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Solid Dicarboxylic Acids as In-Pile Chemical Dosimeters

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Radiolytic decomposition of succinic acid induced by mixed pile radiation was studied with respect to dosimetric use at high reactor power levels, from 2 to 10 MW, and dose rates from 20 to 120 Mrad hr^{-1}. The linear relationship between the absorbed dose and the logarithm of weight losses caused by radiation, like in the case of solid oxalic acid, was found. The radiolytic behaviour of succinic acid and oxalic acid dihydrate is compared, especially the effect of temperature on the radiolysis.

ACIDES DICARBOXYLIQUES SOLIDES COMME DOSIMÈTRES CHIMIQUES DE RAYONNEMENTS DU RÉACTEUR NUCLÉAIRE

La décomposition radiolytique de l'acide succinique induite par les rayonnements mixtes du réacteur a été étudiée l'utilisation dosimetrique au réacteur à puissance élevée de 2 à 10 MW l'intensité de la dose de 20 à 120 Mrad h^{-1}. Il a été trouvé que la perte de poids causée par les rayonnements est proportionelle à l'énergie totale absorbée dans la région étudiée, ce qui est similaire à l'acide oxalique solide. Le comportement radiolytique de l'acide succinique et celui de l'acide oxalique dihydraté ont été comparés. L'effet de la température sur la radiolyse a été particulièrment étudié.

ТВЕРДЫЕ ДИКАРБОНОВЫЕ КИСЛОТЫ В КАЧЕСТВЕ ХИМИЧЕСКИЕ ДОЗИМЕТРЫ ВНУТРИ РЕАКТОРА

Изучено радиолитическое разложение янтарной кислоты, индуцированное смешанным излучением из реактора, в свяеи с дозиметическим применением при высоких уровнях мощности реактора (2–10 Мва) и при мощности дозы 20–120 Мрад $ч^{-1}$. Установлена линейная зависимость поглощенной дозы от логарифма потерь веса из-за излучения, так же как в случае твердой щавелевой кислоты. Дано сравнение радиолитического поведения дигидрата щавелевой кислоты и янтарной кислоты, в частности, влияние температуры на радиолиз.

FESTE DIKARBOXYLSÄURE ALS CHEMISCHE DOSIMETERN FÜR REAKTORSTRAHLUNG

Radiolytische Zersetzung fester Bernsteinsäure durch gemischte Kernreaktorstrahlung wurde wurde bei Reaktorleistungen von 2–10 MW (Dosisleistungen 20–120 Mrad h^{-1}) für die Zwecke der Dosimetrie untersucht. Die Ausbeute der Zersetzung, bestimmt als Gewichtsverlust, nimmt mit absorbierten Dosen regelmässig zu. Das radiolytische Verhalten der Bernsteisäure und Oxalsäure-Dihydrat wurde vergleicht, besonders die Temperaturabhängigkeit der Zersetzung.

IN AN earlier paper[1] the behaviour of solid oxalic acid as a chemical dosimeter for mixed pile radiation has been reported. It was found that this dosimeter is simple to handle and in a defined radiation field gives fairly accurate and reproducible data up to the working temperature of 80°C. In the present work we report some new results on the thermal behaviour of oxalic acid dihydrate under various irradiation conditions and we extend our investigation to the third member of the homologue series of dicarboxylic acids, to solid succinic acid. Earlier data[2,3] have shown that the radiolytic behaviour of solid succinic acid in the field of γ-radiation of ^{60}Co is similar to that of oxalic acid, but in the case of in-pile irradiations some advantages with respect to radiation resistance[2] and thermal stability[4] are anticipated.

The results presented in this paper confirm, indeed, that solid succinic acid can be used successfully as an in-pile dosimeter, and that both dicarboxylic acids, oxalic and succinic, are complementary in a relatively broad range of dose rate and temperature.

EXPERIMENTAL

Measurements were carried out inside the core of the RA reactor at Vinča (a 2 per cent uranium enriched heavy water reactor of nominal power 6·5 MW). The procedure is the same as described earlier:[4] An open quartz ampoule containing 0·2–1·0 g of solid dicarboxylic acid was wrapped in an aluminium foil, placed in a can and irradiated. After irradiation the ampoule was kept at 95°C for 4 and 8 hr in the case of oxalic acid dihydrate and succinic acid,* respectively, and the weight of the remaining amount of sample was determined. Both acids were "Analar" BDH product and have not been additionally purified. For oxalic acid dihydrate the value of the absorbed dose was calculated according to the equation

$$D(\text{Mrad}) = a \log \frac{g_0}{g} \quad (1)$$

with $a = 2{\cdot}11 \times 10^{-3}$ Mrad.[1] In equation (1) g_0 and g are sample weight before and after irradiation (and heating). The absorbed dose rate in all experiments was determined with the aqueous oxalic dosimeter[5] and controlled for reactor power fluctuations by means of cobalt neutron-fluence monitors.[1]

The temperature of all sample was directly measured during irradiation by means of a Chromel–Alumel thermocouple (Sodern, type 2ABAc) within ±0·5°C. In some experimental runs the variation in temperature, in dependence of the reactor power level and sample amount, has been followed.

RESULTS AND DISCUSSION

Figure 1 shows the decomposition of solid succinic acid as a function of the absorbed dose. The ordinate axis represents the chemical effect of decomposition expressed as log g_0/g.

* 95°C has been proven to be optimum for oxalic acid;[6] the same is applied for succinic acid just because of identical treatment of samples.

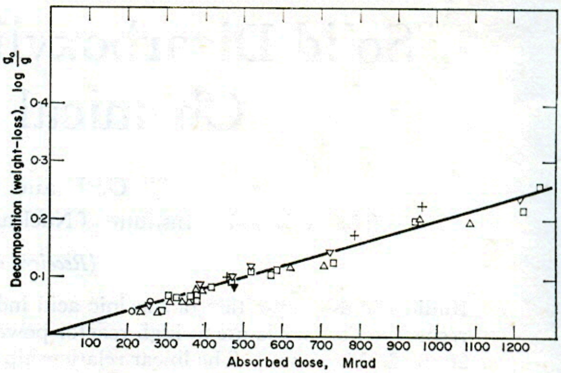

FIG. 1. Decomposition of succinic acid under mixed pile radiation in the RA reactor at Vinča; ○ 2 MW; △ 3 MW; □ 4 MW; ⊠ 4·5 MW; ▽ 5 MW; + 6·5 MW.

The abscissa is the absorbed dose determined with the aqueous oxalic dosimeter, using the proportionality factor specific for the RA reactor which was obtained earlier calorimetrically.[5] The experimental points were obtained at various reactor power levels (2–6·5 MW), irradiations times (3–30 hr), dose rates (20–130 Mrad/hr) and for different initial amounts of sample (0·2–1·0 g).

As in the case of oxalic acid dihydrate the validity of the first order kinetic expression is evident.[1] However, there is a certain difference in the radiolytic change used as the dose measure: the remaining weight after irradiation and heating, is identical to the amount of undecomposed acid for oxalic acid dihydrate, whereas for succinic acid g is the sum of undecomposed acid plus certain solid decomposition products. In the latter case, g exceeds the undecomposed acid by *ca.* 30 weight per cent, as reported previously:[2] the solid radiolytic products contain polymerized derivatives of succinic acid. Nevertheless, the straight line in Fig. 1 confirms that the decomposition of succinic acid under all conditions follows the first order expression (equation (1)) as oxalic acid, and that for both dosimeters the weight-loss is a measure of the absorbed dose.

The results presented in Fig. 1 refer to irradiation up to 6·5 MW power level. At 6·5 MW the experimental points fall slightly above the straight line. This fact and the data of Fig. 2 illustrate the influence of the temperature on the

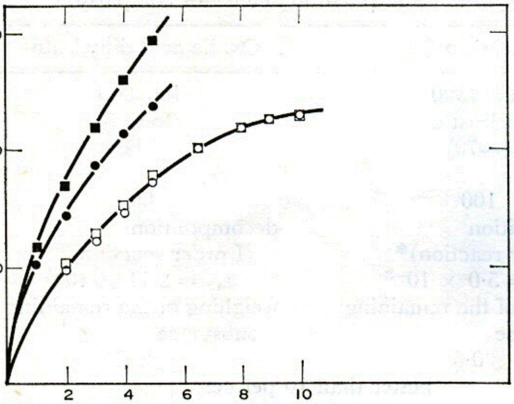

FIG. 2. The temperature in the irradiated oxalic acid dihydrate (circles) and succinic acid (cubes) as a function of the initial amount. Full signs for the 1·0 g samples. Empty signs for the 0·25 g samples.

decomposition rate when samples are irradiated at higher reactor power levels.

Figure 2 shows the effect of the initial amount of sample on the temperature, which has been measured directly in the samples during irradiation. An increase in the amount of sample causes an increase in heat evolution during the irradiation. Thus, in the case of oxalic acid, thermal decomposition seems to be negligible for 0·2 g samples irradiated up to *ca.* 65 Mrad/hr (5 MW power level). However, if the sample amount is increased and the local temperature in the irradiated sample exceeds 85°C, thermal decomposition in addition to radiolysis takes place. In this respect Fig. 3 which refers to succinic acid irradiated at a 10-MW reactor power level is worth noticing. This figure shows that the chemical effect of irradiation, expressed according to equation (1) as log g_0/g, is still linearly dependent on the absorbed dose, but the straight line does not start from the origin. It seems that, at such a high reactor power level, simultaneously with the radiolysis, thermal decomposition due to heat evolution in the sample occurs even with this compound.

Table 1 summarizes the calculated values of the factor a_{succ} of equation (1). These values,

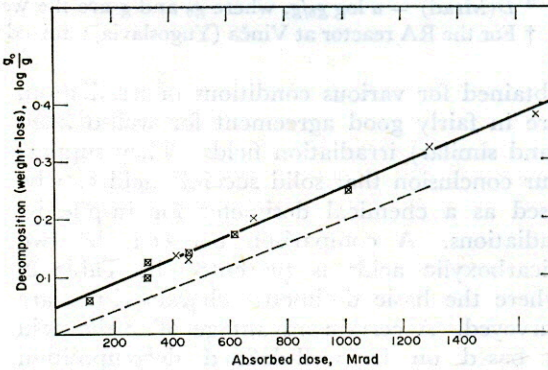

FIG. 3. Decomposition of succinic acid under mixed pile radiation in the RA reactor at 10 MW power level. X—Experiment B; ⊠ Experiment C; Dotted line represents the decomposition curve from Fig. 1.

TABLE 1. Solid succinic acid dosimeter. Reproducibility of a_{succ}-values derived from the measurements at different irradiation conditions during a year. Reactor RA; irradiation position: vertical channel in the core at the maximum thermal neutron flux

Experiment	a_{succ}, $\times 10^{-3}$ Mrad (average)	Reactor power, MW	Irradiation time, hr	Number of samples analysed*	Maximum decomposition %†	Absorbed dose rate, Mrad/MW hr, measured by: Solid oxalic acid dosimeter at 2–5 MW	Aqueous oxalic acid dosimeter at 2 MW
A	5·00 ± 5%	2–5	2–10	28	45	11·0 ± 5%	11·2
B	5·17 ± 5%	3–5	8–30	22	45	11·1 ± 5%	11·8
	4·41 ± 3%	6·5	6–12	6	42		
C	5·02 ± 7%	3; 4	7–28	16	46	12·7 ± 2%	13·0
D	5·05 ± 2%	6·5	3; 6	6	20		

* Initial weights: 0·2–1·0 g.

† As weight-loss.

TABLE 2. Solid succinic and solid oxalic acid dihydrate as in pile-dosimeters—A comparison

System	Succinic acid	Oxalic acid dihydrate
Dose range, Mrad	200–1300	100–800
Reactor power, MW (dose rate, Mrad/hr)	at least 6 (∼70)	up to 5 (∼60)
Upper limit of irradiation temperature, °C	100	80
Reaction observed	decomposition (I order reaction)*	decomposition (I order reaction)*
Proportionality factor,† Mrad	$a_{succ} = 5{\cdot}0 \times 10^{-3}$	$a_{ox} = 2{\cdot}11 \times 10^{-3}$
Method of analysis	weighing of the remaining substance	weighing of the remaining substance
Initial sample amount, gramme	≤0·5	≤0·2
Accuracy	better than 10 per cent	
Relative ease for routine use	about the same	

* $D(\text{Mrad}) = a \log g_0/g$, where g_0 and g are the weights of acids before and after irradiation, respectively.
† For the RA reactor at Vinča (Yugoslavia); mixed pile radiation, gamma to neutron ratio 70/30 in water.

obtained for various conditions of irradiation, are in fairly good agreement for well-defined (and similar) irradiation fields. They support our conclusion that solid succinic acid can be used as a chemical dosimeter for in-pile irradiations. A comparison between the two dicarboxylic acids is presented in Table 2, where the basic dosimetric characteristics are surveyed. A certain advantage of oxalic acid is based on its well-defined decomposition reaction,[6] whereas succinic acid is thermally and radiolytically more stable. In Table 2 the upper temperature limits (taking into account a safety margin of 5–10°) for oxalic and succinic acids are given as 80° and 100°C, respectively. This difference of 20° might be very important for some reactor irradiations. Taking into account all the experimental data, it can be concluded that these two carboxylic acids are complementary with respect to irradiation temperature and absorbed doses. We recommend the use of oxalic acid up to 80°C and *ca.* 65 Mrad/hr of mixed pile radiation whereas succinic acid can be safely used in the range of 80°–100°C and up to *ca.* 80 Mrad/hr of the same radiation.

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