

$$R_m \approx \frac{2R_0}{\alpha} \quad (5a)$$

With $q = -4 \times 10^{-5}$ coulomb/cm², $\alpha = 0.091$ for an aqueous solution of $c = 2$ moles/l. The approximation (5a) is therefore valid for the whole range of concentrations. If the membranic resistance were measured in two solutions with identical values of $(c_1)_0$ but different total concentrations c_1 and c_2 , according to equations (5a) and (6) the resistance ratio would be expected to be

$$\frac{R_m(c_1)}{R_m(c_2)} = \frac{c_2}{c_1}$$

In our experiments with $c_1 = (c_1)_0 = 10^{-2}$ moles/l. and $c_2 \approx 2$ moles/l., a resistance ratio of 130 was found which agrees approximately with the calculated ratio of 200. It can therefore be concluded that the influence of an added indifferent electrolyte on the iodide conductivity of the membrane can be explained by an electrostatic double layer effect.

W. LESSLAUER
J. RICHTER
P. LÄUGER

Institute of Physical Chemistry,
University of Basle,
Switzerland.

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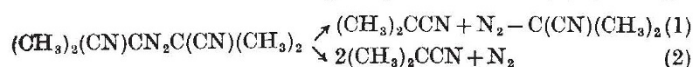
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Pairwise Trapping in Solid State Photo-eliminations

UNDER certain circumstances radicals may be trapped in pairs which are so well separated that there is no chemical bond between them, but sufficiently close that there is a magnetic coupling between the unpaired electrons. If the trapping is sufficiently precise this may be revealed in the electron spin resonance spectrum which will be characteristic of a triplet-state species^{1,2}.

Photolyses or radiolyses sometimes involve the elimination of small stable molecules such as nitrogen or carbon monoxide, and if this occurs in a rigid medium the resulting radicals would seem to be ideally placed for the production of such weakly coupled systems with the precision required for detection. We have recently established that γ -irradiation of crystalline diaryl carbonates, which involves formation of carbon monoxide, gives pairs of aryloxy radicals separated "magnetically" by about 6 Å (ref. 3). The purpose of the present communication is to call attention to the solid state ultra-violet photolysis of azobisisobutyronitrile, which results in a species with an electron spin resonance spectrum which is also characteristic of a triplet.

The reaction was originally written as (1) (ref. 4),



rather than (2), but the spectrum has exactly the form required for radical-pairs (Fig. 2 of ref. 4). The separation of about 280 G between the outer features corresponds

to an effective or "magnetic" separation between the radicals of 5.8 Å which is very close to expectation if the two $(\text{CH}_3)_2\dot{\text{C}}\text{CN}$ radicals simply become planar on the extrusion of a nitrogen molecule. The hyperfine coupling, which is probably dominated by the methyl group protons, is about half that assigned to the protons in separated $(\text{CH}_3)_2\dot{\text{C}}\text{CN}$ radicals⁴ as would be expected for pairs undergoing rapid spin exchange⁵.

This result is of considerable importance because it proves that nitrogen is either extruded in a one-step process or, less reasonably, that the radical $\text{N}_2\text{C}(\text{CH}_3)_2\dot{\text{C}}\text{N}$ loses nitrogen spontaneously even at 77° K.

The alternative interpretation⁴ that a single radical, $\text{N} = \text{NC}(\text{CH}_3)_2\dot{\text{C}}\text{N}$, was responsible for the spectrum is improbable because this radical is expected to be bent at the inner nitrogen atom, with the unpaired electron in a σ -orbital⁶. This is expected to give a spectrum quite different from that detected.

M. C. R. SYMONS

Department of Chemistry,
University of Leicester.

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Voltages produced by Oxygen in Platinum-Sodium Chloride Crystal Cells

It has been found that single crystals of sodium chloride annealed in nitrogen under mild compression between platinum electrodes produce electrical potentials when treated with traces of oxygen at 700°–730° C.

Specimens cleaved to blocks $10 \times 10 \times 3$ mm were placed with the two large surfaces in contact with flat platinum electrodes which rested against recrystallized alumina disks for electrical insulation. The assembly was slightly compressed by springs adjusted to finger tightness. The crystal holder and silica cell were essentially the same as those described in detail by Allnatt and Jacobs^{1,2}. The cell was evacuated to a pressure of 10^{-6} mm of mercury overnight at room temperature and filled with "pure" nitrogen gas (10 p.p.m. of oxygen according to the manufacturer) which had been passed over hot copper turnings. All gases entered the cell through a methanol-solid carbon dioxide trap. The gas flow rates in the experiments mentioned here were all approximately 20 ml./min. When the temperature was initially raised above 500° C a variable voltage of several millivolts was observed similar to that described for

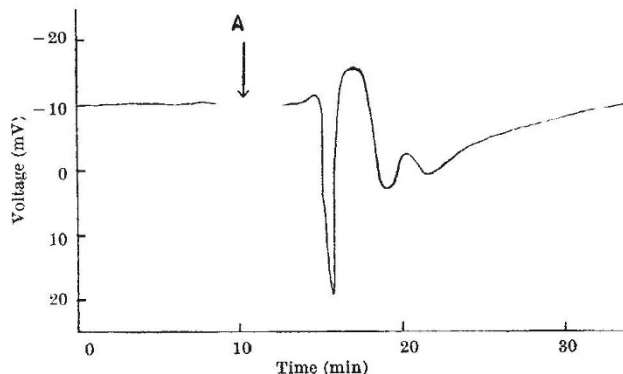


Fig. 1. Voltage-time relation after entry of first portion of oxygen at A. Results are independent of absence or presence of the small thermoelectric voltage at $t=0$ in the graph.