguments are presented in favour of the suggested mechanism.

Despite a great number of papers on the thermal decomposition of metal salts of organic acids, there is no commonly recognized picture of its mechanism even for such relatively simple systems as metal formates and acetates. This is especially true for uranium compounds which are insufficiently studied in general.

In the present work, an attempt is made, by using a variety of methods such as elementary chemical and X-ray phase analysis, IR spectroscopy, modelling separate reactions, measurement of the vapour pressure of volatile decomposition products and time-of-flight mass spectrometry, as well as some methods of isothermal and non-isothermal kinetics, to inquire into the process of the thermal decomposition of hexa- and tetravalent uranium salts of acetic acid, viz. $UO_2(CH_3COO)_2$, $UO_2(CH_3COO)_2 \cdot CH_3COOH$, $UO_2(CH_3COO)_2 \cdot 2H_2O$, $U(CH_3COO)_4$.

Comparison of regularities in the decomposition of uranium tetraacetate and uranyl acetate is of interest in the sense that in each case the solid products contain one and the same oxide, viz. UO_2[1,2]. It could be expected, therefore, that this comparison would lead to an understanding of the process of formation of decomposition products, to get a more comprehensive idea of the thermal destruction of metal acetates and to draw more convincing conclusions about the separate elementary stages.

According to the X-ray spectrographic and IR spectroscopic data obtained by the authors on decomposing the above four compounds, no intermediate stable solid substances are formed[3,4]. As to the final product, it is found to contain 0.45 g at. C/g at. U in the case of uranyl acetate and one order less (~ 0.04 g at C/g at. U) in the case of uranium tetraacetate.

Of the volatile products of decomposition in vacuum, low temperature traps cooled by liquid nitrogen were used to collect and then to separate and identify (by vapour pressure and IR spectra) the following substances: acetic acid, acetic anhydride, ketene, acetone, carbon dioxide, carbon monoxide and water[3,4].

To the authors' knowledge, there is only one paper available[5] in which ketene is mentioned as a product of metal (potassium) acetate decomposition. The radical mechanism of the thermal decomposition of metal acetates suggested by Bell and Reed[6] cannot explain the formation of acetic acid as the main decomposition product of acetates of metals such as copper, silver and others, including uranium acetate.

Poppl's explanation[5], which attributes the formation of acetic acid to hydrolysis, can hardly be satisfactory. At the same time, the occurrence of acetone among the thermal decomposition products of acetates of uranium (as well as other metals) may be conditioned by both the catalytic transformation of acetic acid and the processes leading to the elimination of acetone as an initial product.

These points were to be verified and this was done by means of model reactions*. Study was made of the transformation of vapours of acetic acid, acetic anhydride and acetone on uranium dioxide and trioxide at 300°C ± 2°C. The experiments[3] have shown that

(1) acetone does not undergo any transformation under these conditions;

(2) acetic acid yields acetone, carbon dioxide and water in accordance with the well-known equation of ketonization

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* With this aim, use was made of the devices and the installation schematically depicted in Fig. 1. The reagent (acetone, acetic acid or acetic anhydride) was placed into vessel 1 by vacuum distillation using an appropriate desiccator. The active uranium oxides were prepared just before the experiment by coating a glass wool carrier (reaction tube 2) or cellular glass filter, 3, with the powder of uranyl oxalate to obtain UO_2 or that of uranium peroxide dihydrate to obtain UO_3. After vessel 1 was connected with reaction tube 2 or 3, the whole system was evacuated, then the heater was switched on and the solids were decomposed to form the corresponding oxides. Taps K_1 and K_2 were used to dose out the intake of the vapours of initial organic substances into reaction tube 2 (or 3) as well as the gaseous products of the reaction into the vacuum system containing a number of low temperature traps for separating the components of the mixture. A modified tube 3 was used instead of tube 2 in studying the solid products of a reaction. The spherical branch piece 3S was filled with vaseline oil heated in vacuum to remove very volatile components. After the reaction, the vaseline oil from branch piece 3S was poured over the solid product on filter 3a and the product was then transported in the air.

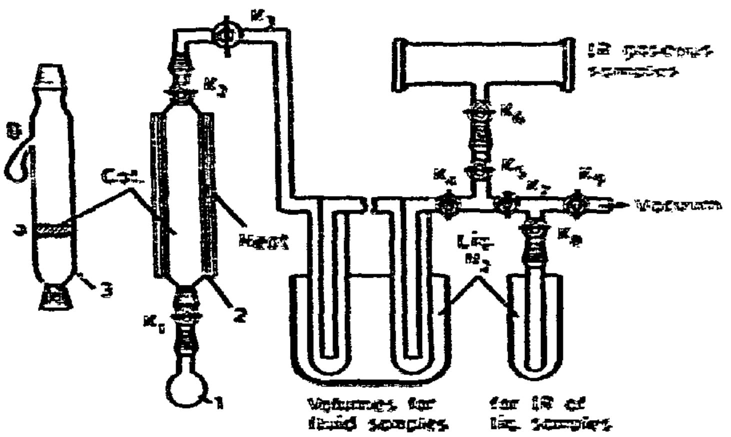


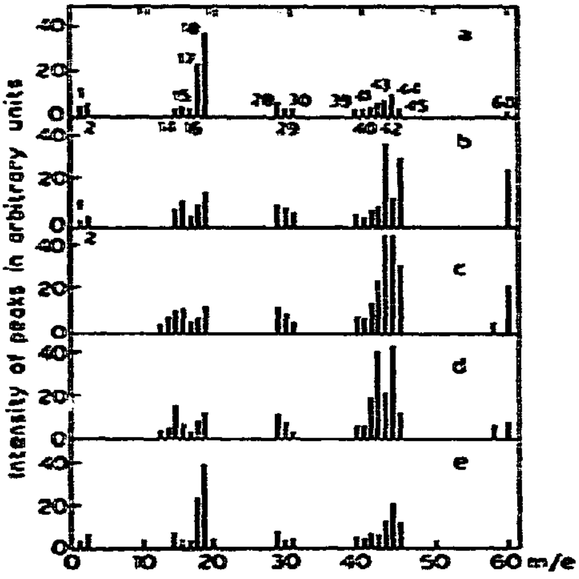
Fig. 1. Diagram of installation and devices for model reactions.

$$2\,CH_3COOH \rightarrow (CH_3)_2CO + CO_2 + H_2O \qquad (1)$$

(In the case of UO_3, a considerable amount of $UO_2(CH_3COO)_2$ and some UO_2 were observed to form. In all other cases, the chemical nature of oxides did not change!).

(3) acetic anhydride readily changes into acetic acid.

The problem of whether acetic anhydride is the primary product of uranium acetate decomposition and ketene the secondary one was solved by the analysis of mass spectra (obtained with the help of a time-of-flight mass spectrometer[3]) of the primary gas products of decomposition with continuous heating in vacuum (3×10^{-6} torr) precluding the secondary processes. The results of two typical experiments are presented below. Above all, these are spectra obtained at different moments of time



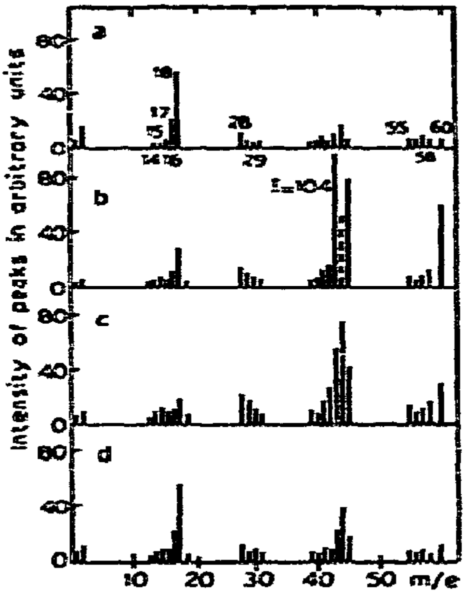


Fig. 2. Mass spectra of the volatile decomposition products of $UO_2(CH_3COO)_2 \cdot CH_3COOH$.

Fig. 3. Mass spectra of the volatile decomposition products of $U(CH_3COO)_4$.

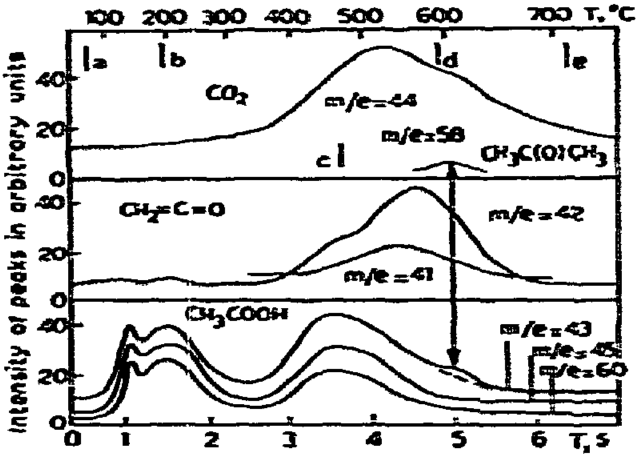


Fig. 4. Time dependence of the intensity of the peaks in the mass spectrum of the volatile products when $UO_2(CH_3COO)_2 \cdot CH_3COOH$ is decomposed in the ion source of a mass spectrometer.

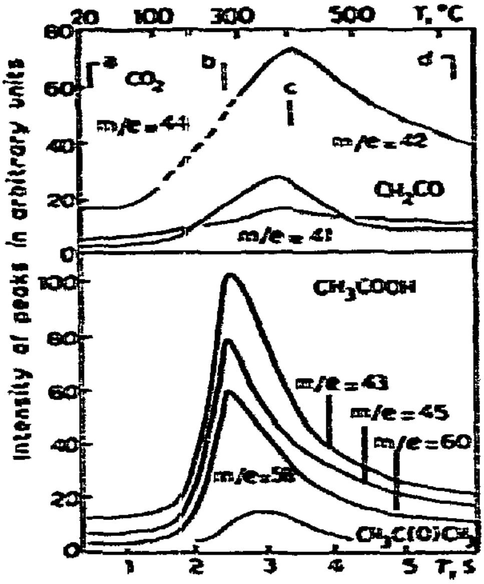


Fig. 5. Time dependence of the intensity of the peaks in the mass-spectrum of the volatile products when $U(CH_3COO)_4$ is decomposed in the ion source of a mass spectrometer.

(Figs. 2 and 3). Their analysis shows the evolution of products to proceed in the sequence acetic acid followed by ketene and carbon dioxide and, finally, acetone.

The sequence of gas product yield can be seen especially clearly from the kinetic curves of time-dependent peak heights characteristic of each of the substances* named (Figs. 4 and 5).

Acetic anhydride was not recorded among the primary products. Nevertheless, it can be argued that, taking into account the results of experiments on modelling (separate reactions) reported earlier, it is acetic anhydride that precedes ketene. This

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* Cf. Table 1.

TABLE I

MASS SPECTRA OF COMPOUNDS DISCOVERED IN THE PRODUCTS OF THE THERMAL DECOMPOSITION OF $UO_2(CH_3COO)_2 \cdot CH_3COOH$[a]

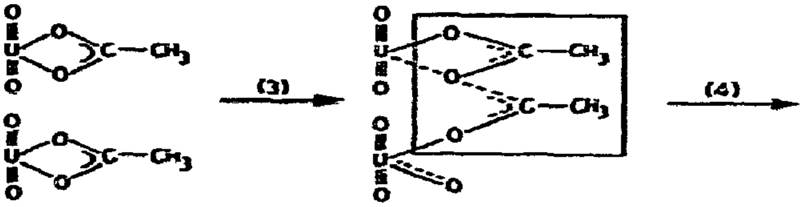
Substance	*M*	M_1/e	J_1	M_2/e	J_2	M_3/e	J_3	M_4/e	J_4	M_5/e	J_5	M_6/e	J_6
CO	28	28	100	12	5	12	2	29	1	14	1	30	1
CO_2	44	44	100	16	9	28	8	12	7	29	1	13	1
	44	44	100	28	7	16	6	22	1	45	1	46	
	44	44	100	28	7	16	6	12	2	22	2	45	1
$CH_2=C=O$	42	14	100	42	94	41	27	13	13	12	12	28	11
$CH_3C(O)CH_3$	58	43	100	58	33	15	31	27	8	42	7	14	6
	58	43	100	58	23	27	8	42	7	26	6	29	4
	58	43	100	58	27	27	8	42	7	26	6	29	4
	58	43	100	58	37	42	7	27	5	28	5	39	4
	58	43	100	58	34	42	7	27	6	28	4	26	4
CH_3COOH	60	43	100	45	90	15	56	60	52	14	22	29	17
	60	43	100	45	94	60	58	29	16	42	15	28	6
	60	43	100	45	87	60	57	15	42	42	14	14	13
	60	43	100	45	94	60	64	15	34	42	20	29	19
	60	60	100	43	99	45	98	44	34	28	29	42	28
$(CH_3CO)_2O$	102	43	100	28	8	42	6	44	3	29	3	45	3

conclusion is supported by the fact that acetic anhydride is readily transformed evolving ketene. Poppl's interpretation[5], according to which ketene can be formed during the thermal decomposition of acetone, is inapplicable here because the products do not contain methane which must be formed from acetone together with ketene.

$$(CH_3)_2CO \rightarrow CH_2CO + CH_4 \qquad (2)$$

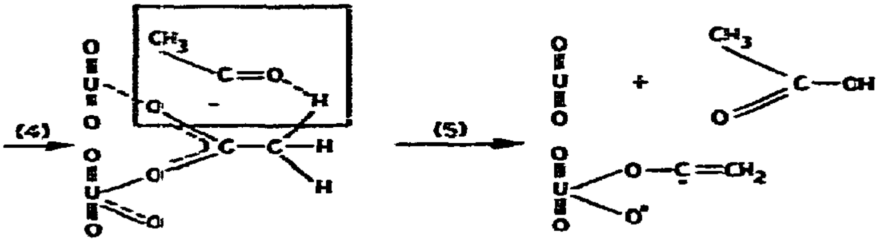
The sum total of experimental data allows the thermal decomposition of uranium acetates to be represented by the following scheme.

(1) The first stage is that of breaking the carbon–oxygen bonds and forming new carbon–oxygen bonds so that an intermediate compound is formed in an adsorbed state with the structure of acetic anhydride.

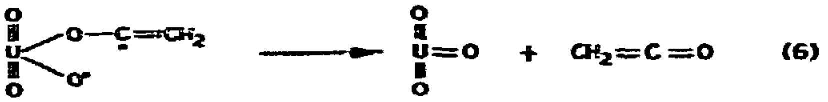


(For simplicity only one of the acetate groups is taken from each of the two adjacent uranium atoms).

(2) Next comes the breaking of the uranium–oxygen bond, the rotation of the acetyl group and the transfer of a hydrogen atom from a neighbouring methyl group which results in the evolution of acetic acid.

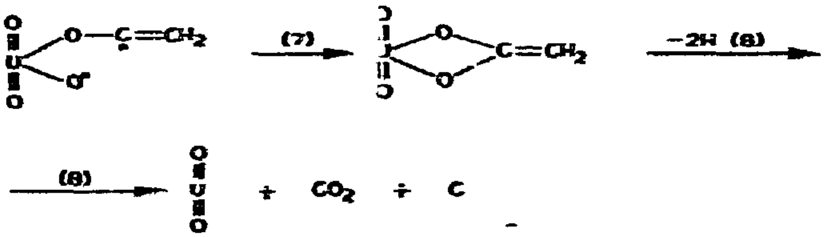


(3) The further changes in the acetate group residue is determined by the possibility of forming a stable molecule, that of ketene, through the reaction


(6)

$$UO_2(OC(=CH_2)O^{\cdot}) \rightarrow O{=}U{=}O + CH_2{=}C{=}O \quad (6)$$

and by that of stabilizing the radical with the subsequent dehydration of the methylene group which yields carbon and carbon dioxide.



In the case of uranium(IV) acetate, only the first course (6) is possible while for uranyl acetate, the parallel reactions (6) and (7) and (8) are possible which accounts for the difference in the decomposition products.

$U(CH_3COO)_4 \rightarrow UO_2 +$ volatile substances (9)

$UO_2(CH_3COO)_2 \rightarrow UO_{2+x} + C +$ volatile substances (10)

Thus acetic acid and ketene turn out to be the primary products of the thermal decomposition of uranium acetates.

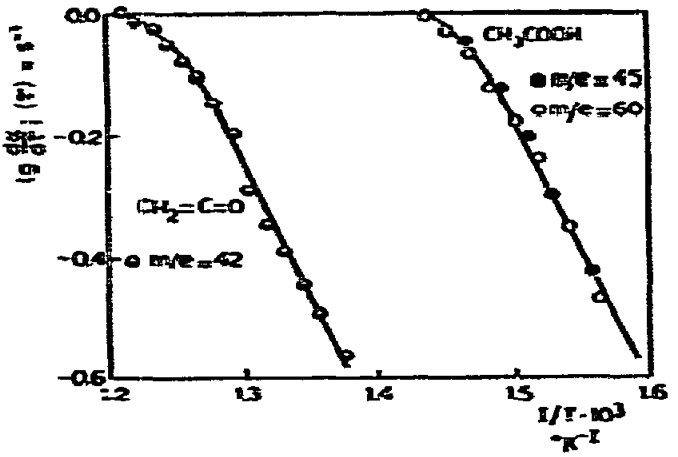


Fig. 6. Dependence of log (dx/dτ) on 1/T for the primary decomposition products of $UO_2(CH_3COO)_2 \cdot CH_3COOH$.

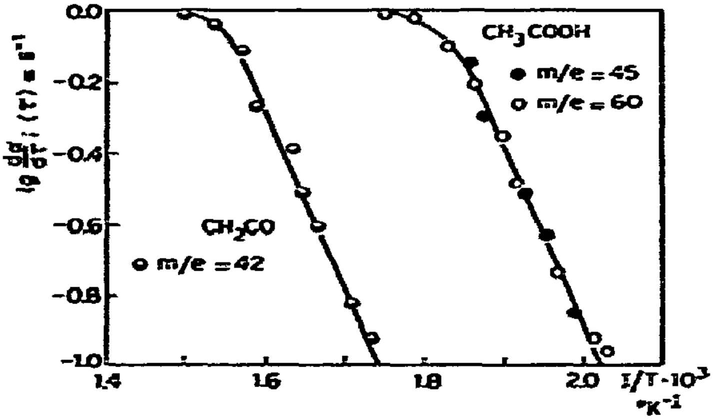


Fig. 7. Dependence of log ($d\alpha/d\tau$) on $1/T$ for the primary decomposition products of $U(CH_3COO)_4$.

Such substances as acetone, water, acetic anhydride in the gas phase and carbon dioxide are formed as a result of secondary reactions of which a significant part is played by the catalytic transformation of CH_3COOH on uranium oxides according to reaction (1).

From the mass spectrometric data, the activation energies were found by means of the kinetic evolution curves of various products of acetic acid and ketene. The corresponding graphs for non-dimensional reaction rates in the coordinates of log ($d\alpha/d\tau$) versus the reciprocal of the absolute temperature are presented in Figs. 6 and 7. In either case, the activation energies were found to equal at ~20 kcal/mole.

The method of isothermal gravimetry in vacuum was used to measure the activation energy values of the process of dissolving $UO_2(CH_3COO)_2 \cdot 2H_2O$ and $UO_2(CH_3COO)_2 \cdot CH_3COOH$ as well as the process of decomposing $UO_2(CH_3COO)_2$ and $U(CH_3COO)_4$. They are all listed in Table 2[4]. The close activation energy values for the processes of desolvation, decomposition of $U(CH_3COO)_4$ and evolution of acetic acid and ketene as primary decomposition products suggest that all these processes are limited by one of the early stages, namely that of breaking the uranium–oxygen bond. The macrokinetic value of $E = 44 \pm 4$ kcal/mole obtained for uranyl

TABLE 2

VALUES OF APPARENT ACTIVATION ENERGY OF THE THERMAL DECOMPOSITION OF URANIUM ACETATES

Compound	*Temperature range (°C)*	*Decomposition product*	*E (kcal/mole)*
$UO_2(CH_3COO)_2 \cdot 2H_2O$	55–74	$UO_2(CH_3COO)_2$	26 ± 3
$UO_2(CH_3COO)_2 \cdot CH_3COOH$	65–84	$UO_2(CH_3COO)_2$	24 ± 2
$UO_2(CH_3COO)_2$	265–302	UO_{2+x}	44 ± 4
$UO_2(CH_3COO)_2$	360–410; 450–520	UO_{2+x}	20*
$U(CH_3COO)_4$	160–274	UO_2	26 ± 2
$U(CH_3COO)_4$	220–270; 320–370	UO_2	20*

* Mass spectrometric data on evolution of CH_3COOH and CH_2CO.

acetate seems to be connected with later stages, among them, possibly, that of breaking the C–C bonds in forming CO_2 and elementary carbon according to the scheme suggested.

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