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# The Influence of Radiation Chemical Effects on X-Ray Structure Determinations†

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Implicit in the use of x-ray diffraction for structural determination is the assumption that the x-rays do not seriously perturb the crystal. This is not true for many organic crystals. X and $\gamma$ rays induce chemical changes including the formation of free radicals. These usually arise by the loss of hydrogen from a molecule or the addition of hydrogen lost from some other molecule, to a double bond. Such effects are quite general and are apart from such special reactions as photodimerization. Normally this would cause minimal perturbation in the usual structural determination. However, free radicals are very reactive. The initial radicals may decompose or undergo chemical change to form more stable trapped radicals. They may react with each other, commonly by dismutation or by addition to another radical or molecule. If oxygen from the surrounding air can penetrate the crystal, the free radicals will react to generate peroxide radicals initiating a chain reaction in which several hundred molecules undergo oxidation for every free radical present.

These effects are quite complex and may result in many kinds of structural damage which can influence a structure determination. An example of this is bromamphenicol.[1] Dunitz noted that the relative intensities of certain reflections changed in the x-ray beam in a manner consistant with bromine loss. The B factor was found to be unusually high and spurious bond lengths were noted apparently because of x-ray damage.

It was considered useful to explore these effects more thoroughly. For this we chose acrylamide since much is known concerning the physical and chemical effects of radiation on it.[2]

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The method adopted was to perform structural determinations by the usual techniques under three different conditions of radiation damage resulting from the x-rays used.

An acrylamide crystal was cooled to −150°C and exposed to the x-ray beam. Under these conditions some radiolysis gas is obtained due to molecular breakdown. In addition free radicals appear due to addition of radiolytic hydrogen to the double bond. Below −135° the free radicals remain trapped. These effects were rather less than is common to a good many organic solids.

It was found that initially several reflections increased in intensity, probably due to a breakup of mosaic blocks. This is a common effect and has been used to decrease extinction.[3] After 2–3 hours the intensities became stable and remained so. Structure I was then determined using counter data.

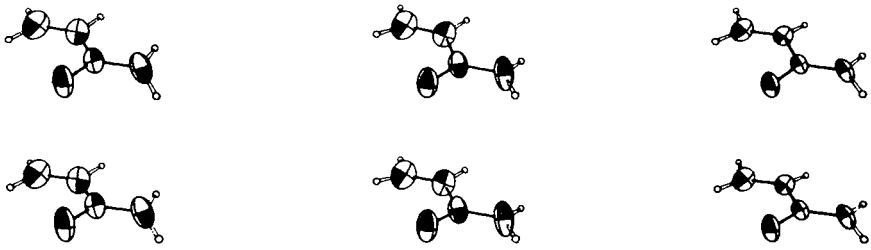
About −135°C the free radical forms dimers by addition to another molecule, probably in the *b*-axis direction. It will not react further until about −20°C. This is a common process and results in products dimensionally different than the molecules from which they arise. This strains and distorts in the lattice. Since the *G*-value for radical formation is low (0.26–0.6) their concentration must still be small.

The crystal used previously was warmed to −40° in the x-ray beam. The *b* axis reflections decreased markedly in intensity while the others showed much smaller changes. When the intensity of 020 decreased 50%, the crystal was recooled to −150°C to stabilize the reflections and structure II was determined.

About −20° the free radicals react to yield amorphous polymer. This case is then characteristic of those situations where the product nucleates a separate phase within the crystal.

A fresh crystal was cooled to −15°C and exposed to the x-ray beam. When the intensity of the 200 reflection decreased 50% it was cooled to −150°C. At this time the crystal was turbid and was more than 50% polymerized. The amorphous polymer gave a broad diffraction ring which added to the background. The structure was then redetermined. Thus we had 3 structures, all determined at the same temperature but each representing a different type and extent of radiation damage to the crystal.

Surprisingly all three structures refined to a weighted *R* factor of about 0.09. However, there were significant differences. The three showed about the same bond length and bond angles between the five heavier atoms. They differed in the hydrogen positions and the thermal parameters. The best structure was probably I since it reflects the smallest amount of structural damage. As expected II was closer to I than the more extensively damaged III. However, standard deviations for II were greater than for III. This probably reflects the preferential weakening of *b* axis reflections, especially



Acrylamide I Acrylamide II Acrylamide III

the high angle ones, as compared to the more general weakening of all reflections, in III. The apparent thermal parameters increased with damage. The orientation of the thermal elipsoids also changed. As expected from the chemical nature of the damage, those of the terminal carbon show a larger change than the amide carbon. The hydrogen parameters differed markedly in the three structures. It proved more difficult to locate them in the extensively damaged structure. The large decrease in the *b* axis reflections in II probably reflects the addition of the free radical to its nearest neighbor in that direction thus causing the largest perturbation along that axis. It should be kept in mind that these structures reflect not uncommon types of radiation damage and that even I, presumably the best structure, probably reflects some radiation damage as indicated by the initial intensity changes and the production of radiolysis gas. These results indicate that the general outline of the structure and the bond angles can be relatively insensitive to radiation damage. The thermal parameters and hydrogen position however, can be seriously perturbed and should be interpreted with caution. However, if properly interpreted, they can shed light on the nature of the chemical damage.

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