Thermal decomposition of solids

RAJESHWAR *et al.*[1] are probably the first to use differential scanning calorimetry (DSC) to study certain solid-state reactions in the presence of high electric fields within 100–400 kV m^{-1}. Shifts in temperature of the DSC peaks, changes of areas under individual peaks, or both were observed. The authors regarded these phenomena as kinetic effects of the field on thermal decomposition, and with this assumption discussed briefly the various mechanisms that may be responsible.

We would like to make two comments. First, we suggest that some of the reactions examined are not thermal decompositions enhanced by the field, but electrically-induced degradations accelerated by the rising temperature. Application of low fields such as 5–25 kV m^{-1} is known to increase the rate of some thermal decomposition reactions (see, for example, refs 2–4). However, when high fields are involved charge carrier injection may occur and a novel type of 'electrochemical' mechanism may operate in ionic metallic compounds including sodium azide[5]. The electric fields applied in the experiments on NaN_3 have not been specified[1] but, if they are of the order of 10^5 V m^{-1} as reported for other substances, they would have been intense enough[6] to cause partial chemical changes in a single crystal at room temperature by this mechanism. Rajeshwar *et al.*[1] have studied samples in powder form at elevated temperatures; the two differences in experimental conditions may be mutually compensating. In the case of AgN_3, the critical field for compacted powder is an order of magnitude greater than that for a single crystal, but the induction period for the onset of electron-hole injection decreases when the temperature is raised[7,8].

The second point concerns the 'pronounced' and 'drastic' increases of exothermicity observed during the decompositions of NaN_3 and $KMnO_4$. The former decomposes according to the equation

$$2NaN_3 \rightarrow 2Na + 3N_2$$

The extent of the above reaction, although dependent on the crystal size and temperature[9], should reach completion in the experiments under discussion since the temperature was raised continuously to 623 K or higher. For metallic azides excepting the alkaline-earth compounds, the measured heats of reactions, Q, closely approach the corresponding heats of formation, ΔH_f. It would be interesting to compare the Q value obtained by the authors with the ΔH_f of NaN_3 which is 322 kJ kg^{-1}. If Q (with electric field) exceeds ΔH_f, then we suspect that joule heating[6] is responsible for their difference. The decomposition of $KMnO_4$ is complex in nature. From its DSC curves[1] we estimate Q at 0 and 200 kV m^{-1} to be ~5 and 300 kJ kg^{-1} respectively. In view of this drastic change in Q, we suggest that chemical characterization of the residues be carried out to clarify both the extent of decomposition and whether the reaction products are the same in both cases.

We also feel that experiments should be performed with the sample placed in an electric field applied through insulating electrodes, as has been done for silver azide[5]. This arrangement will prevent charge carrier injection and eliminate joule heating. Any kinetic or thermochemical effects found in such conditions can be truly attributed to the influence of electric field on thermal decomposition.

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Factors underlying falcon grating acuity

IN investigating falcon visual sensitivity to grating contrast[1], the contrast sensitivity functions of falcon and human observers were determined using stationary and phase changing gratings with a luminance of 40 cd m^{-2}. The study provides a qualitative comparison of falconiforme and human visual performance at that particular luminance, but the data do not warrant the quantitative analysis given for the possible factors underlying spatial acuity in the falconiforme deep fovea.

The extrapolated sensitivity functions show equal visual acuities (expressed in terms of cutoff frequency) for falcon and man. The author argues that the falcon shows an 'extraordinarily high' visual performance because the anatomical proportions of the subjects' eyes indicate a maximum falcon acuity three-quarters that of man. Since the observed human cutoff frequency was 40 cycles deg^{-1}, the expected proportional falcon cutoff frequency would be 30 cycles deg^{-1} rather than the observed value of 40 cycles deg^{-1}. To account for this boost in acuity the theory that the spherical pit of the deep fovea acts as the divergent element in a telephoto lens system[2] is invoked. In this case, the spherical pit needs to provide an image magnification factor of 1.33. We feel that it is not necessary, nor in this case applicable, to suggest such a theory to explain falcon acuity when measured under the relatively low luminance of 40 cd m^{-2}.

To assess whether the falcon's acuity is 'extraordinarily high' or not, its behavioural acuity performance needs to be related to the potential anatomical performance of its own eye, rather than the behavioural performance of another species. The anatomical cutoff frequency of the falcon eye can be defined by the equation and data given in Hirsch's paper[1]:

$$\nu = \frac{F}{d_{cc}\sqrt{3} \times 57.3} \times m$$

where ν is the cutoff frequency in cycles deg^{-1}, F is the falcon focal length of 9.1 mm, d_{cc} represents photoreceptor centre-to-centre spacing of 2 μm, and m is the foveal magnification factor. Assuming no magnification, m is equal to 1. According to this equation the dimensions of the falcon eye allow for a cutoff frequency of 46 cycles deg^{-1}, which is above the behaviourally measured acuity of 40 cycles deg^{-1}. It appears that a measured acuity of 40 cycles deg^{-1} is not 'extraordinarily high'. Note that the last measured response for stationary gratings was obtained at ~25 cycles deg^{-1} The