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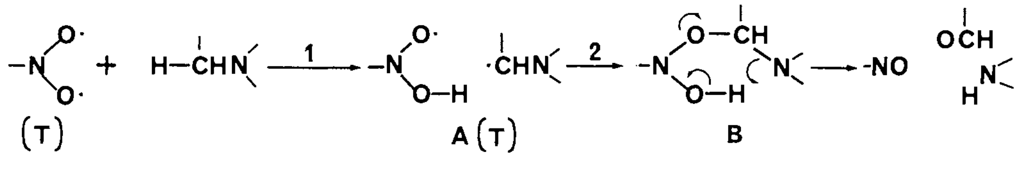
Magnetic Field Effects and Reaction Mechanism in Photoredox Reaction of Nitro Group

Yukiko ISHII, Hideyuki TUKADA, Ryoichi NAKAGAKI,† and Kiyoshi MUTAI*
Department of Chemistry, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro, Tokyo 153
†Faculty of Pharmaceutical Sciences, Kanazawa University,
Takara-machi, Kanazawa 920

Competitive inter- and intramolecular photoredox reactions of the nitro group in homologous series of compound, p-$O_2NC_6H_4O(CH_2)_nOC_6H_4NMe_2$-m (n=2-12) are found to occur at the N-methyl group. The mechanistic aspects of the reactions are discussed in connection with the magnetic field effects on the reaction rate.

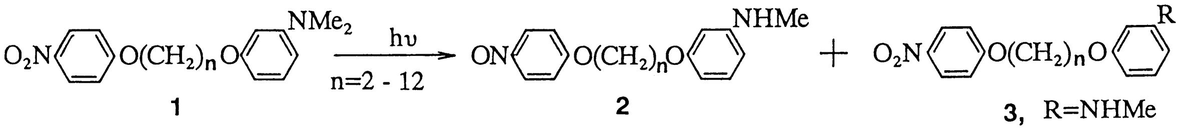
One of the typical photoreactions of aromatic nitro group is photodealkylation of N-alkylanilines, initiated by hydrogen abstraction from the NCH_2 group.[1,2] A similar type photoreaction is well-known for the carbonyl group, termed Norrish Type II, which involves hydrogen abstraction by the excited carbonyl group but the subsequent step stops at the stage of the recombination of a resulting biradical, C-C bond formation. In the case of the nitro group, generation of the corresponding intermediate **B** with N-O-C bond (Eq. 1) has not been confirmed, though its presence is frequently assumed in the photoreactions of the nitro group.[1] The objective of the present study is to provide supporting evidence for this oxygen transfer process in the photodealkylation of nitro compounds.



(1)

The homologous series of compounds adopted for this purpose is **1**, p-$O_2NC_6H_4O(CH_2)_nOC_6H_4NMe_2$-m, in which p-nitrophenoxyl and m-(dimethylamino)-phenoxyl moieties are designed to be capable of working as electron-acceptor and -donor, respectively, for intramolecular electron transfer, because a radical ion pair produced by intramolecular electron transfer is assigned to a key intermediate in some photoredox reactions of nitro compounds.[3]

The reaction was carried out by irradiating a solution of **1** in benzene(10^{-4}mol/dm^3 or less) with a 100 W high-pressure mercury lamp through a Pyrex filter under argon atmosphere, and was monitored by UV spectroscopy and HPLC. The major products, **2** and **3**, were isolated by column chromatography and the structures determined by ^{1}H NMR (270 MHz) and UV spectroscopies. The presence of **4** was also noted from its characteristic ^{1}H NMR spectrum of CHO group in the reaction mixture only as a minor product (less than a few percent of the total product).



1 **2** **3**, R=NHMe **4**, R=NMeCHO

Evidently, **2** is a product of the intramolecular reaction and **3** and **4** are those of the intermolecular one, suggesting the presence of two concomitant pathways in the photoreaction of **1**. In order to understand the effects of the chain length on these two reactions, we determined the initial rate of conversion for the first 60 s of irradiation, as an indication of the relative reactivity of each homolog **1**(n), and the relative quantity of the products in the reaction mixture at the time of 50% conversion of the starting material. The data are summarized in Table 1. The relative reactivity is depicted with a bar graph in Fig. 1, and the distribution of the two products **2** and **3** is plotted against the number of the methylene group n in proportion to the length of the reactivity bar.

Table 1. Relative reactivity in the photoreaction of **1**(n) and molar ratio of **2** and **3**

n	Relative reactivity	Molar ratio/% **2**	**3**
2	1.0	37	63
3	1.2	34	66
4	1.3	56	44
6	1.2	50	50
8	0.9_2	37	63
10	0.7_2	32	68
12	0.7_3	30	70

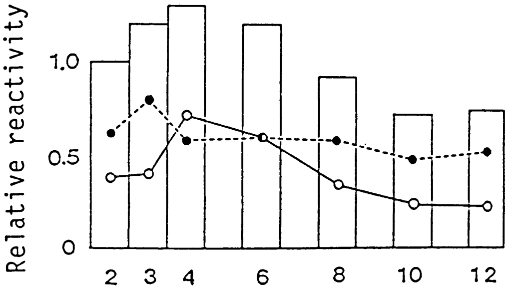


Fig. 1. Relative reactivity (bar) in the photoreaction of **1** and distribution of **2** (---o---) and **3** (- -●- -), plotted in proportion to the bar length.

Throughout the homologs studied, only a small difference of the relative reactivity is observed; at the largest, by a factor of less than 2 between **1**(4) and **1**(12). The slightly larger values observed for the lower homologs are mainly due to the enhanced contribution of the intramolecular pathway, and the contribution of the intermolecular one is almost constant independent of n. The dependence of the reactivity on the chain length is generally noted in intramolecular reactions. The tendency is explicable on the basis of activation entropy and the effect is amplified when an n-dependent intramolecular interaction keeps the reacting moieties in contact or at a close distance. The small dependence observed in **1** suggests an almost negligible importance of the interaction between the terminal aromatic groups, such as charge transfer or electron transfer, in this photoreaction.

It is noteworthy that the intermolecular pathway is competitive or even preferable to the intramolecular one in spite of the entropically disadvantageous bimolecular nature and the low concentration adopted. In contrast, the intermolecular reaction of this type is only a minor pathway in the photoreaction of p-$O_2NC_6H_6O(CH_2)_nNHPh$ 5[3a] and its nitronaphthalene analog.[3b] This difference must be a integral result of several effects. One of the reasons for the large contribution of the intermolecular process in **1** is undoubtedly the absence of an intramolecular interaction. Presumably the difference of the conformational effects on the transition state between the dimethylamino group in the outer sphere of the molecule **1** and the CH_2N group of 5 in the inner sphere as well as the difference in the probable number of the hydrogen atoms to be abstracted is another favorable factor for the intermolecular reaction.

It has been reported that, in the photoredox reactions of some nitroaromatics involving a radical pair intermediate, an external magnetic field reduces the rate of the intramolecular process.[3,4] In order to obtain further insight in the reaction mechanism, we carried out the reaction in the presence of a magnetic field (0.64T). As an example, the spectral change of the solutions of **1**(12) in the absence and presence of the magnetic field is illustrated in Fig. 2.

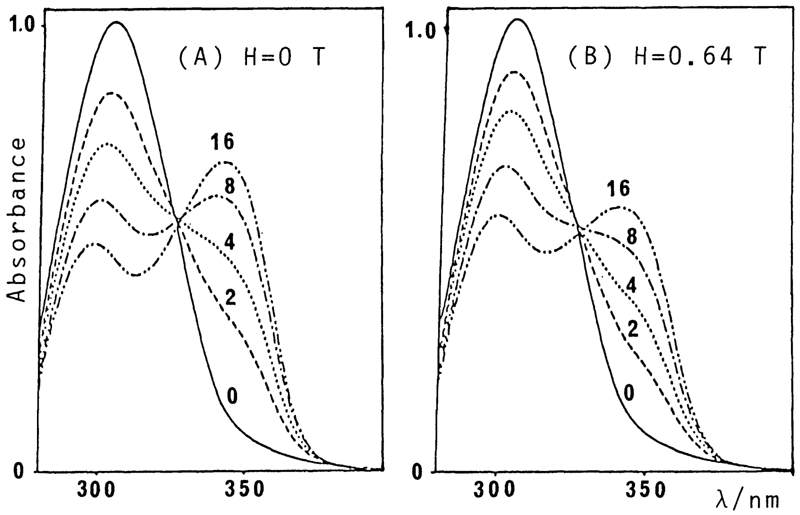


Fig. 2. UV-Absorption spectra of the solution of the n=12 homolog of 1 in C_6H_6; (A) in the absence of and (B) in the presence of an external magnetic field (0.64 T). The numerals attached to the curves denote the irradiation time (min).

An absorption peak observed at ca. 305 nm for the starting material is mainly due to the p-nitrophenoxyl chromophore and an increase at ca. 345 nm during irradiation is due to the p-nitrosophenoxyl chromophore in **2**.[3a] Obviously, the intensity increase of 345-nm band is slower in the presence of the magnetic field; i.e. the rate of the intramolecular process for the formation of **2** is reduced.

The magnetic field effects have been interpreted as being concerned with an intersystem crossing process by splitting the degenerate triplet states and thus narrowing the possible pathways for the crossing.[5] Considering that under the present reaction conditions the excited chromophore is only the p-nitrophenoxyl group, which undergoes rapid conversion to the triplet state, the possible process involving intersystem crossing is recombination of the radical pair **A** to yield **B** (Eq. 1), since **A**, generated through abstraction of the hydrogen by the triplet nitro group, is in the triplet state and the recombination to form N-O-C bond requires a singlet radical pair.

The apparent reduction in the intenstity increase of the 345-nm band in the presence of the magnetic field (Fig. 2B) is interpreted as follows; the process generating the singlet radical pair in the solvent cage is thus retarded, while the intermolecular reaction corresponding to the out of cage process is free from the restraint of the multiplicity and correspondingly becomes more favorable process.

References

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