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Role of Water of Crystallization in Thermal Annealing of Neutron Activated Lithium Permanganate

V G DEDGAONKAR*, S MITRA & S A KULKARNI

Department of Chemistry, University of Poona, Pune 411 007

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Manganese-56 activity distribution between Mn^{7+}, Mn^{2+} and Mn^{4+} states in neutron activated $LiMnO_4.3H_2O$ and $LiMnO_4.H_2O$, is nearly the same, the ratio being ~7:93:0. Subsequent heat treatment over the temperature range 328-393 K shows higher recovery rate for the trihydrate. Activation energy for the annealing process is 13.2 and 28.7 kJ mol^{-1} for $LiMnO_4.3H_2O$ and $LiMnO_4.H_2O$, respectively. A relationship is sought between the annealing data and the dehydration characteristics.

The thermal annealing behaviour of permanganates has been extensively studied[1,2], but the role of water of crystallization in thermal annealing of permanganate is still unclear. In the present note kinetics of isothermal annealing is considered in conjunction with isothermal dehydration with a view to understanding the role of water of crystallization.

$LiMnO_4.3H_2O$ was prepared from $Ba(MnO_4)_2$ and Li_2SO_4 by a double decomposition reaction and its purity checked. $LiMnO_4.H_2O$ was obtained on isothermally heating the trihydrate at 363K for 2 hr. Thermalized neutrons from a ^{252}Cf fission neutron source (flux : $\sim 10^6$ n cm^{-2} s^{-1}, γ-dose : 1 mGy s^{-1}) were used for activation and an electronically controlled oil bath was employed for isothermal annealing. An adsorption-elution technique[3] was employed for the ^{56}Mn activity separation using alumina as an adsorbent for Mn^{2+}.

The initial retention values of $LiMnO_4.3H_2O$ and its monohydrate are nearly the same, i.e. 7.0 ± 1 %. Standard deviation observed in the results of heating experiments is within ± 1.5 % and this treatment given over the temperature range 328-373 K shows an increasing pattern of retention with temperature dependent saturation values (Fig. 1). It is interesting to note that annealing in monohydrate is only to a very small extent reaching a limiting value well within 15 min, while the trihydrate salt anneals to a considerable extent and the time required to reach its saturation is longer. The role that water of crystallization plays in aiding recovery in lithium salt appears unique; no such recovery over the dehydration temperature range is noted in the case of $NaMnO_4.3H_2O$ and hexahydrates of alkaline-earth and transition metal permanganates[4]. The linear relationship between logarithm of the fraction to be annealed and the heating time is indicative of the fact that the recombination of the fragments yielding the parent form follows first order kinetics. Arrhenius treatment to the isothermal annealing data gives the energy of activation as 13.2 and 28.7 kJ mol^{-1} for $LiMnO_4.3H_2O$ and $LiMnO_4.H_2O$ respectively.

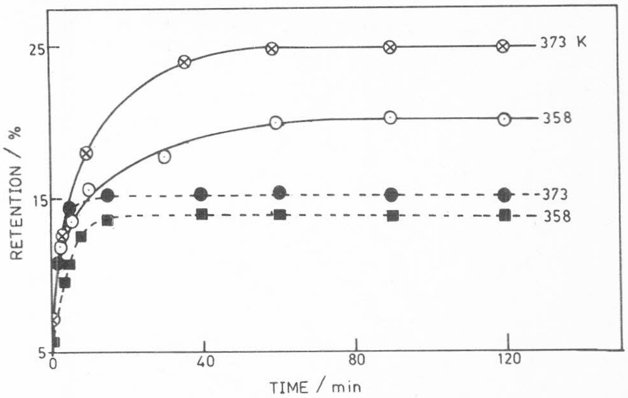

Fig. 1—Isothermal annealing characteristics of $LiMnO_4.3H_2O$ (solid lines) and $LiMnO_4.H_2O$ (dashed lines)

The plateau values of retention on isochronally heating $LiMnO_4.H_2O$ for 1 hr are 5.7, 10.4, 11.3, 12.3, 13.9, 15.2 and 12.2 % at 298, 328, 333, 343, 358, 373 and 393K respectively. The corresponding values for $LiMnO_4.3H_2O$ are 7.1, 12.3, 13.0, 14.8, 20.4, 25.3 and 18.1 %. It may be noted that the recovery is always higher in the case of the trihydrate. The non-retained fraction in either form of lithium permanganate was Mn^{2+} with the annealing taking place at its cost. Above 373K the parent and/or the annealable species decomposes so that the retention decreases in both the forms with a simultaneous increase of activity in the Mn^{2+} fraction; no $^{56}MnO_2$ is observed, however.

The kinetics of isothermal dehydration of neutron activated $LiMnO_4.3H_2O$ reveal that above 380K concomitant decomposition of the salt occurs indicating that the recoil sites act as nucleation centres creating localized strains in the crystal which eventually lower the decomposition temperature. Fractional dehydration (α) which has been followed with time over the temperature range 357-378K (Fig. 2) shows that a linear rate law is applicable for the loss of two water molecules. Arrhenius treatment to the data gives the activation energy as 63.4 kJ mol^{-1}.

Thermogravimetric and differential thermal analysis data (Fig. 3) show that the total mass loss corresponding to the two endotherms at 390 and 432K is equivalent to the loss of two water molecules. The

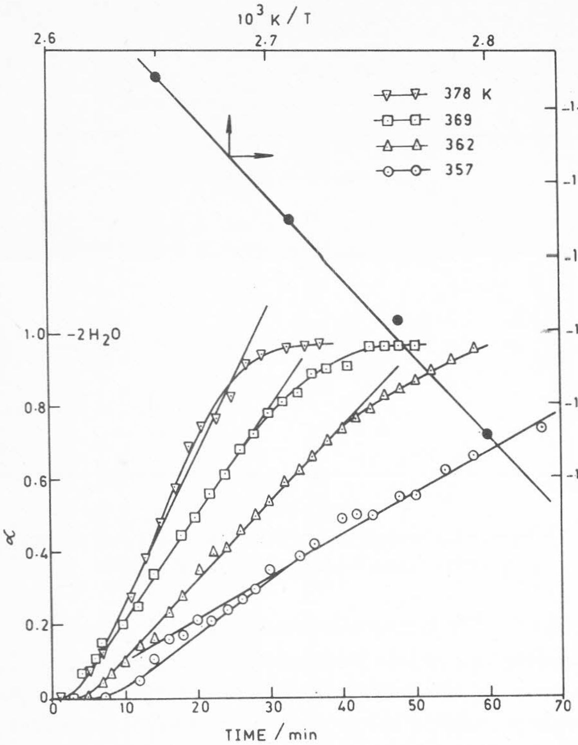

Fig. 2—Isothermal dehydration of $LiMnO_4.3H_2O$ at different temperatures and the Arrhenius plot for the dehydration (●)

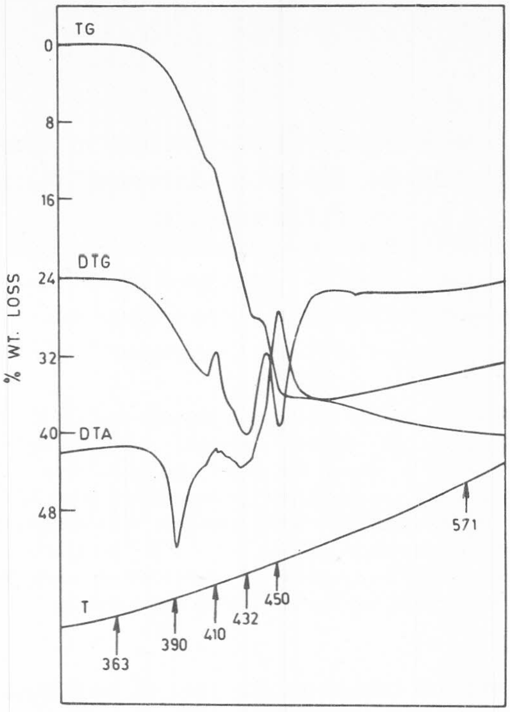

Fig. 3—Simultaneous DTA, DTG and TG for 25 mg sample of $LiMnO_4.3H_2O$ [Heating rate 5 K/min]

exotherm at 450K signifies a phase transformation during removal of the third water molecule. This is immediately followed by decomposition. The gradual mass loss then occurs upto 570K and the final value is in accordance with the reaction : $2\ LiMnO_4 \rightarrow Li_2MnO_4 + MnO_2 + O_2$.

A comparison of the isothermal dehydration and annealing data reveals that $^{56}MnO_4^-$ recovery in $LiMnO_4.3H_2O$ is maximum during the time interval in which the rate of loss of water molecules is high. Following the recoil event, oxygen containing fragments are likely to be held by water molecules through hydrogen bonds particularly in the case of the trihydrate. These fragments become available for recombination when released during the dehydration process. The higher extent of annealing in the case of trihydrate also supports this. Lower recovery in the monohydrate may be a consequence of a less tightly packed crystal structure which allows the recoil fragments to move farther away from the parent site so that recombination reactions become less probable even on heat treatment.

References

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