Comparison of the Electrical Conductivities of the Perchlorates of Ammonia and Rubidium: a Test for Proton Migration in the Solid State

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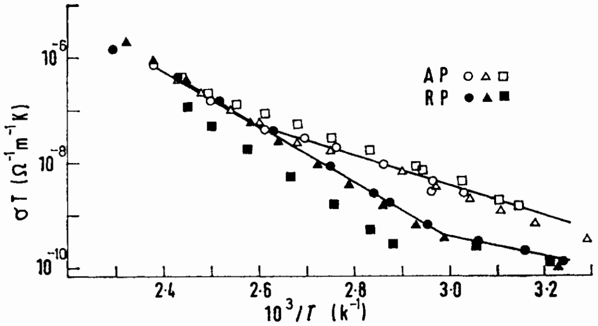
The d.c. conductivity, and its variation with temperature, of single crystals of NH_4ClO_4 and the crystallographically related $RbClO_4$ strongly suggests that detached protons and transient NH_3 species are not involved in the bulk migration of charged carriers in NH_4ClO_4, contrary to what happens in NH_4Cl.

THE recently established [1] importance of proton transfer in the decomposition of ammonium perchlorate (AP) has prompted us to examine whether proton migration is the principal mode of transport of charged carriers through this solid. By analogy with Staveley's and others' results [2,3] on ammonium halides—in which it was shown that the electrical conductivity of solid NH_4Cl was several decades larger than that of the corresponding solid alkali-metal chlorides—we should expect proton migration to operate in AP *via* structural vacancies and transient NH_3 species. Two brief studies of the electrical conductivity of AP have recently been reported.[4,5] Whereas the results of Maycock *et al.*[4] are not readily amenable to interpretation in terms of proton migration, the work of Boldyrev and Khairetdinov,[6] who detected H_2 liberation at the cathode during electrolysis (a characteristic which is not, of itself, adequate, see ref. 7 to identify protonic conductivity), does reveal that, at least in powdered AP, the migration of protons could be significant.

Apart from the possibility that in powdered samples proton migration may occur preferentially at surfaces (*cf.* behaviour of ice [7] and other [8,9] solids), it is important to know to what extent bulk proton migration occurs at higher temperatures. We have, accordingly, made appropriate electrical measurements on AP and a closely related solid, rubidium perchlorate (RP) which crystallizes not only in the same symmetry class and with the identical space-group (*Pnma*) but which has, in addition, unit-cell dimensions remarkably close to those of AP (a = 9·202, b = 5·816, c = 7·449 Å for AP and a = 9·269, b = 5·814, c = 7·490 Å for RP), a fact which is a consequence of the near-identical ionic radii of the (rotating) NH_4^+ (1·43 Å) and Rb^+ (1·47 Å) ions.

Results for the bulk conductivity on dried single crystals of the two salts are summarized in the Figure, from which it may be seen that the classic kinked-plot, symptomatic of an extrinsic process giving way to an intrinsic one at higher temperatures, is obtained in each case. Of considerable significance is the near identity



σT versus $1/T$ plots for dry single crystals of AP and RP (see text). The d.c. measurements were generally made from the highest temperature downwards. Earthed guard rings were employed. Note close similarity of activation energies for the two solids in the intrinsic region. Results of different runs on same sample are shown as circles, triangles, and squares

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of the activation energies (1·1 and 1·2 eV) and of the absolute values of σT for the two materials at high temperatures (contrast the situation that obtains for NH_4Cl and NaCl). It is, therefore, extremely unlikely that detached protons, transient NH_3 species, and structural vacancies are involved in the bulk migration of charge carriers through AP. It also follows that, if, as seems likely, the conduction process is principally ionic in character, the mobility of the NH_4^+ ion as a unit is closely comparable to that of Rb^+ in the respective solid perchlorates. (At the surfaces [9] of these two solids the situation may, however, be different, and this is currently under investigation.) It is of relevance to note that the fluorophosphates of ammonia and rubidium (as pellets) also have near-identical [2] conductivities ($\sigma_{333\ K} \sim 6 \times 10^{-9}\ \Omega^{-1}\ m^{-1}$) indicating that our conclusions for the perchlorate may also be valid for NH_4PF_6.

The d.c. conductivity of a number of single-crystal samples (grown from aqueous solution) fitted with earthed guard-rings, was recorded in dry nitrogen over a range of temperatures. A step-voltage supply provided the field across the crystals and the resulting charging and discharging transient and steady currents measured using either a F.E.T.-input operational amplifier (Carwyn Instruments, type 101A) or an electrometer (Keithley model 602) linked to a chart recorder (TOA model EPR/2T). Temperature control of a silicone-oil bath was maintained using a controller (Eurotherm PID/SCR) and the temperature of the samples (±0·1 K) measured using a copper constantan thermocouple. So long as the samples were heated up to the highest temperatures of measurement (*ca.* 410 K) for a length of time sufficient to drive off vestiges of moisture, the results were found to be reproducible. Repeat runs in nitrogen on different crystals yielded σI values within a factor of 10 and the activation energy was reproducible to within ±0·1 eV.

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