# EMANATING ABILITY AND RELEASE OF A SURFACE GAS LABEL DURING THE THERMAL DECOMPOSITION OF COPPER, NICKEL, AND THORIUM OXALATES

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## Abstract

## Full Text

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# EMANATING ABILITY AND RELEASE OF A SURFACE GAS LABEL DURING THE THERMAL DECOMPOSITION OF COPPER, NICKEL, AND THORIUM OXALATES

The pyrolysis of transition-metal oxalates is one of the favorite objects of study in topochemistry ([1], [2]). Nevertheless, the mechanism of the processes and the nature of the factors determining the structure and properties of the solid products have not been sufficiently clarified. It seemed of interest to include these reactions among the processes studied by us with the use of emanation methods, which have shown their effectiveness in investigations of the pyrolysis of hydroxides and carbonates ([3]).

The copper ($CuC_2O_4 \cdot \frac{1}{2}H_2O$), nickel ($NiC_2O_4 \cdot 2H_2O$), and thorium ($Th(C_2O_4)_2 \cdot 6H_2O$) oxalates studied in this work, containing radiothorium, were prepared by joint precipitation of the corresponding nitrate salts with a solution of ammonium oxalate. The thorium-232 content was 2 at.%; in this case thorium-228, which served as the isotope label, was about $3 \cdot 10^{-10}\%$. The method of introducing radioactive inert gases into a solid and monitoring their release have been described previously ([4]). The experiments were carried out in a stream of nitrogen with continuous temperature increase and parallel recording of differential thermograms.

Fig. 1. Change in the emanating ability (1) and release of $Kr^{85}$ (2) and radon (3) during the thermal decomposition of nickel oxalate

In Fig. 1 the change in the emanating ability for thoron (emanogram) (1) and the release of the surface gas label ($Kr^{85}$) (2) from the surface of nickel oxalate in the hydrated form are compared.

The first maximum on the emanogram at 140° can probably be associated with the removal of hygroscopic water, which causes no thermal effect on the thermogram but leads to enhanced release of emanation together with the evaporating water (5). The second maximum on the emanogram at 270° is due to the release of water of crystallization, which is also matched by the endothermic effect on the thermogram (Table 1). The increase in emanating ability at 340° is directly connected with the decomposition of the oxalate, as is indicated by the presence of an endothermic effect at 340° on the thermogram. We note that during the decomposition of nickel oxalate in an atmo-

in an oxygen atmosphere an exothermic effect is observed, and the temperature of maximum emanation release increases somewhat. Carrying out the reaction in a $CO_2$ atmosphere shifts the emanation maximum corresponding to the direct decomposition of the oxalate toward lower temperatures. The results obtained are in good agreement with the thermographic data reported in the work of R. Della [6]. The radon-release curve is analogous to the emanogram, while the release of radioactive krypton-85 from the surface of nickel oxalate (Figs. 1, 2) does not increase at the temperature corresponding to decomposition of the oxalate, since practically all of the introduced krypton is removed already during dehydration of the oxalate.

**Table 1**

**Extremal points recorded on thermograms during decomposition of oxalates**

| Sample | Endoeffect temperature, °C |
|---|---|
| $NiC_2O_4 \cdot 2H_2O$ | I |
| $NiC_2O_4 \cdot 2H_2O$ | II 230 |
| $NiC_2O_4 \cdot 2H_2O$ | III 340 |
| $CuC_2O_4 \cdot \frac{1}{2}H_2O$ | I 110* |
| $Th(C_2O_4)_2 \cdot 6H_2O$ | I 150 (140-180) |
| $Th(C_2O_4)_2 \cdot 6H_2O$ | II 255 (240-330) |
| $Th(C_2O_4)_2 \cdot 6H_2O$ | III 385 (370-410) |
| $Th(C_2O_4)_2 \cdot 6H_2O$ irradiated with a dose of $3.3 \cdot 10^8$ rad | I 140 |
| $Th(C_2O_4)_2 \cdot 6H_2O$ irradiated with a dose of $3.3 \cdot 10^8$ rad | II |
| $Th(C_2O_4)_2 \cdot 6H_2O$ irradiated with a dose of $3.3 \cdot 10^8$ rad | III—390 |

* Temperature of exoeffect II 290°.

As can be seen from Fig. 2 and the data of Table 1, the curves of emanation (1) and release of the surface gas label (2) during heating of copper oxalate

Fig. 2. Change in emanating ability (1), release of radioactive krypton (2) during decomposition of copper oxalate

Figure 2: Fig. 2. Change in emanating ability (1), release of radioactive krypton (2) during decomposition of copper oxalate

Fig. 3. Change in emanating ability (1), release of radioactive krypton (2), and radon (3) during decomposition of thorium oxalate

Figure 3: Fig. 3. Change in emanating ability (1), release of radioactive krypton (2), and radon (3) during decomposition of thorium oxalate

have a similar shape. The first peak in the region of 120–140° is apparently associated with the release of water of crystallization, and the second, in the region of 260–280°, with decomposition of the oxalate, which is also confirmed by thermographic analysis.

The short-term increase in the release of radioactive krypton at 290° is probably connected with the exothermic character of the process taking place.

In Fig. 3 the emanogram and the release of the gaseous radioisotope label for thorium oxalate are compared. Three peaks of the emanogram in the intervals 140-160°, 250-330°, and 410-420° indicate, as in the preceding cases, the sequential appearance, as the temperature is raised, of several processes that enhance the emanating ability. On the thermogram these maxima correspond to three endothermic minima (see Table 1). The first maximum on the emanogram in the region of 140–160° is obviously associated with the gradual removal of water of crystallization. The broad maximum in the region of 250–330° and the subsequent increase in emanation at 410–420° can apparently be explained by the superposition of the processes of continuing dehydration and stepwise decomposition of thorium oxalate through the intermediate formation of carbonate, as is also indicated in the work of R. M. Della and V. I. Veler [6].

**Fig. 2.** Change in emanating ability (1), release of radioactive krypton (2) during decomposition of copper oxalate

**Fig. 3.** Change in emanating ability (1), release of radioactive krypton (2), and radon (3) during decomposition of thorium oxalate

The release of forcibly introduced radon (Fig. 3, 3) from the surface of thorium oxalate also causes the appearance of three peaks, of which the first and third approximately coincide with the first and third maxima of the emanogram, while the second is shifted toward higher temperatures relative to the extreme points on the emanogram and thermogram. For radiokrypton (curve 2) this maximum is absent, and the first and third are analogous to the peaks for radon and thoron. In addition, there is a very small peak at 240°, corresponding, according to literature data (7), to the second stage of dehydration of the oxalate.

It was of interest to apply these radiochemical methods to the study of the

Fig. 4. Change in emanating ability (1) and release of radioactive krypton (2) during thermal decomposition of preliminarily $\gamma$-irradiated thorium oxalate

Figure 4: Fig. 4. Change in emanating ability (1) and release of radioactive krypton (2) during thermal decomposition of preliminarily $\gamma$-irradiated thorium oxalate

decomposition of preliminarily irradiated oxalates, since the creation of surface and bulk defects under $\gamma$-irradiation can make it possible to make fuller use of the features of emanation and surface gas-label methods (8). The oxalate samples under study were placed in sealed glass ampoules and irradiated in a cobalt $\gamma$-installation with a dose rate of 750 rad/sec. The total irradiation dose was $0.8 \cdot 10^8$ rad for nickel oxalate and $3.3 \cdot 10^8$ rad for thorium oxalate.

**Fig. 4.** Change in emanating ability (1) and release of radioactive krypton (2) during thermal decomposition of preliminarily $\gamma$-irradiated thorium oxalate

It was established that preliminary irradiation of nickel and copper oxalates does not lead to a change in their emanating ability and does not affect the character of release of the surface gas label. It should be noted, however, that for the irradiated nickel oxalate sample the appearance of a small peak is observed on the krypton-release curve at a temperature corresponding to its decomposition (340°). The most significant changes, clearly recorded by both radiochemical and thermographic methods, are observed for irradiated thorium oxalate. In this case, on the emanogram (Fig. 4, 1) and thermogram (Table 1) of the irradiated sample, the maximum in the region 250–330° disappears. Irradiation also leads to a lowering of the temperature of the maximum corresponding to dehydration of the oxalate and to the appearance of an additional peak on the krypton-release curve. At the same time, the radon-release peak at 370° increases in comparison with the peak at 420°, which is observed for both the irradiated and the non-irradiated sample.

X-ray diffraction data established that the structure of the preliminarily irradiated sample is identical to that of non-irradiated thorium oxalate calcined to no higher than 300–330°, i.e., at a temperature equal to or slightly higher than the temperature of the second maximum of emanating ability. This structure may be attributed to the presence of dehydrated oxalate or thorium carbonate. Taking into account that in the work of R. Dell (6) stepwise decomposition of thorium oxalate via carbonate is proposed, it seems more probable to regard the intermediate phase formed as thorium carbonate. Considering, on the one hand, the disappearance of the maximum of emanating ability between 250–330° and, on the other hand, the appearance of an additional maximum in the release of $Kr^{85}$ at 370° upon heating preliminarily irradiated thorium oxalate, it may evidently be considered that, in this case, the processes responsible for the increase in emanating ability and for the release of radioactive krypton have different natures.

As was shown earlier (4), for simple topochemical processes of the transformation of hydroxide into oxide, the extrema of emanation release and of the radioactive gas label, as a rule, coincided. In essence, there apparently should not be any significant difference between these methods, since in all cases the radioactive gas is found in the lattice of the solid as a result of radiation effects. When the radioisotope of thorium ($\mathrm{Th}^{228}$) is introduced into the solids under study, as a result of successive radioactive decay the ThX that is formed, and then thoron, are introduced into the lattice of the solid owing to recoil energy.

The radioactive gas label ($\mathrm{Rh}, \mathrm{Kr}^{85}$) is introduced into the lattice of the solid during ion bombardment in an electric discharge. Thus, in both cases the methods of introducing radioactive gases are radiation methods. However, in the first case the radioactive gas formed, according to calculations carried out by the formula of Flügge and Zimens (9), is located at a depth of 300–400 Å and is generated continuously. In the second, the radioactive gas is located at a depth measured in tens of angstroms, and is not replenished during release.

In connection with this, in some cases fixation of high-temperature processes by the surface gas-label method is made difficult, and thermally activated release of radioactive gas, caused by diffusion, and the state of the sample surface before forced introduction of the radioactive gas label, acquire considerable importance. In addition, the surface layer may be destroyed during the introduction of radioactive radon or krypton atoms, and part of the radioactive gas is released in the process of annealing of defects at 50–100°. In this connection the low-temperature and fairly broad peaks of $\mathrm{Kr}^{85}$ release observed during the decomposition of all the oxalates studied may be regarded as being due to thermal diffusion with the simultaneous superposition of partially occurring dehydration. Possibly, these features of the methods explain the differences that appear in the study of more complex multistage processes, such as the processes of decomposition of oxalates. Here cases are possible in which the gas label is practically not captured by one of the solid phases formed during decomposition, as was shown by the example of thorium oxalate, where the first and third maxima were recorded by the emanation and gas-label methods, while the second maximum, corresponding to the formation of an intermediate bulk phase, was recorded only by the emanation method. The additional radon and krypton peak in irradiated thorium oxalate may be associated with a change in the energy state of the sample surface or with the interaction of gaseous decomposition products with the surface directly during irradiation.

Thus, preliminary irradiation of the samples made it possible to reveal a definite difference in the results obtained, arising from the characteristic features of the methods used, and showed the prospects for their further application.

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*Note: Figure translations are in progress. See original paper for figures.*