

Annealing of Recoil Damage by Ultra-violet Light

ANNEALING of the chemical damage caused by thermal neutrons is well known for ionizing radiations such as γ -rays and high-energy electrons^{1,2}. However, only one report of annealing by ultra-violet light is recorded in the literature. W. Herr³ found that the yield of rhenium (VII) from potassium chlororhenite irradiated with neutrons decreased more by heating at 100°C. and irradiating with a mercury ultra-violet lamp than by heating alone. No attempt was made to determine the annealing kinetics or to relate the process to annealing by ionizing radiations. Harbottle⁴ reported that four hours bright sunlight had no influence on the retention of potassium chromate.

We have observed the recombination of recoil fragments by ultra-violet light in ammonium dihydrogen phosphate, and have made a comparison of this with high-energy electron annealing. The ammonium dihydrogen phosphate crystals were irradiated with thermal neutrons in *Bepo* at Harwell for 6 hr. at p.f. 0.1. Annealing was carried out using a Hanovia *U.V.S.* 250 mercury lamp, giving a dose of 4.5×10^8 ergs. cm.⁻² hr.⁻¹ at 20 cm., and using 1.8-MeV. electrons from a Van der Graaf accelerator. In both cases care was taken to ensure that the temperature of the samples did not rise above 30°C. Typical plots of the nonphosphate fraction versus dose are given in Fig. 1. The phosphate activity was separated by precipitation of magnesium ammonium phosphate. Although it is not yet possible to compare quantitatively the dose-rate by each annealing method, calculation of the energy from the ultra-violet source incident on the sample shows that the dose-rate cannot be greater than the equivalent of 1 *M* rads/hr. and is probably much less.

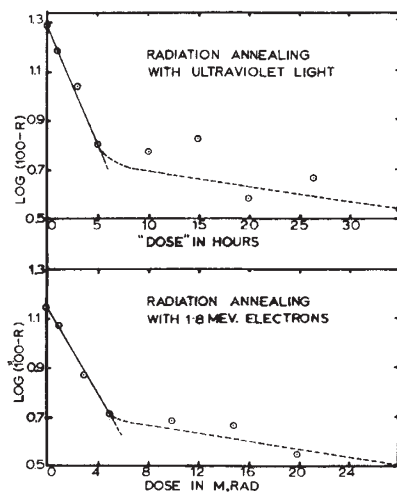


Fig. 1

The similarity of the behaviour of the material towards both ultra-violet radiation and electrons indicates that both mechanisms of annealing are the same. Both show an initially linear portion indicative of a monomolecular recombination process. At higher doses the speed of reaction decreases and a much slower process of unknown kinetics takes over when the retention reaches 95 per cent. The sensitivity of the material to ultra-violet light can be taken as evidence that radiation annealing occurs

by an electronic process probably controlled by the defect concentration in the crystal lattice.

Further investigation of the sensitivity of the material to the wave-length of the radiation used is in progress and will be reported in full later.

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¹ Williams, R. R., *J. Phys. Chem.*, **52**, 603 (1948).

² Green, J. H., Harbottle, G., and Maddock, A. G., *Trans. Faraday Soc.*, **49**, 1413 (1953).

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⁴ Harbottle, G., *J. Chem. Phys.*, **22**, 1083 (1954).

A Correlation between the Shift in the Ultra-Violet Absorption Maxima and the Electronegativity of the Adjacent Atoms in some Aliphatic Carbonyl Compounds

DURING the course of our recent work on the photochemistry of butyric acid and its methyl ester¹, some spectroscopic confirmation was sought that their absorption spectra and those of the aldehydes and ketones are due to the same electronic transition. The absorption spectra are similar in form and have comparable extinction coefficients, but the absorption maxima of the acids and esters are displaced to lower wave-lengths, as column 2, Table 1, illustrates. There is little

1 Compound	2 Wave-length of absorption maximum in Å.	3 Reference	4 Shift (wave numbers)	Electro-negativity
Acetaldehyde	2930	8	0	4.6
Acetic acid	2040	9	14930	6.0
Acetone (in water)	2645	8	3730	5.0
Acetone (in hexane)	2790	8	1750	5.0
Acetyl chloride	2345	10, 11	8550	5.5
Acetyl bromide	2400-2600*	10	5910-7570	5.3
Butyric acid	2050	10	14690	6.0
Dimethyl carbonate	1700-1800*	10	21480-24470	7.0
Ethyl acetate	2100	10	13520	6.0
Formaldehyde	3150†	12	-1910	4.2
(in ether)				

* Estimated range: measurements not extended to maximum.

† Estimated from maximum intensity of partially banded—partly continuous spectrum in reference.

doubt that they are due to the same transition, for the primary photochemical reactions are similar and the carbonyl group in the acids maintains its identity, although it is naturally modified by the neighbouring hydroxyl group².

According to Mulliken³ and McMurray⁴, the low extinction of the long-wave absorption of the aldehydes indicates a transition which is forbidden by local symmetry. The spectrum is due to the excitation of an electron from a non-bonding orbital, localized near the oxygen atom of the carbonyl group, to an anti-bonding orbital, spread out over a larger part of the molecule⁵. The upper electronic state is not repulsive, but internal transitions from it to other excited states which are repulsive, lead to the observed photochemical decomposition⁶. The shift in the absorption maximum in going from an aldehyde to an acid may be regarded as an effect of the adjacent atoms to the carbonyl group on the binding of the non-bonding electrons. They will be attracted more by the oxygen atom of the acid than by the hydrogen of the aldehyde and so more tightly bound. Consequently,