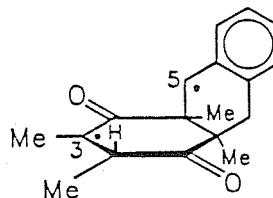


04.3-1 THERMAL DECOMPOSITION OF TRICYANO-METHANIDES. By B.J Poppleton, CSIRO Division of Materials Science and Technology, Clayton 3168, Australia.

The tricyanomethanides crystallize as coordination polymers or simple salts dependent on the particular cation. The simple salts (of the alkali metals for example) when heated melt before decomposition. In contrast, the salts of Mn, Pb and Tl decompose through an exothermic solid state polymerization at a characteristic temperature.

The crystal structure of the thallium derivative has been studied at several temperatures and the thermal parameters of the light atoms correlated with the decomposition pathway.



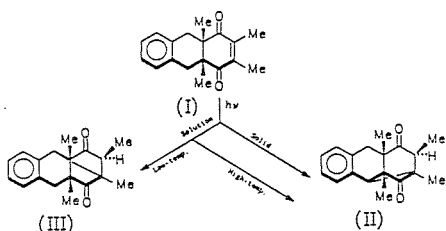
The proposed detailed reaction pathway can be analysed in terms of the following motions:

- (i) Transfer of H(5) to C(2) to form a biradical.
- (ii) Reduction of the C(3)...C(5) non-bonded distance to a final bonded distance; the motion can be analysed as:
 - (a) folding about C(4a)-C(8a) by 20°;
 - (b) folding about C(1)...C(4) by 50°;
 - (c) partial pyramidalization of C(3);
 - (d) minor atomic movements to maintain approximate planarity of carbonyl functions.
- (iii) Minor adjustments of the resulting photoproduct geometry to minimize the overall energy.

The complete reaction pathway involves a minimum of intramolecular motion, with an accompanying movement of the whole reacting molecule by about 1.0 Å allowing accommodation of the photoproduct in the reactant lattice, in a topochemically favourable process.

04.3-2 REACTION PATHWAY IN THE PHOTOCONVERSION OF A TETRAHYDROANTHRACENEDIONE TO ITS SOLID STATE PHOTO-PRODUCT. By Sara Ariel, Syed H. Askari, John R. Scheffer, James Trotter and Fred Wireko, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6.

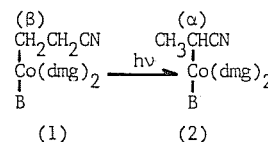
Photolysis of crystals of (I) gives only product (II), while photolysis in solution gives mainly (II) at high temperature and predominantly (III) at low temperature. The crystal structure of (I) has been determined in an effort to rationalize the observed photochemical behaviour, and that of (II) to provide details of possible reaction pathways.



The crystal structures of diketones (I) and (II) allow the proposal of a detailed reaction pathway for the formation of (II). The proposed mechanism involves a γ -hydrogen abstraction by ethylenic carbon to form an intermediate biradical, followed by C-C bonding to generate the tricyclic compound (II). The reaction pathway for (I) \rightarrow (II) involves a reduction of the C(3)...C(5) non-bonded distance of 3.133(6) Å to a bonded C(3)-C(5) length of 1.570(3) Å, which can be achieved with minimum total atomic movement (of about 1.5 Å).

04.4-1 RATE-ACCELERATION DUE TO HYDROGEN BOND OF REACTIVE GROUP IN THE SOLID-STATE PHOTOREACTION. By Y. Ohashi, E. Shimizu and K. Hori, Department of Chemistry, Ochanomizu University, Otsuka 2-1-1, Tokyo 112, Japan

It has been found that the cobaloxime complex (1) is transformed to (2) in the solid state on exposure to visible light. For the



mixed crystal composed of (1) and (2), the rate of the isomerization depends on the volume of the cavity for the β -cyanoethyl (β -cn) group (Uchida, Ohashi & Sasada, Nature(London), 1986, 320, 51-52).

In order to ascertain the relation between the cavity size and the reaction rate, several crystals with different axial base ligands (B) were examined. The correlation holds good for all the crystals except one with 3-aminopyridine as a ligand, which has a greater rate in spite of its smaller cavity. In the 3-aminopyridine complex, the β -cn group is hydrogen bonded with the amino group of the neighboring molecule. This hydrogen bond would stabilize the β -cn radical produced by visible light and facilitate the radical change to α -cn radical which is recombined with the cobalt atom.