The Use of Metastable Colour-centres in Alkali-metal Halide Crystals and in Silica Gel to catalyse Exchange between Tritium Gas and Hydrocarbons

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Summary Colour-centres of low stability induced by γ-radiation in sodium chloride, potassium chloride, and silica gel act as effective catalysts for the exchange reaction between tritium gas and hydrocarbons although the exchange is accompanied by extensive fragmentation and polymerisation.

RABE and JOPPIEN have recently shown[1] that *F*-centres induced in sodium chloride crystals by γ-radiation are discharged when azoethane is admitted, and that this latter compound is decomposed at the same time to yield nitrogen. Burns and Williams[2] have shown that colour-centres of much higher stability produced by very intense irradiation of NaCl by electrons and γ-rays are active in initiating the polymerization of acrylonitrile. These reactions were attributed to the action of "free atoms." There do not appear to be any reports of the use of colour-centres to catalyse isotopic exchange reactions of organic molecules.

We have prepared colour-centres by irradiating sodium chloride crystals (doped with $2{\cdot}5 \times 10^{-2}\,\%$ of calcium chloride) with ^{60}Co radiation ($1{\cdot}3 \times 10^{6}$ rads), having stability similar to those produced by Rabe and Joppien in that bleaching occurs within a few minutes on exposure to air or daylight. On admitting tritium gas and n-pentane we have found that the colour of the irradiated crystals fades over 20 h at room temperature. When the hydrocarbon is removed and analysed by g.l.c. (using both a flame ionisation detector and an ion chamber sensitive to tritium β-particles) it was found that between 10 and 80% of the tritium used (*ca.* 20 mCi) had been incorporated into hydrocarbon molecules, and further, that considerable fragmentation had occurred to produce tritium-labelled fragments. Some polymerised labelled products were also detected. Yields of labelled products were variable, and in some runs only fragment products were observed. Results of a typical run in which polymers were produced are: (yields are in mCi of incorporated tritium per ml of pentane) methane 11·0; ethane 6·0; propane 1·0; n-butane 1·0; 2-methylhexane 9·8; 2-methylheptane 2·2; cyclooctatetraene 2·2; n-decane 0·2; n-dodecane 1·4. Results of another run in which only fragments appear are: methane 45·8; ethane 29·6; propane 6·0; n-butane 0·8; n-pentane 0·3. In runs with unirradiated sodium chloride very little, if any, activity was found in hydrocarbons.

Irradiated potassium chloride as catalyst gave 85% of the incorporated tritium in the form of parent hydrocarbon. Attempts to discover factors responsible for the lack of reproducibility are proceeding, as are investigations into the use of other salts.

Silica gel is known[3] to produce *F*-centres when exposed to γ-radiation. We found this to be true if the silica gel were first thoroughly degassed at 600° for several hours, when a strong blue colour was observed on irradiation. This preparation gave rise to considerable fragmentation of pentane, detected as labelled products. If the silica gel were not well degassed, neither coloration nor labelling was seen. A typical result is: propane 0·15; 2-methylpropane 0·08; but-1-ene (?) 0·03; 2-methylbutane (?) 0·83; pent-1-ene (?) 0·47; 2-methylbut-1-ene 0·33; pent-2-ene 3·8; cyclopentene 0·07. Again, the results were variable.

In neither set of experiments was any mass peaks seen, so that the reactions reported were detectable only by virtue of the radioactivity of the labelled products, implying that conversions were all less than 0·2%.

(*Received, June 28th,* 1971; *Com.* 1058.)

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[1] J. G. Rabe and G. Joppien, *Z. Naturforsch.*, **1969**, **24a**, 796.

[2] W. G. Burns and T. F. Williams, *Nature*, **1955**, **175**, 1043.

[3] J. G. Rabe, B. Rabe, and A. O. Allen, *J. Phys. Chem.*, 1966, **70**, 1098.