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Hydration-Annealing of Chemical Radiation Damage in Calcium Nitrate

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The effect of hydration on the annealing of chemical radiation damage in anhydrous calcium nitrate has been investigated. Rehydration of the anhydrous irradiated nitrate induces direct recovery of the damage. The rehydrated salt is susceptible to thermal annealing but the extent of annealing is small compared to that in the anhydrous salt. The direct recovery of damage on rehydration is due to enhanced lattice mobility. The recovery process is unimolecular.

A considerable amount of work has been done on the thermal annealing of chemical radiation damage in ionic nitrates and the influence of various factors thereon[1-4]. It has been observed that phase transformations in irradiated crystals induce rapid recombination of damage fragments and the recombination virtually ceases once the phase transformation has taken place[5-7]. The effect of lattice rearrangement accompanying loss of water of crystallisation on the annealing of chemical radiation damage in calcium bromate monohydrate-anhydrous system has also been reported[8]. However, published information on the effect of post irradiation hydration on the annealing of chemical radiation damage is not available. It was of interest, therefore, to investigate the effect of regain of water of crystallisation on the annealing of chemical radiation damage in anhydrous salts. Ionic nitrate, such as calcium nitrate has been chosen for this investigation because it is formed as crystalline nitrate with water of crystallisation and the regain of water by the anhydrous nitrate to form the tetrahydrate takes place at room temperature. Moreover, the kinetics of thermal annealing of chemical radiation damage in this system has been investigated in detail[9]. A preliminary note on the effect of hydration on the annealing of chemical radiation damage in cadmium nitrate has already appeared[10].

Experimental

Calcium nitrate tetrahydrate (A. R. grade) was dehydrated to constant weight at 170° in a thermostated electric hot air oven and stored over phosphorus pentoxide in a vacuum desiccator. Portions of the anhydrous salt sealed *in vacuo* in pyrex glass ampoules were irradiated at room temperature with ^{60}Co γ-rays to a dose of 52 Mrad at a dose rate of 0.2 Mrad h^{-1}. The irradiated samples were preserved over phosphorus pentoxide in vacuum desiccator. Due to the highly hygroscopic nature of the anhydrous salt it was always handled in a dry box.

The damage nitrite was estimated spectrophotometrically with a Beckman DU2 instrument by Shinn[11] method as modified by Kershaw and Chamberlin[12] to an accuracy of $\pm 1\%$.

The effect of regain of water of crystallisation on the initial nitrite content in γ-irradiated anhydrous calcium nitrate was studied by keeping known weights of the irradiated sample in a constant humidity controlled atmosphere[13] of relative humidity 93.9% for various time intervals, from 0-265 h at room temperature and estimating the NO_2^- content at the end of each time interval. The weight of the irradiated salt at the end of the above time interval agreed with the uptake of four molecules of water of crystallisation indicating complete rehydration.

Isothermal annealing runs were made in air in glass tubes in a thermostated electric hot air oven maintained to within $\pm 1°$ of the desired temperature, with samples of the irradiated anhydrous salt, the irradiated sample rehydrated at room temperature and also with the sample desiccated after rehydration.

Results and Discussion

The damage induced by 52 Mrad ^{60}Co γ-rays in anhydrous calcium nitrate was 4058 p.p.m. of NO_2^-. There was progressive diminution of NO_2^- content during rehydration. Typical plots of nitrite concentration *vs* time of rehydration are given in Fig. 1. The plots are linear which implies an unimolecular recombination process. The velocity constant is $3.84 \times 10^{-4} h^{-1}$.

The thermal annealing characteristic of irradiated anhydrous calcium nitrate at 300° along with those of the rehydrated sample and the sample desiccated after rehydration are shown in Fig. 2. The regain of water of crystallisation by the irradiated anhydrous

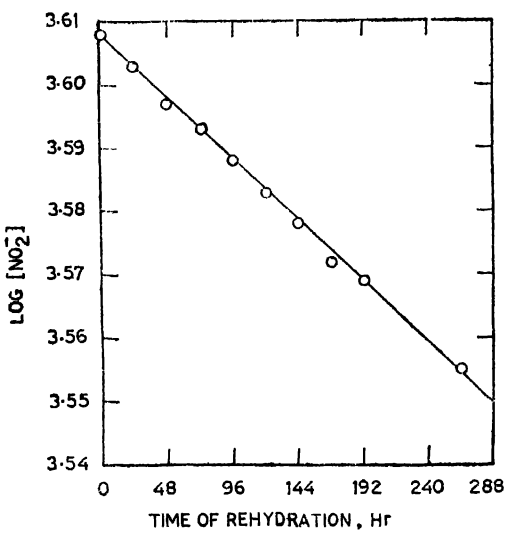

Fig. 1. Annealing of chemical radiation damage in anhydrous calcium nitrate on rehydration.

appreciable energy of activation and that the energy input to the system is only utilised for the release and migration of the damage oxygen. The annealing on rehydration of the anhydrous salt and subsequent thermal annealing of the rehydrated salt can therefore be explained as follows. The rehydration of the anhydrous salt results in phase change. The lattice mobility during the phase change liberates the damage oxygen and a proportion of these combine with nitrite to give nitrate ions. This results in the annealing observed on rehydration. However, a small portion of the fragments could survive the lattice rearrangement[16]. These fragments anneal back to nitrate on heating. Since the proportion of these fragments is small the extent of thermal annealing after rehydration is very small as observed.

The thermal annealing of chemical radiation damage in ionic nitrates is a combination of a first order process, which corresponds to the recombination of close correlated nitrite ion-oxygen atom pairs, and a second order process involving random

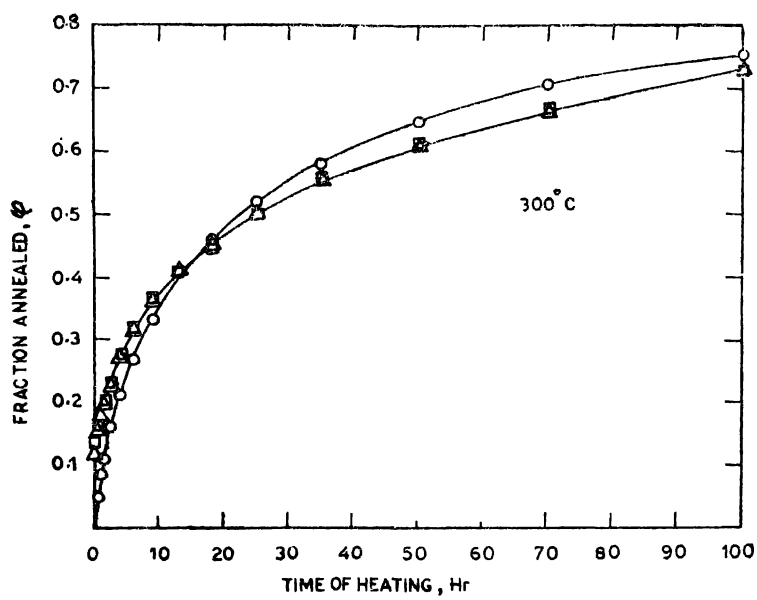

Fig. 2. Effect of rehydration and subsequent desiccation on thermal annealing of chemical radiation damage in calcium nitrate, (O) irradiated anhydrous salt, (△) irradiated anhydrous salt rehydrated, (□) irradiated anhydrous salt desiccated after rehydration.

nitrate at room temperature to form the tetrahydrate results in the recovery of damage, to the extent of $\phi=0.116$, where ϕ is the fraction annealed[14]. The subsequent thermal annealing behaviour of the rehydrated salt is quite normal although the extent of annealing is smaller than that for the irradiated anhydrous salt. Desiccation of the rehydrated salt produces an additional recovery of $\phi=0.02$. The thermal annealing behaviour of the sample desiccated after rehydration is also similar to that of the rehydrated sample.

In the model of annealing developed by Maddock and Mohanty[1,15] it has been proposed that the recombination of the damage fragments (NO_2^- and O in the case of nitrates) occurs without recombination of the damage fragments throughout the crystal[17]. The percentage of NO_2^- that recombine by the first order mechanism in irradiated calcium nitrate is 12 and the corresponding energy of activation is 16.9 kcal mol^{-1}. The extent of hydration annealing is smaller in the case of calcium nitrate compared to that in cadmium nitrate[10]. This low magnitude of annealing is due to the small percentage of the primary fragments and the higher energy of activation involved.

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References

1. A. G. MADDOCK, and S. R. MOHANTY, *Discuss. Faraday Soc.*, 1961, 31, 193.
2. E. CHANDUNNI and S. M. K. NAIR, *Rad. Eff. Lett*, 1981, 58, 5.
3. E. CHANDDUNI, Ph. D. Thesis, University of Calicut, 1981.
4. M. S. KRISHNAN, Ph. D. Thesis, University of Calicut, 1981.
5. A. G. MADDOCK and S. R. MOHANTY, *Radiochim. Acta*, 1963, 1, 85.
6. S. R. MOHANTY and S. R. UPADHYAY, *Indian J. Chem.*, 1965, 3, 285.
7. E. CHANDUNNI and S. M. K. NAIR, *Radiochim. Acta*, 1979, 26, 177.
   M. KHARE and S. R. MOHANTY, *J. Inorg. Nucl. Chem.*, 1967, 29, 853.
9. S. M. K. NAIR, C. JAMES and C. S. PEARLY, *Radiochim. Acta*, 1983, 32, 202.
10. S. M. K. NAIR and C. JAMES, *Indian J. Chem., Sect. A*, 1982, 21, 504.
11. M. B. SHINN, *Ind. Engg. Chem., Anal. Ed.*, 1941, 13, 83.
12. N. F. KERSHAW and N. S. CHAMBERLIN, *Ind. Engg. Chem., Anal. Ed.*, 1942, 14, 312.
13. E. CHANDUNNI, M. S. KRISHNAN and S. M. K. NAIR, *J. Indian Chem Soc.*, 1978, 55, 574.
14. M. S. KRISHNAN and S. M. K. NAIR, *J. Indian Chem. Soc.*, 1979, 56, 805.
15. S. R. MOHANTY and S. R. UPADHYAY, *Z. Phys. Chem.*, 1968, 57, 3.
16. J. R. BOLTON and K. J. MCCALLUM, *Can. J. Chem.*, 1957, 35, 761.
17. S. M. K. NAIR, M. S. KRISHNAN and C. JAMES, *Rad. Eff.*, 1983, 71, 87.