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Photo-Smiles Rearrangement (IV) Electron-Transfer Mechanism of an Intra-Molecular Aromatic Nucleophilic Substitution

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PHOTO-SMILES REARRANGEMENT (IV) ELECTRON-TRANSFER MECHANISM OF AN INTRAMOLECULAR AROMATIC NUCLEOPHILIC SUBSTITUTION

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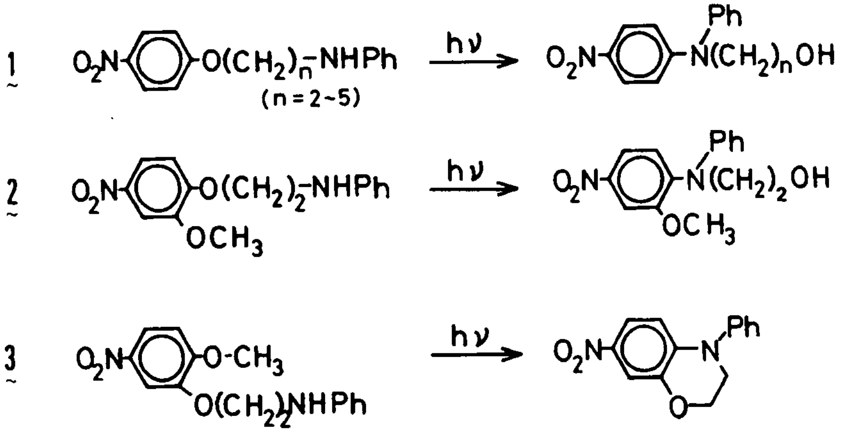
Abstract The mechanism of the photo-Smiles rearrangement involves formation of an intramolecular radical ion-pair and a spiro-type Meisenheimer complex. The complete reaction pathways can be qualitatively described by the use of potential energy surfaces for the ground, the charge-transfer, and the locally-excited states. This can be regarded as an extention of the charge-transfer theory for aromatic substitution reactions developed by Nagakura to photochemical reactions.

Although a great number of photochemical aromatic nucleophilic substitutions have been reported,[1] the detailed mechanism has been studied for only a few reactions. One of the typical examples is the photo-Smiles rearrangement, an intramolecular nucleophilic photo-substitution, the mechanism of which has been elucidated by means of laser photolysis.[2] In the present work, we show that the photo-Smiles rearrangement can be reasonably described by the charge-transfer theory for aromatic substitutions developed by Nagakura.[3]

On photo-excitation of aromatic species, 1-3, into the locally-excited states of the nitroanisole moiety, 4-nitrodiphenylamine derivatives are produced (scheme 1). Two reaction intermediates have been detected by nanosecond laser photolysis. The first, short-lived species is a radical ion pair formed after photoelectron transfer from the aniline moiety to the excited nitroanisole moiety. The second, long-lived species, is a spiro-type Meisenheimer complex.



SCHEME 1

The schematic illustration of photo-Smiles rearrangement is given in Fig. 1. The primary process of the photoreaction consists of an electron transfer from the nucleophile to the aromatic substrate. The second step is σ-complex formation between the two species. This kind of reaction mechanism is essentially the same as that previously proposed by Nagakura for thermal aromatic substitutions.[3] The para-substitution with regard to the nitro group observed for photo-Smiles rearrangement can be explained in terms of free valencies of the nitroanisole anion. Thermal aromatic nucleophilic substitutions have been observed for highly electron-accepting substrates, e.g. 2,4,6-trinitroanisole,[4] tetra-cyanoethylene,[5] and

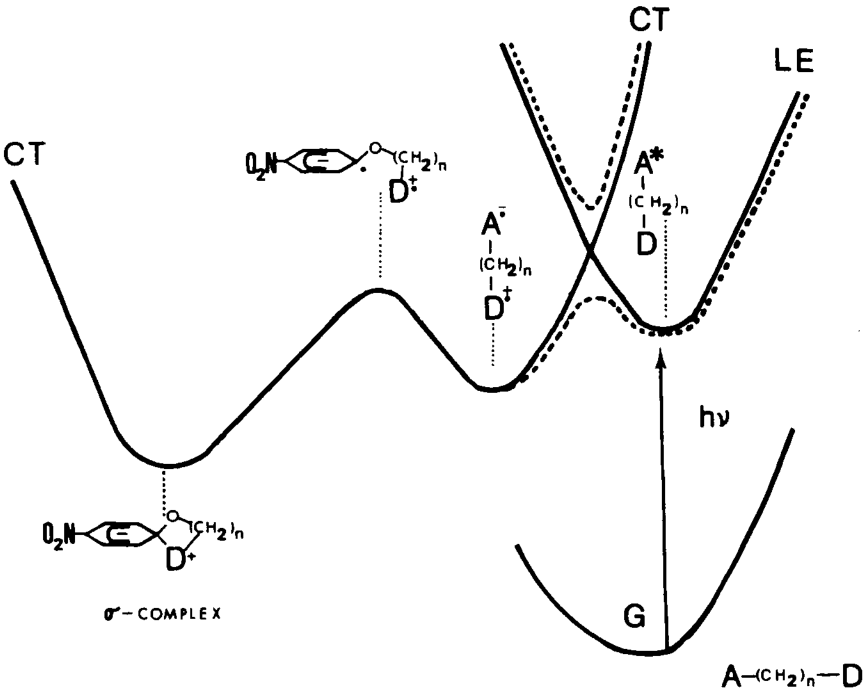
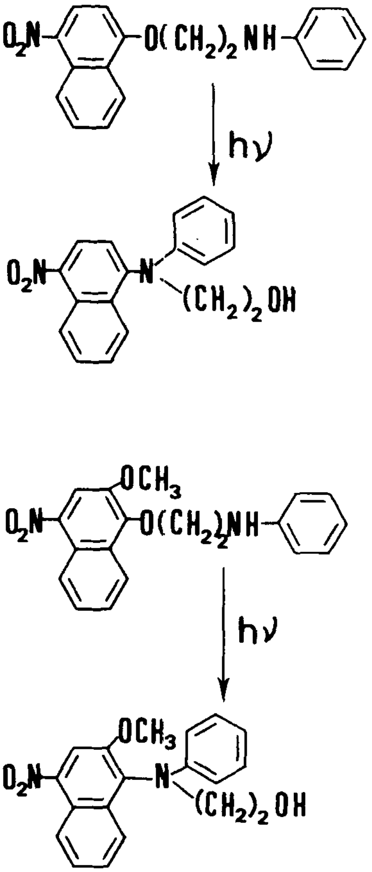


FIGURE 1. Schematic illustration of σ-complex formation in the course of photo-Smiles rearrangement.

A and D denote the electron acceptor moiety and electron donor moiety, respectively. Solid and broken lines represent non-adiabatic and adiabatic potential energy surfaces, respectively. An asterisk refers to an excited state. Positive and negative signs represent the charge. Before the bond formation between the D cation radical and A anion radical fragments, the carbon atom at the para-position with respect to the nitro group changes from the sp^2 to sp^3 hybridization. This corresponds to the activation process in the σ-complex formation.

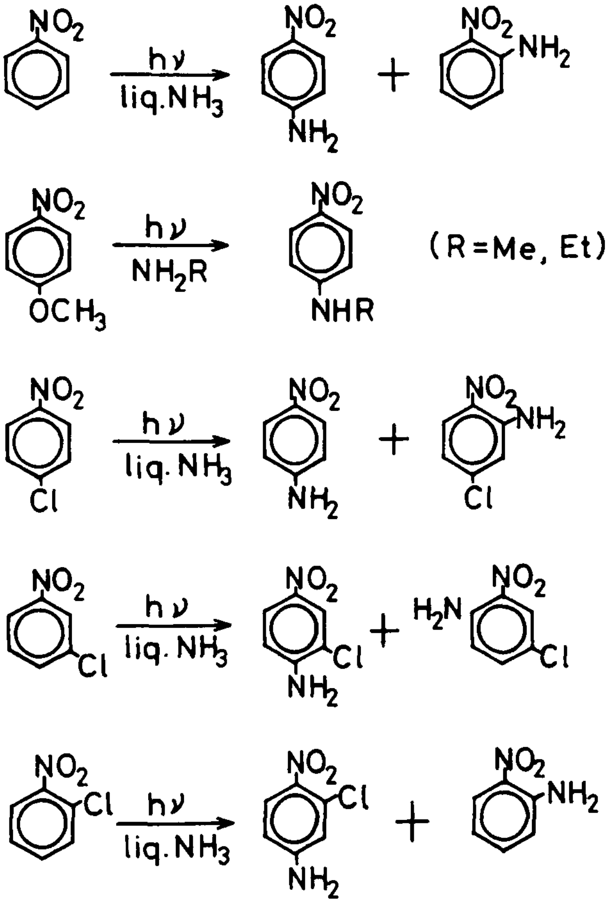
chloranil.[6] The photochemical substitution reaction, however, occurs even for weakly electron-accepting molecules such as p-nitroanisole. The electron affinity becomes greater in the excited state than in the ground state, since the singly occupied HOMO behaves as an



SCHEME 2

electron-accepting orbital in the excited state.

Although the meta-activation with regard to a nitro group is well known in photochemical aromatic nucleophilic substitutions,[1] we have found several para-substitutions in photochemistry of 4-nitrophenyl and 4-nitronaphthyl ether derivatives (schemes 1 and 2). In addition, there have been many other ortho/para substitution reactions in the literature (scheme 3).[1]



SCHEME 3

This kind of photochemical reactivity is the same as in thermal substitutions, and has hitherto been explained in terms of merging resonance stabilization during product formation, which has been proposed by Havinga and collaborators as one of the empirical rules for photochemical nucleophilic substitutions.[1] As has been admitted by themselves, this rule has no sound theoretical basis. We propose that an ortho/para orientation rule in nucleophilic substitutions can be applied to reactions involving one-electron transfer prior to σ-complex formation. According to this mechanism, para-substitutions with regard to the nitro group observed for both thermal and photochemical substitutions can be rationalized in terms of the free valencies of the nitrobenzene anion radical by the use of charge-transfer theory.[3] The present schematic description of photochemical reaction pathways in Fig. 1 is more comprehensive than the conventional interpretation so far given by Havinga and co-workers.

In conclusion, the charge-transfer theory has thus been shown to be generally useful and readily applicable to many photochemical systems of interest. This method is also expected to be extended to many other types of aromatic photo-reactions involving electron-transfer processes, e.g. electrophilic substitutions. Since the present description of reaction pathways based upon charge-transfer theory is simplified and schematic, it is apparently useful to practising organic photochemists in interpreting and predicting the reaction mechanism of complex polyatomic molecules accompanying photo-induced electron transfer.

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