A Radiation-induced Isomerisation in Organic Crystals

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DURING the *X*-ray crystallographic analysis of the *p*-bromophenacyl ester of hirsutic acid, Comer and Trotter observed an unusual and highly specific intramolecular rearrangement (involving the migration of two H atoms) induced by the *X*-ray beam.[1] After 10 hr. exposure, they found the crystals consisted of an approximately equimolar mixture of the original molecule and the isomer and that further irradiation casued no additional change. The rearrangement barely altered the lattice parameters but did lead to O—H · · · O hydrogen bonding between pairs of dissimilar molecules.

An estimation of the radiation intensity used by Comer and Trotter has been made by absorbing the collimated *X*-ray beam, essentially completely, in a Fricke dosimeter solution. From (i) the observed total oxidation of Fe^{2+} to Fe^{3+} (ii) the known G for the Fricke dosimeter for 8 kv *X*-rays, (iii) the absorption coefficient of the crystals for this radiation, (iv) the density of the crystals, and (v) the reported irradiation time (<10 hr.) for 50% conversion, a lower limit to the G value (radiation yield per 100 ev absorbed) has been evaluated, such that G (isomerisation) $\geqslant 57$.

This high G value indicates either a chain reaction involving a chemically active propagating species (difficult to envisage in this case) or a highly efficient energy transfer process, probably peculiar to the crystalline state and requiring the exothermicity of the hydrogen-bond formed. In any event, Comer and Trotter's observation represents a unique and interesting radiation chemical reaction. If such highly efficient and selective radiation-induced isomerisations in the pure crystalline state are not exceptionally rare then this observation affords the synthetic or preparative organic chemist a valuable technique and the crystallographer a warning.

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[1] F. W. Comer and J. Trotter, *J. Chem. Soc.* (*B*), 1966, 13.