Effect of Radiation on the Chemical Changes accompanying Nuclear Isomeric Transition (Tellurium-121m, -127m, and -129m) in Crystalline Telluric Acid

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Ionising radiation increases the retention of the ground-state species from the isomeric transition of the tellurium isomers in telluric acid. The change in retention with length of irradiation resembles that taking place on heating. The plateau value depends on the dose rate of the irradiation. On ceasing irradiation a new generation of ground-state species grows in and the retention returns to the original value at a rate determined by the decay constant of the ground-state species. The growth and decay of the retention can be duplicated in a series of irradiations and interruptions. An interpretation of these data is provided.

THE advantages of studying the effects of ambient conditions on the isomeric transition rather than the radiative thermal neutron-capture reactions have been discussed in a previous paper[1] in which the effect of temperature on an isomeric transition was reported. In this paper the effect of a steady dose rate of ionising radiation from a ^{60}Co source is explored.

The telluric acid system was chosen partly because of the desirability of comparison with the thermal effects and partly because the system presents the possibility of simultaneous measurements with the three transitions due to ^{121m}Te, ^{127m}Te, and ^{129m}Te. These have the advantage of covering a wide range of half-lives of the ground states. The half-lives of the excited states are 154, 109, and 34 d, and of the ground states 17 d, 9.4 h, and 69 min, respectively. All the states are produced in sufficient quantity by neutron irradiation of natural tellurium. Andersen *et al.*[2] reported that ^{127}Te formed in ^{127m}Te(OH)$_6$ can be radiation annealed.

EXPERIMENTAL

Materials and Equipment.—Natural tellurium metal samples were irradiated in the reactor in the Nuclear Centre at Salazar, Mexico, for 65—72 h at a flux of *ca.* 10^{12} neutron cm^{-2} s^{-1}. The other reagents used were of AnalaR quality. The irradiated tellurium was purified from trace impurities, using a procedure described previously,[1,3] and converted into telluric acid *ca.* 15—30 d after the end of the irradiation. The tellurium(IV) carrier solution used was 4 mol dm^{-3} in hydrochloric acid and contained 1 μg cm^{-3} of tellurium.

The gamma irradiation source was a Gammabeam 650 (Atomic Energy of Canada) containing *ca.* 5×10^4 Ci of ^{60}Co located in the University of Mexico (U.N.A.M.). Activity measurements were made with a Ge–Li solid-state detector used in conjunction with a Nuclear Data 1 024-channel pulse analyser.

Separation Procedure.—The sample was dissolved in the tellurium(IV) carrier solution and the Te^{IV} was extracted into tributyl phosphate as described previously.[1] The decay of the ground-state tellurium in the organic phase and its growth in the aqueous phase was followed by activity measurements.

Measurement of Activities.—The activities of ^{121}Te, ^{127}Te, and ^{129}Te in the aqueous phase were measured by integrating under the well resolved 0.417, 0.455, and 0.573 MeV photopeaks.† Measurements were made with the Ge–Li detector immediately after separation of the phases in the solvent-extraction separation. The retention as Te^{VI} was calculated by expressing this aqueous activity as a fraction of the activity of an equal aliquot portion of the original telluric acid solution.

Radiation Annealing.—For the measurements on ^{127}Te and ^{129}Te the crystals were stored for 3—4 d to ensure transient radioactive equilibrium of the isomer pairs. In order to reduce the magnitude of corrections to the tellurium-121 data, the telluric acid sample was stored for 6 months to reach radioactive equilibrium; 50—250 mg of telluric acid was used for each measurement.

Small samples of the telluric acid were then irradiated for periods of 0—180 min at various dose rates with the ^{60}Co radiation. All the irradiations were at ambient temperature. The temperature of the irradiation chamber wa

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† 1 eV ≈ 1.6×10^{-19} J, 1 rad = 10^{-2} J kg^{-1}.

[1] S. Bulbulian and A. G. Maddock, *J. Chem. Soc.* (*A*), 1971, 2810.

[2] T. Andersen, L. Johansen, and K. Olesen, *Trans. Faraday Soc.*, 1967, **63**, 1730.

[3] S. Bulbulian, *Kerntechnik*, 1970, **12**, 123.

usually 4 °C higher than that of the laboratory, which was *ca.* 18 °C. The temperature of the irradiated crystals varied according to the dose rate and the irradiation time; the maximum temperature registered was 42 °C. Results were corrected for temperature effects by using data from our previous work.[1] The dose rates were measured at the University by a modified Fricke method with the aereated iron(II)–copper(II) system.[4] A $G(Fe^{3+})$ value of 0.66 was used for this system. The telluric acid samples were dissolved and analysed immediately after the irradiation for ^{129}Te determination. In the case of ^{121}Te and ^{127}Te, the time elapsed between the end of the irradiation and dissolution of the crystals varied from 3 to 90 min.

Calculation of the Retention.—Using the method described previously,[1] $R_0 = [ka_2 - a_1(1 - e^{-\lambda t_2})]/a_1e^{-\lambda t_2}$ where a_2 is the ground-state activity observed in the aqueous extract and a_1 is the corresponding activity of the equilibrium solution: t_2 is the time interval between phase separation and measurement of a_2, and k is an efficiency factor allowing for the different compositions of the two solutions on which measurements are made. The measurement of k has been described previously.[1] The decay constant of the daughter species is λ. No corrections for decay of the parent isomers were necessary, but a finite time, t_3, usually elapsed between the end of the irradiation with ^{60}Co and dissolution of the sample in 4 mol dm^{-3} HCl. A further time, t_4, elapsed before phase separation during the analysis. If the retention in the unirradiated crystals is R_u and that of the irradiated crystals is R, then R_0, the observed value, is given by (1) where R_s = retention following isomeric decay in 4 mol

$$R_0 = R_s(1 - e^{-\lambda t_3}) + Re^{-\lambda t_3} + R_u(1 - e^{-\lambda t_4}) + Re^{-\lambda t_4} \qquad (1)$$

dm^{-3} HCl. Hence we obtain expression (2). Typical

$$R = \frac{R_0 - R_s(1 - e^{-\lambda t_3}) - R_u(1 - e^{-\lambda t_4})}{(e^{-\lambda t_3} + e^{-\lambda t_4})} \qquad (2)$$

values for t_2 and t_3 are 12 and 3 min respectively. A typical value of t_4 for ^{129}Te is 3 min, but for ^{127}Te and ^{121}Te t_4 varied from 3 to 90 min. The retentions R_u and R_s were measured in control experiments: $^{121m}Te/^{121}Te$, 0.77 and 0.05; $^{127m}Te/^{127}Te$, 0.67 and 0.04; and $^{129m}Te/^{129}Te$ 0.63 and 0.04, respectively.

RESULTS AND DISCUSSION

The results for the three isomeric pairs are shown in Figure 1(*a*)—(*c*). In each case the retention increases, at first rapidly, then more slowly, eventually reaching a pleateau at a value that is dependent on the dose rate. The data for a set of measurements at constant dose rate are compatible with a linear relation between log $(1 - R)$ and the time of irradiation, but the precision of the measurements is insufficient to attach much significance to this relation. More important, it is clear that the very different half-lives of the ground states of ^{121}Te, ^{127}Te, and ^{129}Te have no very marked effect on the approach to the equilibrium value. This implies that the radiation affects the existing radioactive fragments and is not only effective at, or immediately after, the isomeric transition. There are few comparable published data: Costea[5] investigated the change in retention with time of neutron irradiation of samples of hexa-amminecobalt(III) nitrate at different positions in a reactor. He associated the different curves obtained with the dose rate, due to concurrent ionising irradiation, applied to the sample at the different positions. Although these experiments concern radioactive fragments generated by the (n, γ) process, the data are very similar to those obtained for the isomeric transition. The progress of the process could be represented by the equation $\Delta R_\infty - \Delta R = \Delta R_\infty e^{-\kappa t}$ where ΔR is the observed change in retention up to time t, ΔR_∞ is the change up to the plateau value, and the constant κ is independent of the dose rate. In our experiments the same relation is obeyed; κ does not depend on the particular isomeric

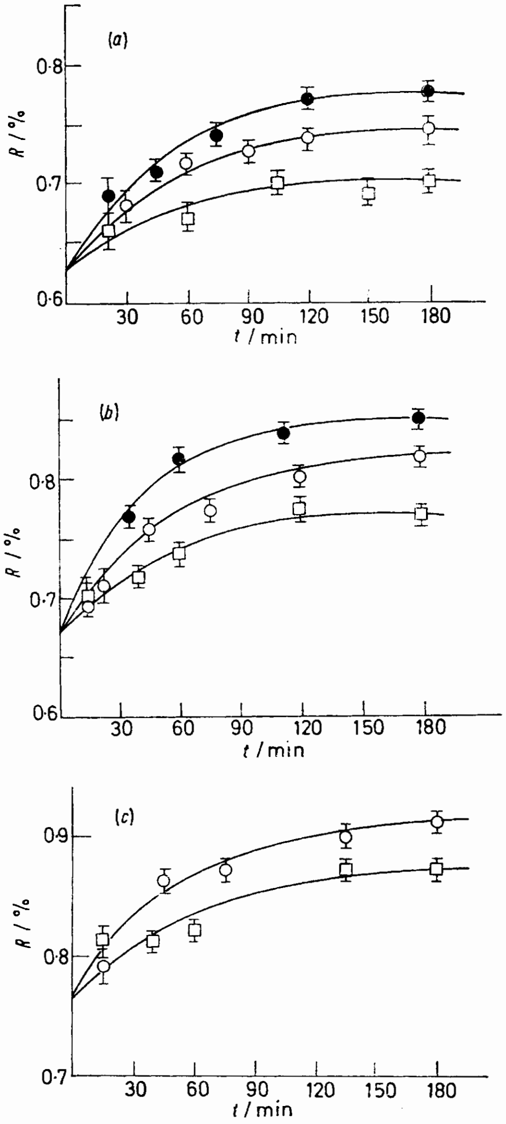

FIGURE 1 Radiation annealing: (*a*) ^{129}Te, dose rates 1.34 (□), 4.59 (○), and 6.66 Mrad h^{-1} (●); (*b*) ^{127}Te, dose rates 1.31 (□), 4.49 (○), and 6.88 Mrad h^{-1} (●); (*c*) ^{121}Te, dose rates 1.31 (□) and 4.49 Mrad h^{-1} (○)

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[4] C. Archundia, R. Herrera, and I. Garcia, 17th Congress Mexican Phys. Soc., 1974.

[5] T. Costea, *J. Inorg. Nuclear Chem.*, 1961, **17**, 20.

transition studied but it does depend on the dose rate. However, Costea found that ΔR_∞ was proportional to the logarithm of dose rate, whereas our data give a more nearly linear relation between ΔR_∞ and the dose rate:

Dose rate/Mrad h^{-1}	1.3	4.5	6.9
$\Delta R_\infty/\%$	10	15	18

Costea did not state whether the temperature of the samples was maintained constant at the different irradiation positions, and differences might be expected to affect his results.

Andersen *et al.*[2] only made measurements on $^{127\mathrm{m}}\mathrm{Te}$ at one dose rate which was not reported. Since a 10-MeV electron bombardment was used, the irradiation was presumably carried out at a very high dose rate and the curve reported (Figure 4, ref. 2) appears to be tending towards a plateau at a retention of *ca.* 81 or 82% which is consistent with the presumably very high dose rate in this experiment and the data in Figure 1(*b*) above.

The simplest model for the change in R would be to suppose that at given dose rates the rate of the conversion of ground-state $\mathrm{Te}^{\mathrm{IV}}$ back into $\mathrm{Te}^{\mathrm{VI}}$ by the radiation is proportional to the number of ground-state tellurium(IV) fragments present in the sample. The proportionality constant λ_2 has the same characteristics as a decay constant. Suppose the number of ground-state tellurium(IV) fragments of the given isomeric pair is a_y and the number of $\mathrm{Te}^{\mathrm{VI}}$ is a_r: let the decay constant of the ground-state isomer be λ_1 and the retention in the absence of the radiation R_0, which will determine the proportion of ground-state fragments of $\mathrm{Te}^{\mathrm{IV}}$ and $\mathrm{Te}^{\mathrm{VI}}$ formed at the moment of isomeric transition; this will be supposed independent of the radiation. Then $a_r + a_y = a_t$ where a_t is the transient equilibrium number of ground-state tellurium atoms. Expression (3) may be

$$\mathrm{d}a_r/\mathrm{d}t = \lambda_2 a_y + R_0 \lambda_1 a_t - \lambda_1 a_r \qquad (3)$$

written, supposing transient equilibrium is maintained, *i.e.* a_t is constant. Thus we obtain (4). As $t \longrightarrow \infty$,

$$\frac{(\lambda_1 + \lambda_2)(R - R_0)}{\lambda_2(1 - R_0)} = 1 - \mathrm{e}^{-(\lambda_1 + \lambda_2)t} \qquad (4)$$

$R_\infty = [\lambda_2/(\lambda_1 + \lambda_2)](1 - R_0) + R_0$, and introducing $\Delta R = R - R_0$, equations (5) and (6) follow. If λ_2 is

$$\Delta R = \frac{\lambda_2}{\lambda_1 + \lambda_2} \cdot (1 - R_0)(1 - \mathrm{e}^{-(\lambda_1 + \lambda_2)t}) \qquad (5)$$

$$\Delta R_\infty = \frac{\lambda_2}{\lambda_1 + \lambda_2} \cdot (1 - R_0) \qquad (6)$$

taken as a variable and assumed to be proportional to the dose rate, we can write (7).

$$\frac{\mathrm{d}\Delta R_\infty}{\mathrm{d}\lambda_2} = \frac{\lambda_1(1 - R_0)}{(\lambda_1 + \lambda_2)^2} \qquad (7)$$

This model would explain the observed dependence of ΔR on t but would require the rate constant for the process to depend on dose rate, if it is supposed that λ_2 is proportional to the dose rate. But the data in this paper demand that ΔR changes much more slowly with dose rate than is implied by equation (7). The model becomes completely untenable when one considers the ΔR values. As seen from equation (6), ΔR_∞ only assumes values appreciably different from 1 or 0 if λ_1 and λ_2 have comparable magnitudes. Now the different tellurium ground states involved in these experiments have widely different values of λ_1, so that unless the λ_2 value for the same dose rate changes in some related way λ_1 and λ_2 cannot always be of similar magnitude. In fact one would hardly expect large differences in λ_2 at constant dose rate for the different isomeric pairs.

It is also useful to compare the results with those published on the radiation annealing of fragments produced by the (n, γ) reaction. There appear to be a number of significant differences. Although the question has not been studied very exhaustively, the present data[6-8] suggest that the extent of radiation annealing of (n, γ) products is determined predominantly by the dose given to the neutron-irradiated sample and is little affected by the dose rate. The changes reported here are clearly dose-rate dependent, as was the effect of concomitant ionising radiation during the neutron irradiation studied by Costea.[5]

The exponential dependence of the extent of annealing on the dose of ionising radiation absorbed, which is characteristic of the radiation annealing of (n, γ) fragments at modest doses, is known to break down at larger doses[9-11] when the process slows down and eventually reaches a plateau value. However, the possibility that this plateau is dose-rate dependent has not been investigated. It should also be observed that the plateau is reached at much lower doses and the extent of annealing is smaller for the isomeric transition-produced species than for the (n, γ) products. The radiation annealing proceeds in a similar manner to, but is slower than, the thermal process. Like other cases of radiation annealing it is temperature dependent and must involve a thermally controlled step.

So far these data are compatible with a model for the radiation annealing suggested previously by Al-Siddique and Maddock.[11] It supposes that the isomeric transition process in telluric acid leads to the production of daughter species having a distribution of energies of activation for thermal annealing such as is shown in Figure 2. At a given ambient temperature T, practically all the daughter species with energies of activation lying to the left of the step function shown, T, will suffer thermal annealing before decay. The effect of the ionising radiation will be to transfer part of the population lying to the right of the step function to the left. These centres will then suffer

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[6] G. Harbottle, *J. Chem. Phys.*, 1954, **22**, 1083.

[7] J. W. Cobble and G. E. Boyd, *J. Amer. Chem. Soc.*, 1952, **74**, 1282.

[8] A. G. Maddock, F. E. Treloar, and J. I. Vargas, *Trans. Faraday Soc.*, 1963, **59**, 924.

[9] T. Andersen and A. G. Maddock, *Trans. Faraday Soc.*, 1963, **59**, 2362.

[10] F. Baumgärtner and A. G. Maddock, *Trans. Faraday Soc.*, 1968, **64**, 714.

[11] F. R. Al-Siddique and A. G. Maddock, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3007.

rapid thermal annealing. However, not all the population lying to the right of T is eligible for this process.

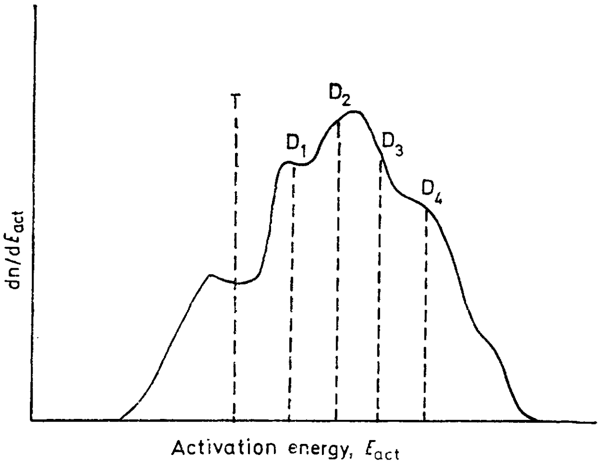

FIGURE 2 Hypothetical spectrum of energies of activation for thermal annealing of fragment centres: T, centres lying to the left of this line anneal rapidly at temperature *T*; D$_1$D$_2$, *etc.*, maximum radiation-initiated reduction in energy of activation can transfer population D$_2$ — D$_3$ to D$_1$ — D$_2$, *etc.*

So far the model does not specify whether the radiation produces a direct effect on the damage centres, or whether the effect is due to some radiation-induced change in the bulk of the material. Because of the low concentration of the damage centres, the former process would probably imply transfer of excitation, or ionisation, over several lattice units to reach the damage centres.

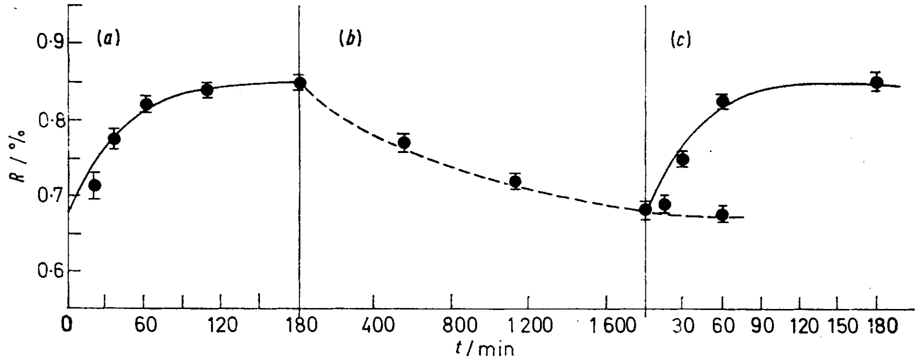

FIGURE 3 Recovery and repeat annealing of ^{127}Te after a first radiation annealing: (*a*) first 180-min first-radiation annealing; (*b*) 0—1 600 min recovery in the absence of radiation; (*c*) second 180-min second-radiation annealing. Dose rate, 6.88 Mrad h^{-1}

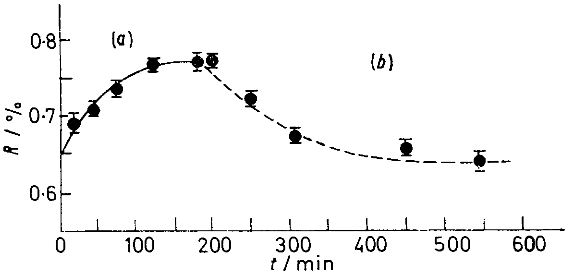

FIGURE 4 Radiation annealing and recovery measured with ^{129}Te. Irradiation stopped at 180 min. Dose rate, 6.66 Mrad h^{-1}

These alternatives have been investigated by measuring the rate of return of the retention in the telluric acid to its initial value after removal from the ionising radiation and the re-establishment of a steady retention on irradiating for a second time. The results for ^{127}Te are shown in Figure 3. The recovery after irradiation of the ^{129}Te retention is shown in Figure 4. These data show that the recovery after irradiation is determined by the time constant for growth of a new population of daughter species in the matrix. Thus recovery is much slower for ^{127}Te than for ^{129}Te (compare Figures 3 and 4). One cycle of irradiation and recovery does not affect the behaviour of the sample during a subsequent irradiation. This shows that the effect directly concerns the damage centres and is not simply due to radiation-induced changes in the matrix.

The similarity of the radiation and thermal-annealing isotherms suggests the possibility that the ionising radiation quickly modifies the energy of activation spectrum and the subsequent thermal annealing is the only rate-controlling process. If this were the case, a short ionising radiation, only part of the way to the plateau retention value, might lead to a further change in retention on storage of the sample at the same temperature, but in the absence of ionising radiation. The data from such an experiment are shown in Figure 5. The retention values after removal from the radiation are corrected for growth of the ground-state species. Only a very small amount of additional annealing appears to take place after removal from the radiation, so that some, but not all, of the centres suffering a change in the energy of activation for the thermal annealing anneal during the irradiation. Clearly the effect of the radiation does not take place rapidly compared with the rate of thermal annealing at the ambient temperature and thus the radiation process is slower to reach its plateau than the thermal process.

It has been suggested[10] that the radiation annealing of (n, γ)-generated damage centres slows down with increasing dose, eventually reaching a plateau, because the radiation steadily generates defects in the solid which compete with the (n, γ) centres for the excitation or ionisation produced by the ionisating radiation and dissipates them so that they can no longer produce annealing. This explanation is excluded, at least in the present system, by the repetitive radiation-annealing curves (Figure 3). In addition it does not lead to the dependence of the plateau on the dose rate (see equations on p. 719 of ref. 10). The similarity of the thermal and radiation-annealing curves can be explained if one supposes that the rate constant for radiation annealing decreases with increasing activation energy for thermal annealing about as rapidly as does the rate constant for the thermal process, that is to say as a negative exponential dependence.

A previous proposal[11] that each radiation event reduces the energy of activation for thermal annealing of the affected centre by a much smaller amount than the span of activation energies in the spectrum, so that centres with high activation energies may need several radiation events before crossing the step-function thermal-annealing threshold, T Figure (2), will not lead to dose-rate-dependent plateaux.

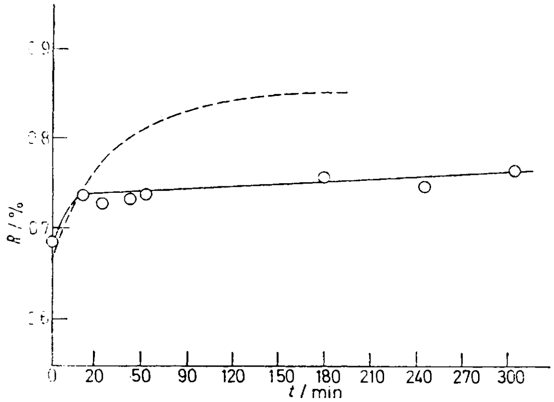

FIGURE 5 Radiation annealing interrupted at 12 min. Dose rate, 6.88 Mrad h^{-1}

A physical model which will lead to a sufficiently rapid decrease in radiation-annealing rate constant is to attribute the annealing to local heating produced by the radiation. As the activation energy for thermal annealing increases the volume of crystal raised to a sufficiently high temperature for annealing by a single radiation event will decrease. At constant dose rate this will lead to a decrease in the rate constant for the radiation annealing. At still higher energies of activation an overlap of heated zones due to two, or more, nearly simultaneous radiation events may be necessary. Such a model will yield rate constants which decrease smoothly and rapidly with increasing energy of activation for thermal annealing of the centres. It can also be expected to yield dose-rate-dependent plateaux.

Such an explanation would hardly be possible for photoannealing, but preliminary experiments show that photoannealing of the ground-state species in telluric acid can occur. An experiment combining thermal and radiation annealing also excludes this explanation. A sample giving a retention of 66% for ^{129}Te gave a plateau retention of 84% during heating for 3 h at 89 °C. Irradiation for 3 h at 5.3 Mrad h^{-1} gave the same retention, but when the irradiated sample was heated to 89 °C, after the end of the ionising irradiation, the retention rose further to a plateau value of 93%. Thus the ionising radiation does not simply recombine those fragment centres with the lowest energies of activation first, as would be the case if its mode of action was purely thermal, but must reduce the energies of activation for thermal annealing of some of the less readily thermally annealable centres.

One is forced to conclude that (*i*) the irradiation must produce its effect in the immediate vicinity of the fragment centres, because there is no effect on a new generation of fragments (Figures 3 and 4), (*ii*) the radiation-annealing effect is not purely thermal, some change occurring in the vicinity of the decay centres, (*iii*) all centres can be affected, and (*iv*) the immediate effect of the irradiation manifests itself in a lowering of the energy of activation for thermal annealing.

Irradiation of a solid often leads to a steady-state concentration of a radical, or reactive, species. The various ways in which such an equilibrium concentration can arise are discussed, for instance, by Vasil'ev and Tal'rose.[12] The lowering of the energy of activation for reoxidation of the ground-state species might then be due to the formation of a radical in its close vicinity. The proportion of ground-state species with nearby radicals increases with the dose rate and the radicals decay fairly rapidly ($t_{\frac{1}{2}} < 1$ h) in the absence of the radiation. Oliveira and Alcacer[13] recently showed that the radiolysis of solid telluric acid generates $HO_2^{\cdot}$ radicals which have a half-life of *ca.* 50 h. They suggest $HO_2^{\cdot}$ formation *via* $OH^{\cdot}$ and the latter could well function as the above postulated species.

Such a model accounts for the practically constant time taken to reach the radiation-annealing plateau for all three isomers. This is a little more than the time required to reach a steady-state concentration of nearby $OH^{\cdot}$ radicals. It may well imply some migration of excitation to generate radicals close to the fragment centres, but energy transfer resulting in radiolysis near lattice imperfections is well established. It is compatible with the data of Figures 3—5. The model implies that the radiation annealing is closely associated with the radiolytic properties of the matrix.

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[12] G. K. Vasil'ev and V. L. Tal'rose, *Kinetika i Kataliz*, **1963**, **4**, 497.

[13] C. M. Oliveira and L. J. Alcacer, *J. Radiation Phys. Chem.*, 1975, **7**, 577.