MAGNETIC FIELD AND MAGNETIC ISOTOPE EFFECTS ON PHOTOCHEMISTRY OF BIFUNCTIONAL CHAIN MOLECULES CONTAINING NITROARYLOXY AND ANILINO MOIETIES.

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We have been investigating behaviour of bichromophoric chain species containing hydrogen-donor and acceptor moieties which efficiently undergo intramolecular hydrogen abstraction reactions on photo-excitation. The intramolecular remote photoredox reactions for chain-linked compounds consisting of potential oxidants and reductants have some advantages over the corresponding intermolecular counterpart. While intermolecular photoredox reactions involving nitro-aromatic species and reductants are rather complex due to the secondary processes of primary photoproducts with nitroso-aromatic chromophores,[1] we can minimize the secondary reactions by choosing lower concentration of the intramolecular bifunctional compound with similar chromophores.[2-4]

Extremely large magnetic field effects have been observed on photoredox reaction yields of 4-nitro-1-naphthoxy derivatives containing anilino chromophore. This is one of few cases where the unimolecular cage reaction predominates in the zero-field and the bimolecular escape process becomes a major reaction pathway on application of external magnetic fields. Figure 1 shows the cage and escape reactions for the chain-linked biradicals which are initially populated through hydrogen abstraction from the methylene group adjacent to anilino nitrogen by the nitro-aromatic moiety in the excited triplet state. Thus, the biradical consists of nitroxide and anilino-alkyl radicals. The cage product yield is increased on heavy carbon (C-13) substitution of the N-terminal methylene carbon which enhances the transition probability between the triplet and singlet biradicals.

Our findings on nitro-aromatic photochemistry are summarized as follows: Magnetic field and magnetic isotope effects are observed on photoredox product yields derived from the bifunctional parent compound. Magnetic field and magnetic isotope effects are useful probes for photoreactions involving radical pairs and biradical intermediates.