

branches of the experimental curves correspond to a mean chain lifetime of about 200 msec. When assuming a purely bimolecular disappearance, we obtain $k_2/\alpha = 3.5 \times 10^6 \text{ M}^{-1}$, independently of dose-rate in the range studied.

As distortion of the curves due to the electronic circuit could be excluded, a discrepancy arises between both the rising portions of the curves and the results of the stationary measurements on one hand, and the decay curves on the other. It appears as though there would be both first and second order reactions during irradiation, and only second order reactions in the absence of irradiation. Thus, the simple mechanism we proposed as a working hypothesis needs to be extended.

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Dehydroxylation of Muscovite

It is well known that large, well-crystallized sheets of muscovite mica are resistant to thermal decomposition at temperatures above 500° C. Hidnert and Dickson¹, for example, reported that heating at 600° C for 1 h produced little or no change in the properties of a large number of different muscovite samples. Finely divided muscovite, however, begins to lose its structural water at an appreciable rate at temperatures as low as 400° C (ref. 2). Related dioctahedral aluminosilicates, such as the montmorillonite clays, are also dehydroxylated at temperatures below 500° C (ref. 3). This process occurs without a general destruction of the crystal lattice in dioctahedral minerals. It has been recognized⁴ that the rate of decomposition may be limited by diffusion of water from the lattice.

When a thin sheet of muscovite is heated for a long enough time at 600° C, it is possible to demonstrate the loss of structural hydroxyl groups by the infra-red spectrum. For example, a sheet of Brazilian muscovite 1.4 μ thick was held at 600° C for 760 h; at the end of this time, the OH peak at 3,628 cm^{-1} had decreased to 30 per cent of its initial intensity. The sample was still transparent, had the appearance of a single crystal, and its thickness was not measurably changed. This sample was afterwards re-hydroxylated at 600° C and about 16 atm. water pressure for 485 h, after which the OH content was restored to 84 per cent of its original value. The OH absorption band at 3,628 cm^{-1} showed the same dichroism as in the original sheet, which may be interpreted to mean that no major rearrangement of the aluminosilicate lattice takes place on dehydroxylation.

When a sheet of muscovite is heated at 700°–800° C, the rate of water loss increases markedly, and extensive delamination of the crystal occurs. The thickness of a sample exposed to a temperature in this range for a short time may increase 20-fold while 50 per cent of its hydroxyl content is lost. There is a corresponding increase in the surface area (measured by the Brunauer–Emmett–Teller method). The true density of the solid, as measured by helium displacement, changes by less than 5 per cent. Finely divided muscovite, however, exhibits slightly decreased surface area after dehydroxylation.

It would appear, therefore, that three processes are involved in the dehydroxylation of micas. Depending on the nature of the sample and the conditions, any one of

them may be the rate limiting step. The primary step is the formation of water molecules from structural OH groups. This is an entirely local and reversible reaction; in the absence of any other processes, it leads to a temperature dependent equilibrium water concentration. The extent of this reaction depends on the details of the lattice arrangement; it occurs much more readily in dioctahedral than in trioctahedral micas⁵.

If diffusion of water molecules through the lattice is a slow process compared with the attainment of this equilibrium, the rate of the overall dehydroxylation will be diffusion limited, and this appears to be the case for muscovite at temperatures below ~ 650° C. At about 700° C, however, the concentration of water molecules inside a thick sheet of muscovite reaches a point where the pressure is sufficient to produce delamination, substantially reducing the diffusion distance and correspondingly accelerating the loss of water. With finely divided samples, however, the pressure necessary for delamination is not reached and diffusion remains the controlling step over a larger temperature range.

One would expect delamination to occur along the normal potassium ion cleavage planes, and this view is supported by the fact that the ion-exchange capacity⁶ per unit of surface area is the same for normal muscovite and for material which has been 50 per cent dehydroxylated at 760° C.

It is obvious that, even though the basic mechanism of water loss by diffusion does not change, the rate of the overall dehydroxylation process will change drastically with temperature. It will also vary with the degree of dehydroxylation and under most conditions the apparent kinetics will be of a complicated mathematical form. Further detailed investigations of the infra-red spectral changes occurring on dehydroxylation have been made by one of us (W. V.), and will be presented elsewhere.

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BIOPHYSICS

Effects of Low-dosage Gamma-radiation on Soluble Collagen

THE effects of low-dosage radiation on soluble collagen molecules have not been reported. This low-dosage radiation is suitable for producing initial radiation-induced molecular changes which are described and interpreted in this communication.

Samples were prepared and examined as follows: citrate soluble human skin collagen was prepared by methods of Bakerman¹. Salt soluble preparations were similar to those of Jackson and Bentley². Collagen concentrations were calculated from nitrogen values determined by Conway diffusion technique³ after Kjeldahl digestion. Viscosity measurements were made in a calibrated Cannon–Manning semimicro-capillary viscometer in a water bath regulated to $20^\circ \pm 0.015^\circ \text{C}$. Determinations of optical rotation were made with a Rudolph photoelectric polarimeter with sodium and xenon light sources. The samples showed one distinct peak at 20°C in a Spinco model *E* ultracentrifuge. The limiting viscosity numbers were 1,340 and 1,150 and the optical rotation readings were -370° and -390° for salt- and citrate-soluble collagens respectively. Concentrations of soluble collagens were approximately 2 mg/ml. 2-ml. samples were irradiated in citrate buffer at 24°C in 'Pyrex' beakers covered with