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PHOTOUREIDOMETHYLATION OF 9-CYANOPHENANTHRENE WITH TETRAMETHYLUREA INVOLVING THE CHARGE-TRANSFER PROCESS IN THE EXCITED TRIPLET STATE

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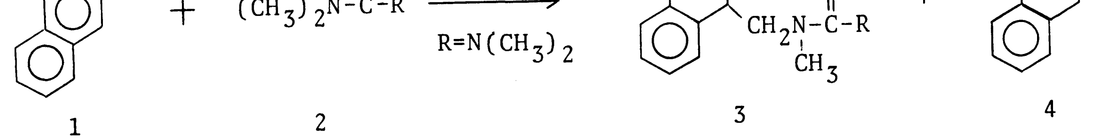
Irradiation of an acetonitrile solution of a mixture of 9-cyanophenanthrene and tetramethylurea gave an ureidomethylated product in a high yield, the reaction being regioselective and solvent-dependent. It is indicated that the reaction involves the charge-transfer process in the excited triplet state of 9-cyanophenanthrene.

There has recently been growing evidence that the exciplex and the cation-anion radicals generated by electron transfer are intermediates in numerous photochemical reactions. Although whether the charge-transfer process takes place in the excited siglet or triplet state depends upon reaction systems, the examples of the charge-transfer reaction which occurs in the excited singlet state have been more accumulated than those involving the excited triplet state. In particular, only definite examples are available with regard to the reaction involving the intermediacy of the triplet state exciplex.$^{1-4)}$ As a part of our studies on the photochemical reaction of the compounds containing N,N-dimethylcarbamoyl groups,$^{5-8)}$ we have carried out the photochemical reaction of tetramethylurea with 9-cyanophenanthrene, finding that ureidomethylation occurs. We wish to report that the photoureidomethylation reaction of 9-cyanophenanthrene is regioselective and solvent-dependent, for which the operation of the charge-transfer process in the excited triplet state is responsible.



1 2 3 4

Upon irradiation of an acetonitrile solution of 9-cyanophenanthrene (1, 0.06 mol/l) and ten molar excess of tetramethylurea (2) in a pyrex tube with a 500W high pressure mercury lamp for 20 hr, an ureidomethylated product was obtained in 73% yield, together with 9,10-dihydro-9-cyanophenanthrene (4) in 11% yield. By contrst, the reaction in benzene afforded the ureidomethylated product only in 3% yield. The ureidomethylated product obtained in the reaction was solely 9,10-dihydro-9-cyano-10-(N-methyl-N',N'-dimethylureidomethyl)phenanthrene (3) as determined from the NMR spectrum.

Since the urea (2) does not absorb the incident light (λ=313, 331 nm), the excited 9-cyanophenanthrene (1) is the active species for the reaction. No appreciable quenching of the fluorescence of 1 occurred in the presence of 2 ([1]= 5×10^{-4} mol/l, [2]= 0.5 mol/l) as observed from the measurements of both the fluorescence intensity and lifetime (τ_f=24 nsec in the presence and absence of 2 in degassed acetonitrile at room temp.), which rules out the reaction in the excited singlet state of 1, indicating that the excited triplet of 1 is operative as the active species for the reaction. It may be conceivable that the excited triplet of 1 abstracts a hydrogen atom from 2 as has been observed for 1,1-diphenylethylene$^{9)}$; however, this mechanism cannot account for the regioselectivity and the solvent dependency of the reaction. If the excited triplet nitrile abstracts a hydrogen atom from 2, the resulting ureidomethylated product would be 9,10-dihydro-9-cyano-(N-methyl-N',N'-dimethylureidomethyl)phenanthrene in view of the stability of the intermediate radical generated by the initial hydrogen abstraction.

The regioselectivity and solvent dependency observed for the present photochemical reaction can be explained in terms of the operation of the charge-transfer process, *i.e.*, formation of either the triplet state exciplex or the cation-anion radicals, *via* the excited triplet state of 1.$^{10)}$ A supporting evidence for the operation of the charge-transfer process in the present reaction system was obtained from the phosphorescence quenching measurement. As shown in Fig. 1, the phosphorescence of 1 (10^{-3} mol/l) was partially quenched in the presence of large amounts of 2 (1.0 mol/l) in 2-methyltetrahydrofuran (MTHF) at 77 K, while no fluorescence quenching was observed under the same

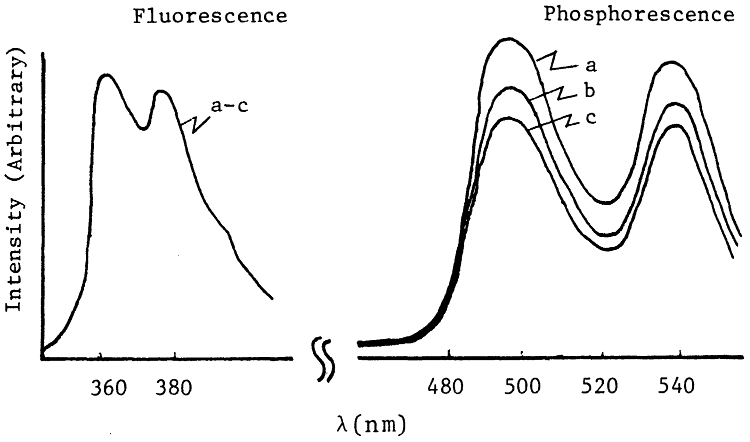
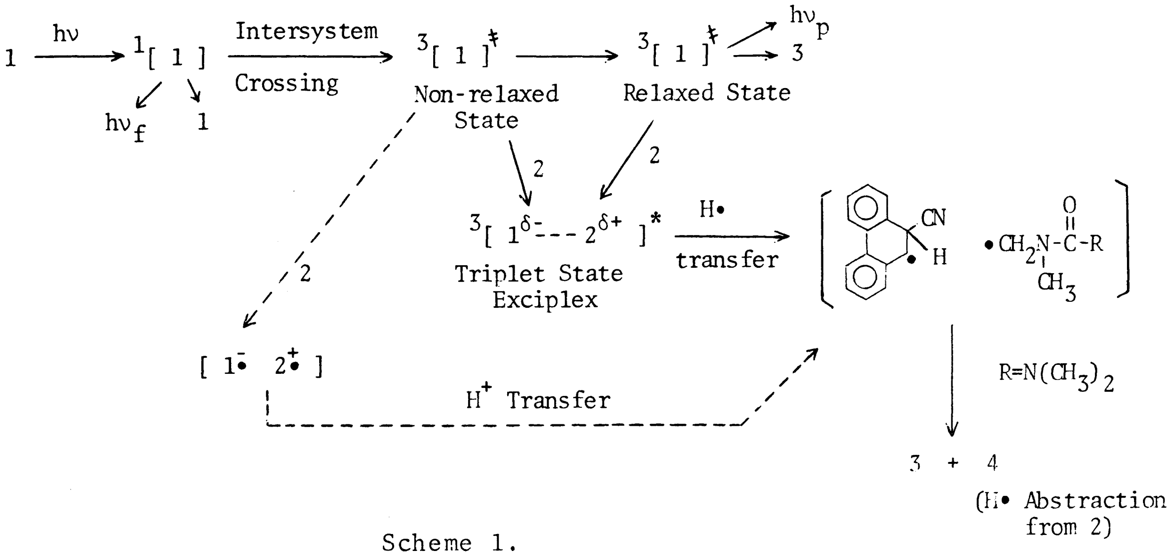


Fig. 1. Emission spectra of 9-cyanophenanthrene (1) in the absence and presence of tetramethylurea (2) in MTHF at 77 K. Excitation wavelength: 320 nm. a: [1]=10^{-3} mol/l; b: [1]=10^{-3} and [2]=10^{-1} mol/l; c: [1]=10^{-3} and [2]=1.0 mol/l.

conditions. The urea (2) does not function as an inner filter in this measurement, since its absorption band lies in a much shorter wavelength region. No ground state charge-transfer interaction was observed for this system at 77 K as well as at room temperature as evidenced from the UV absorption spectra together with the fact that no appreciable fluorescence quenching was observed under the same conditions. Consequently, the occurrence of the charge-transfer process between the excited triplet nitrile (1) (electron acceptor) and the nearby ground state urea (2) (electron donor) will be responsible for the phosphorescence quenching behavior. Whereas the intensity of the phosphorescence decreased in the presence of large amounts of 2, its lifetime was not affected by 2 under the same conditions (τ_p=2.4 sec with or without 2 in degassed MTHF at 77 K). It is suggested that in a rigid matrix at 77 K only the excited triplet molecules nearby the urea undergo the charge-transfer interaction in the emitting state in a time region of much shorter than that of the lifetime measurement. It is also conceivable that the charge-transfer interaction takes place in the non-relaxed excited triplet state of 1. Although the experimental results obtained for the rigid matrix system are not directly applied to the reaction in a fluid solution, the two possible mechanisms as shown in Scheme 1 are suggested for the ureidometylation of 1.



Scheme 1.

One involves the initial hydrogen atom transfer from 2 to 1 *via* the intermediate non-emitting triplet state exciplex. The charge-transferred nature of the complex will be more enhanced in polar solvents leading to the stabilization of the complex, and the charge-tranferred nature of the complex or the geometry of the complex will be responsible for the regioselectivity observed for the reaction. An alternative mechanism involves the intermediacy of the 9-cyanophenanthrene anion radical and the tetramethylurea cation radical generated by electron transfer. The electron transfer, which is facilitated in polar solvents, and the following proton transfer and radical coupling processes will account for the regioselectivity observed. The calculated free energy change for the electron transfer[13] from the ground state of 2 to the lowest triplet state of 1 is significantly endothermic ($\Delta G=20.9$ kcal/mol)[14] and indicates that the electron transfer would be improbable; however, if the electron transfer occurs in the non-relaxed excited triplet state of 1, there will be an energy gain favorable for the electron transfer.[15]

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10) Related to the present study, it has been reported that the photocycloaddition of 1 with anethole proceeds *via* the excited singlet state exciplex.[11] There has also a report that the excited triplet state of 1 is involved in the photocycloaddition with electron deficient olefins.[12]

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14) The half-wave potential for the reduction of 1 ($E_{1/2}$) was determined by means of polarography with dropping mercury as a working electrode in DMF. The half-peak potential for the oxidation of 2 (irreversible process, $E_{p/2}$) was determined by means of cyclic voltammetry with platinum as a working electrode in CH_3CN.

$E_{1/2}$ (for reduction of 1) = -2.24 V vs. Ag/Ag^+ 0.1 N, $E_{p/2}$ (for oxidation of 2, sweep rate 200 mV/sec) = 1.22 V vs. Ag/Ag^+ 0.1 N, E_{0-0} (triplet excitation energy for 1) = 2.5 eV (57.5 kcal/mol), $e^2/\varepsilon r$ (coulombic attraction term in CH_3CN) = 0.05 eV (1.2 kcal/mol).[13]

15) The free energy change for the electron transfer process in the energy level of the lowest singlet nitrile ($E_{0-0}=78.2$ kcal/mol) is close to zero kcal/mol.

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