On the Anomalously Large Electrical Conductivity of Ammonium Perchlorate–Ammonia (1/2)

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A.c. measurements on the diammonia compound of ammonium perchlorate (AP) along with electrical data relating to rubidium perchlorate, its ammonia compound, and liquid ammonia, suggest that the exceptional room temperature conductivity of AP,$2NH_3$ arises from protonic migration.

ON cooling single crystals of ammonium perchlorate (AP) to liquid nitrogen temperatures in the presence of ammonia gas anomalously large and somewhat erratic currents were recorded. The effect was tentatively attributed *in transitu*, to the electret properties of ammonia.[1] Upon their removal from the measuring

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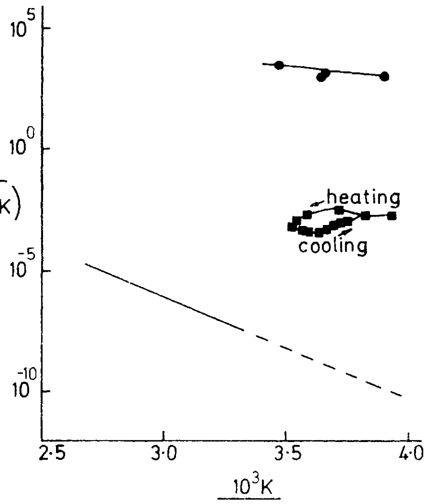
[1] D. C. Lainé and R. C. Sweeting, *Phys. Letters*, 1971, **36A**, 469.

system at room temperature, the (originally single-crystal) samples were found to be loosely packed, polycrystalline, masses. The uptake of ammonia, recorded microgravimetrically in separate experiments, was anomalously large and far in excess of that corresponding to either physical adsorption or chemisorption.[2,3] The above effects may be rationalized in terms of the reaction of AP with ammonia since it is now known that AP,[3,4] in common with other alkali metal (M) perchlorates,[5] forms compounds of the type $MClO_4,nNH_3$ where *n* are integers ranging from 1 to 6. Clearly a given ammonia compound is stable under a definite equilibrium pressure of ammonia and addition of an excess of ammonia may lead to its dissolution in the compound. Confirmation of these changes is readily obtainable by simple optical microscopy (see micrographs in refs. 2 and 3), and by microbalance techniques.

The electrical conductivity of AP–ammonia compounds was considered to be particularly interesting because of the possibility of proton conduction in such systems, there being potentially facile proton transfer in the $NH_4^+ + NH_2$ Brönsted conjugate pair. Measurements are reported here on the electrical conductivity of the system $NH_4ClO_4,2NH_3$ in the range 257—298 K taken employing an a.c. technique (1592 Hz).† The ammonia compound formation was achieved, knowing the data of Fridman and Pastevich,[4] by admission into the measuring cell of the calculated amount of ammonia and maintenance of the correct gas pressure during the course of the experiment. Inert, stainless steel, electrodes were employed with the ammonia compound (a liquid in the temperature range studied) contained in a Teflon cup.

At room temperatures the a.c. conductivity of $NH_4ClO_4,2NH_3$ is *ca.* 10^{12} times as large as that of an AP disc (Figure) and is characterized by an activation enthalpy of *ca.* 0·25 eV (24 kJ mol^{-1}). Analogous measurements were carried out on rubidium perchlorate (RP). Even though it is not feasible, because of the slowness of the reaction, to identify the various ammonia compounds of RP (not hitherto reported in the literature), the temperature variation of the conductivity of a sample of RP after the establishment of an equilibrium pressure of ammonia was also recorded (Figure). The conductivity is lower by a factor of some 10^5 than that of $NH_4ClO_4,2NH_3$.

In suitable systems[6,7] large values of the absolute conductivity together with a very low activation enthalpy of conduction strongly indicate a mechanism involving intermolecular (and possibly some intramolecular) proton jumps. Recently Delpuech and co-workers[8] have computed by *ab initio* methods an energy barrier of *ca.* 0·1 eV for the proton jump from NH_4^+ to NH_3 in solution so that our roughly determined activation enthalpy, which encompasses both the intra- and inter-molecular terms, suggests protonic motion. Furthermore, the difference between the AP and RP ammonia compounds together with the fact that the conductivity of $NH_4ClO_4,2NH_3$ is *ca.* 10^6 times as large as that of liquid ammonia[9] further supports the proposal that protons from NH_4^+ species are the dominant charge carriers.‡



Log$_{10}$ σT *vs.* $10^3/T$ dependence * for NH_4ClO_4–ammonia (1/2) (●) and $RbClO_4$–ammonia under ammonia 400 Torr (■). The broken line refers to extrapolated a.c. measurements at 1600 Hz on an NH_4ClO_4 disc. The difference between heating and cooling cycles for $RbClO_4$–ammonia is attributed to the inherent irreproducibility in this system.

* A. B. Lidiard in 'Handbuch der Physik,' vol. 20, ed. S. Flugge, Springer, Berlin, 1957; G. P. Owen, J. M. Thomas, and J. O. Williams, *J.C.S. Faraday I*, 1972, 2356.

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† A.c. methods were employed in preference to d.c. methods to minimize electrochemical deposition and polarization effects.

‡ Since this paper was submitted a report has appeared (A. Potier and D. Rousselet, *J. Chim. Phys.*, 1973, **70**, 873) on the electrical conductivity of the closely analogous oxonium perchlorate ($[H_3O^+][ClO_4^-]$). It has been established that in the orthorhombic *Pnma* phase (which is the same space group as that of ammonium perchlorate), the exceptionally large intrinsic conductivity arises primarily from the facile transport of the proton. The proton transport mechanism is obviously very similar to that which is discussed here.

[2] S. V. Moore, Ph.D. Thesis, University of Wales, Aberystwyth, 1974.

[3] S. V. Moore and J. M. Thomas, Proc. 7th Int. Symp. on Reactivity of Solids, Bristol, 1972, eds. J. S. Anderson, M. W. Roberts, and F. S. Stone, Chapman and Hall, London.

[4] A. I. Fridman and I. V. Pastevich, *Russ. J. Inorg. Chem.*, 1968, **13**, 60.

[5] C. Smeets, *Nature W. Tijdschr.*, 1935, **17**, 83, 213.

[6] G. P. Owen, J. M. Thomas, and J. O. Williams, *J.C.S. Dalton*, 1972, 808.

[7] T. M. Herrington and L. A. K. Staveley, *J. Phys. Chem. Solids*, 1964, **25**, 921.

[8] J. J. Delpuech, G. Serratrice, A. Strich, and A. Veillard, *J.C.S. Chem. Comm.*, 1972, 817.

[9] International Critical Tables, vol. 6, McGraw-Hill, New York, 1929, p. 142.