RADIATION CHEMISTRY

Radiation-induced Formation and Reactions of the Formyl Radical Ion

We have recently reported the formation of the CO_2^- radical ion and the related CO_2H radical by the action of ionizing radiation on aqueous solutions of carbon dioxide and bicarbonate¹.

It seemed of interest, therefore, to examine the corresponding reaction with carbon monoxide which should lead, in the first instance, to the CO^- radical ion and the COH radical. Some direct proof for the presence of CO^- in aqueous solutions has been obtained now from experiments in which oxygen-free aqueous solutions containing suitable organic solutes have been irradiated with ionizing radiations in the presence of carbon monoxide. It could be demonstrated that in certain cases the CO^- ion (or the COH radical respectively) could be combined with an organic radical with the formation of the corresponding formylated compound.

For example, the irradiation of aqueous solutions of methanol ($10^{-1} M$) in the presence of carbon monoxide (1 atm.) with Co-60 γ -rays (1.4×10^{19} eV. ml.⁻¹) gave glycolaldehyde with a yield of $G = 0.2$ (molecules/100 eV.) at pH = 5.4. The glycolaldehyde was identified by the formation of a coloured derivative with the 2 : 3-diaminophenazine reagent in concentrated sulphuric acid².

It is again important that the reaction is carried out in deoxygenated solutions because otherwise the negative polarons (H_2O^-), which are the reducing entities³ produced by the action of radiation on water, may be scavenged to a greater or lesser extent by the molecular oxygen according to:

In general, this formylation process depends on the formation of a free radical from the organic solute by the action of the radiation-produced OH or (H_2O^+), for example, in the case of methanol:

and association of the organic free radical with the COH (CO^-) according to the reaction:

the formyl radical being formed by the reduction of CO according to:

In this way it should be possible to produce some ¹⁴C-carbonyl compounds labelled in the CO group.

We wish to thank the Rockefeller Foundation for financial support; one of us (J.H.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

JOHN HOLIAN
GEORGE SCHOLES
JOSEPH J. WEISS

Chemistry Department,
King's College
(University of Durham),
Newcastle upon Tyne.

The neutron spectrometer used was similar to that described by Antal and Goland². A mica monochromator was used with beryllium and beryllium oxide filters. The results are shown in Fig. 1 plotted

as $\ln\left(\frac{I_u}{I_t}\right)$ versus wave-length, where I_u is the number of neutrons transmitted by 14 cm. of unirradiated beryllium oxide and I_t is the number transmitted by an identical specimen after irradiation. The doses quoted are the integrated doses over the fission neutron spectrum. It can be seen that the amount of extra scattering due to defects increases with neutron dose. For one set of specimens an annealing study was made by repeating the measurements after annealing the specimens at 200° C. intervals from 200–1,400° C. These results are shown in Fig. 2.

It can be seen that there are two distinct effects, a decrease in attenuation near the Bragg cut-off, which anneals steadily from 200° C. to 1,000° C., and an increase at longer wave-lengths, which anneals between 1,200° C. and 1,400° C.

The initial decrease in extra scattering near the cut-off wave-length could be explained if irradiation broadened the Bragg reflexions. However, this seems unlikely because the X-ray line broadening appears to be insufficient to account for the effect and this line broadening does not anneal until 1,400° C. A defect configuration which would explain the sharp decrease with wave-length is that proposed by Huntington³ for copper, in which two interstitial atoms appear at each side of a vacant lattice site with an I-V spacing of less than 1 Å.

The theory developed by James⁴ for the scattering of X-rays by polyatomic gases has been applied to the increase in scattering observed at long wave-lengths. A model which fits the observed dependence on wavelength is one in which the vacancies are clustered into close-packed groups containing 14 vacancies and the interstitials are randomly distributed. Values for the number of defects have been calculated on this model and these are shown in the Table 1.

Table 1

Specimen	Mean fission neutron dose (n.v.t.)	Irradiation temperature	Fraction of primary collisions	Fraction of displaced atoms	Displacements per primary collision
X22	2.8×10^{19}	70–75° C.	7×10^{-3}	$4.5 \pm 4.0 \times 10^{-4}$	1–13
X4	1.8×10^{20}	80–100° C.	4.5×10^{-4}	$4.5 \pm 0.4 \times 10^{-3}$	9–11
X39	6.8×10^{20}	80–100° C.	1.7×10^{-3}	$2.2 \pm 0.1 \times 10^{-3}$	12–14

The number of primary collisions was calculated by assuming a cross-section of 2.5 barns as the average of beryllium and oxygen atoms over the fission spectrum.

Further work on X-ray line broadening and other physical properties are being carried out in order to obtain more information on the nature of the defects.

T. M. SABINE
A. W. PRYOR
B. S. HICKMAN

Australian Atomic Energy Commission
Research Establishment,
Lucas Heights,
New South Wales.

¹ Antal, J. J., Weiss, R. J., and Dienes, G. J., *Phys. Rev.*, **99**, 1081 (1955).

² Antal, J. J., and Goland, A. N., *Phys. Rev.*, **112**, 103 (1958).

³ Huntington, H. B., *Phys. Rev.*, **91**, 1092 (1953).

⁴ James, R. W., *The Optical Principles of the Diffraction of X-rays* (G. Bell and Sons, Ltd., 1958).

¹ Scholes, G., Simic, M., and Weiss, J. J., *Nature*, **188**, 1019 (1960).

² Dechary, J. M., Kun, F., and Pitot, H. C., *Anal. Chem.*, **26**, 449 (1954).

³ Weiss, J., *Nature*, **186**, 751 (1960).