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On the Dynamics of the Accumulation of Stabilized Paramagnetic Centres at Low Temperature: Radiolysis of a Molecular Matrix

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The problem of limited concentrations of atoms and radicals at low temperature in a molecular matrix has been investigated and a model, describing the experimental results, is proposed, according to which the radical yield for low dose rates is significantly higher than that for high dose rates.

The stabilization of limited concentrations of atoms and radicals at low temperature in molecular matrices was intensively studied in the early sixties.[1] Along with extensive experimental investigation the problem was theoretically considered to ascertain the maximum possible concentrations of stabilized radicals. Refs. 2 and 3 report the calculation, based on a statistical coordination model, of the maximum concentration of radicals. These calculations were based on the simple assumption that the formation of a radical in a position adjacent to the stabilized radical would result in their recombination. This estimation (~ 10%) should probably be considered as the highest possible boundary for accumulation of stabilized radicals, as it is one to two orders of magnitude higher than the observed maximum concentrations.[4,5] In order to explain the experimentally recorded concentrations of stabilized radicals, a dynamic theory was suggested.[6] This theory was later developed,[7,8] to connect extremely low concentrations of atoms and radicals with the thermal instability of such systems with respect to the heat wave spreading over the sample from the centre of random recombination.

It has been proposed[9] that the recombination of centres during radiolysis might also be caused by a quite different factor: the brittle fracture of a sample. The accumulation of metastable states on radiolysis of a solid matrix[10] may lead to the appearance of local microcracks in the sample. Sufficient molecular mobility for recombination of the stabilized centres is created in the surrounding volume as the microcracks are formed.

When a helium flow containing minor admixtures of N_2 and atomic N was put into superfluid helium, the formation of a snow condensate, containing extremely high relative concentrations of atoms, was observed.[11] However, these maximum concentrations do not actually exceed the theoretical statistical predictions, since they are caused by the formation of a helium 'coat' around the nitrogen atom.

During the complex formation and stabilization of radicals during the low-temperature radiolysis of organic compounds, the following processes lead to retarded accumulation of frozen radicals, along with an increase in their concentration (*i*) Formation of radicals (mobile) at 77 K (atomic hydrogen, atomic fluorine, *etc.*) that can recombine with stabilized 'heavy' radicals during their migration over the matrix. (*ii*) Charge transfer and excitation transfer processes. (*iii*) A wave of recombination caused by heat from the random recombination. (*iv*) Recombination in the region of microcrack formation. (*v*) Decay of radicals on localization of irradiation energy (this process has been reported previously[4,5] and confirmed by a large amount of experimental evidence).

The kinetics of radical accumulation during the course of n-heptane radiolysis at 77 K over a wide range of doses (up to 20 MGy; Gy = J kg^{-1}) and with low dose rates (100 kGy h^{-1}) have been investigated.[12] The rate of radical accumulation in n-heptane at 77 K was found to decrease monotonously, however, being substantially different to zero even at maximum irradiation doses. The results obtained are in sharp contrast to the previous ideas: the maximum concentrations of stabilized radicals were not observed, those observed being higher than previously recorded values. The contradiction is evidently connected with the use of low dose rates uncharacteristic of earlier experiments.

We propose the mechanism of eqns. (1)–(4) to explain the results obtained. A radical formed by the interaction of irradiation with a molecule may either recombine with the other unstabilized radical (R) or become trapped and stabilized (R_{st}). Mobile atoms of hydrogen or fluorine, for instance, can serve as unstabilized radicals. A stabilized radical affected by irradiation may become stabilized (*e.g.*, by the reaction $—CH_2—CH_2— \rightarrow —CH{=}CH_2 + H_2$).

$$M \xrightarrow{\gamma} R \qquad (1)$$

$$R \longrightarrow R_{st} \qquad (2)$$

$$R \xrightarrow{\gamma} R \qquad (3)$$

$$R + R \longrightarrow \text{decay} \qquad (4)$$

The process will then be described by a system of two differential equations (5) and (6),

$$d[R]/dt = k_1I - k_2[R] + k_3I[R_{st}] - k_4[R]^2 \qquad (5)$$

$$d[R_{st}]/dt = k_2[R] - k_3I[R_{st}], \qquad (6)$$

where I is the dose rate, and k_1–k_4 are the rate constants for eqns. (1)–(4). The kinetics of accumulation of $[R_{st}]$ obtained by solving the system of eqns. (5) and (6) gives a definite limited concentration [eqn. (7)].

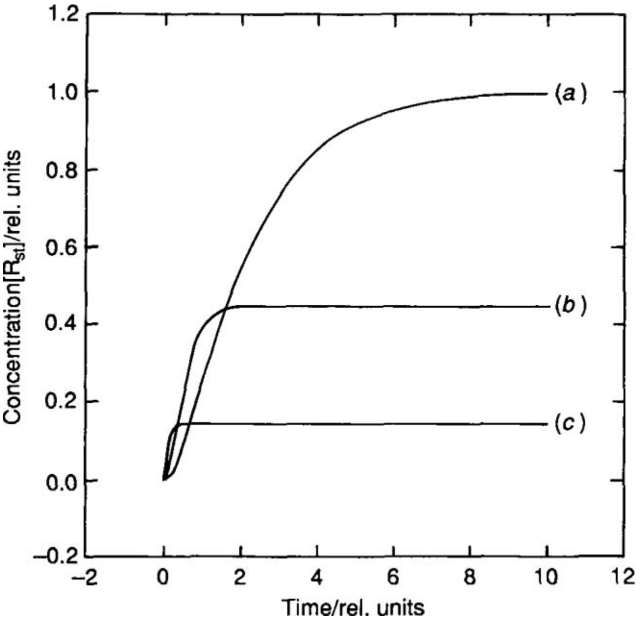

Fig. 1 Kinetic curves for the accumulation of stabilized radicals with respect to time, computed according to the model suggested for different dose rates: (*a*) dose rate 1, (*b*) 5, (*c*) 50 rel. units; $k_1 = k_2 = k_3 = k_4 = 1$

$$[R_{st}]^{\infty} = k_2/k_3[k_1/k_4I]^{0.5} \qquad (7)$$

A numerical solution of eqns. (5) and (6) was carried out which showed that the maximum concentration of accumulated radicals is inversely proportional to the square root of the dose rate (see Fig. 1).

Thus the proposed model relates the anomalously high concentrations $[R_{st}]$ produced experimentally on low-temperature radiolysis of n-heptane[12] to a specific dependence of their yield on the dose rate.

It is interesting to note that the kinetic curves have an S-character. This fact has important consequences for the ambiguous notions of 'radiation yield' and the relation between the $[R_{st}]$ yield at a fixed dose and the dose rate used in the experiment. Fig. 2 shows the initial curves for the accumulation of stabilized radicals *vs.* the integral dose, calculated for different dose rates. There is a significant difference in the values of $[R_{st}]$ obtained with different dose rates but with the same integral dose. The radical yield is observed to increase with decreasing dose rate. However, for very low dose rates, the S-character of the accumulation curves degenerates and the yield of stabilized radicals is no longer dependent on the dose rate.

Experimental data on the accumulation of paramagnetic centres during radiolysis of alkyl ketones at 77 K are given in ref. 13. Kinetic curves for the accumulation were obtained for two very different dose rates, using ^{60}Co γ-irradiation and an electron beam. Whereas the maximum concentration was observed for high dose rates (electron beam), the $[R_{st}]$ yield for small dose rates (^{60}Co γ-irradiation) grew practically linearly with increase in dose rate within the whole range of dose rates. The radical yield for low dose rates is sufficiently higher than for high dose rates. Therefore the experimental data[13] are fully in accordance with our model.

If our suggested model is correct, then two anomalous phenomena should be observed in the low dose rate region.

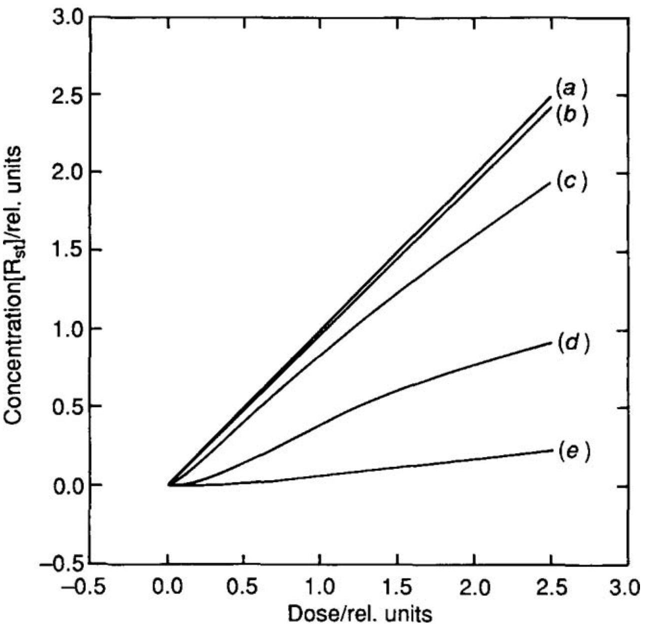

Fig. 2 Initial portions of accumulation curves for stabilized radicals *vs.* integral dose, calculated for various dose rates: (*a*) dose rate 0.0005, (*b*) 0.005, (*c*) 0.05, (*d*) 0.5, (*e*) 5 rel. units; $k_1 = k_2 = k_3 = k_4 = 1$

(*i*) Accumulation of very high concentrations of stabilized radicals, and (*ii*) the lower the dose rate used, the higher the yield of radicals for the fixed doses.

These conclusions are significant for the study of the long-term action of ionizing irradiation at low dose rates on humans.

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