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# Mechanism for Light Induced Hydrogen Isotope Exchange in Benzonitrile

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Light induced tritiation of benzonitrile with diethylamine[N$^3$H] or triethylamine-tritiated water was studied with respect to quenching of benzonitrile fluorescence by the amines and the tritium distribution in the nucleus. A mechanism involving an exciplex possessing charge transfer nature was proposed.

It is well known that photolysis of thiols yields hydrogen atoms, and this method has been used to study the properties of the hydrogen atom in solution.[1,2] Thus, Pryor and his co-workers[2] have reported the aromatic substitution by tritium atoms generated by photolysis of benzenethiol[S$^3$H]. We have also studied[3] the light induced tritiation of aromatic compounds with 1-propanethiol[S$^3$H] in respect of the tritium distribution in the nucleus and the relative rate of tritiation, and found that the nuclear tritium distribution data are different from those reported by Pryor.[2] Kinetic studies[4] have shown that the rate constants for the reaction of hydrogen atoms with aromatic compounds vary only between $2.4\times10^8$ and $26\times10^8$ M$^{-1}$ s$^{-1}$. Electron-donating substituents on the aromatic nucleus enhance the rate and electron-withdrawing groups retard the rate, indicating an electrophilic character of hydrogen atoms for the reaction.[4] On the contrary, our work with 1-propanethiol showed that the rate of nuclear tritiation relative to benzene, obtained in competitive methods, is extremely high in benzonitrile,[3] methyl benzoate,[3] and terephthalonitrile.[5] Furthermore, fluorescence of terephthalonitrile in benzene was quenched by 1-octanethiol with the quenching rate constant near to the diffusion-controlled value.[5] On the basis of these results a mechanism involving a reaction of singlet excited aromatic compounds with thiols was proposed for the tritiation reaction, at least in the case of benzonitrile, methyl benzoate, and terephthalonitrile.

This consideration reminds us the photoreaction of aromatic compounds with amines, in which singlet excited aromatic compounds are demonstrated to interact with amines.[6] Thus, the possibility that such interaction may be followed by hydrogen exchange led us to investigate the positional reactivity of light induced tritiation of benzonitrile with amines as well as quenching of the lowest excited singlet state of aromatic nitriles by amines. The results are interpreted in terms of a mechanism involving formation of an exciplex followed by its decay to a radical pair.

## Results and Discussion

*Fluorescence Quenching of Aromatic Nitriles.* Fluorescence of benzonitrile, α-naphthonitrile, and terephthalonitrile was strongly quenched by diethylamine and triethylamine in benzene. The Stern-Volmer plots of the reciprocal of relative fluorescence intensities against amine concentrations were linear in all compounds investigated, and the slopes of the Stern-Volmer plots ($k_q\tau_s$) are shown in Table 1, where $k_q$ is the rate constant of the bimolecular quenching process, and $\tau_s$ is the lifetime of the singlet state in the absence of the amines in aerated benzene. Assuming diffusion-controlled oxygen quenching ($1.5\times10^{10}$ M$^{-1}$ s$^{-1}$),[7] the effect of air saturation on fluorescence intensity affords an estimate of $\tau_s$ (air) in benzene; benzonitrile, 25 ns; α-naphthonitrile, 12 ns; terephthalonitrile, 18 ns. The observed $k_q\tau_s$ values for the amines are divided by the $\tau_s$ values and the resulting $k_q$ values are listed in Table 1. The quenching rate constants ($k_q$) of diethylamine are several times larger than those of triethylamine and are close to the diffusion limit. The higher efficiency of the quenching, therefore, indicates the interaction of the singlet excited aromatic compounds with the ground state amine. Furthermore,

Table 1. Quenching of fluorescence from aromatic nitriles by amines in aerated benzene

| Fluorescer | Quencher | $k_q\tau_s$, M$^{-1}$ | $k_q\times10^{-9}$, M$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| Benzonitrile | $HN(C_2H_5)_2$ | 56.9 | 2.3 |
| | $N(C_2H_5)_3$ | 9.43 | 0.38 |
| α-Naphthonitrile | $HN(C_2H_5)_2$ | 92.6 | 7.5 |
| | $N(C_2H_5)_3$ | 10.5 | 0.85 |
| Terephthalonitrile | $HN(C_2H_5)_2$ | 174 | 9.8 |
| | $N(C_2H_5)_3$ | 18.8 | 1.1 |

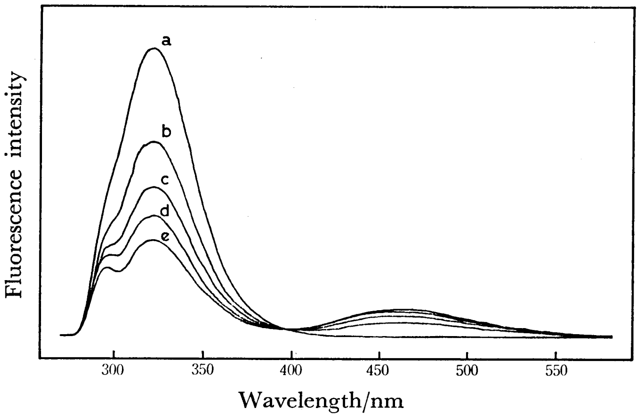


Fig. 1. Fluorescence of benzonitrile ($6.14\times10^{-3}$ M) in benzene in the presence of triethylamine. Concentration of quencher (M): a, nil; b, $5.64\times10^{-3}$; c, $1.13\times10^{-2}$; d, $1.69\times10^{-2}$; e, $2.26\times10^{-2}$.

the quenching of benzonitrile by triethylamine was accompanied by the appearance of a new emission at longer wavelength (Fig. 1), which may be assigned to an exciplex formed between the two components, while no exciplex emission was observed in the quenching of benzonitrile by diethylamine in benzene.

*Hydrogen Isotope Exchange in Benzonitrile.* Irradiation of a mixture of benzonitrile and diethylamine-[N$^2$H] with a 1 kW high pressure mercury arc lamp for 20 h resulted in minor amounts of deuterium incorporation (0.9%) in the recovered benzonitrile as determined by mass spectrometry. When a solution of benzonitrile in acetonitrile was irradiated in the presence of diethylamine[N$^2$H] under the same conditions, the amino-deuterium is transferred to benzonitrile to the extent of 4.5%. A labelling experiment of benzonitrile with triethylamine in acetonitrile was carried out in the presence of deuterated water to elucidate the mechanism. It is of interest to note that the deuterium was involved in the starting material recovered (4.1%).

In view of the incorporation of deuterium in benzonitrile the light induced tritiation of benzonitrile was undertaken with diethylamine[N$^3$H] or with triethylamine–tritiated water to determine the tritium distribution in the nucleus and the relative rate of tritiation.

A mixture of diethylamine[N$^3$H], benzene, and benzonitrile was irradiated with a high pressure mercury arc lamp. After a usual work-up, the aromatic compounds were recovered by distillation. Benzene fraction was purified by fractional distillation and submitted to tritium assay. Benzonitrile was degraded by the known procedures[8] in order to determine the tritium distribution. Similarly, a solution of benzonitrile in acetonitrile was irradiated with a high pressure mercury arc lamp in the presence of triethylamine and tritiated water. The benzonitrile was recovered in a similar way and degraded.

The tritium distribution in the recovered benzonitrile and the relative rate of tritiation (per C–H bond) are shown in Table 2 together with related data. The tritium distribution pattern is very similar to that obtained with 1-propanethiol[S$^3$H] and acetic acid[O$^3$H],[3] but differs greatly from that reported for the addition of tritium atoms[2] (Table 2). The order of reactivity among the nuclear positions is *para*$\gg$*ortho*$>$*meta* in the present study, whereas it is *meta*$\approx$*ortho*$>$*para* for the addition of tritium atoms.[2] The relative rate of the tritiation on benzonitrile to benzene is extremely high with diethylamine[N$^3$H] and its value is larger than that with 1-propanethiol-[S$^3$H] by a factor of seven, although the tritium distribution is similar in patterns in both reagents. The decrease in the relative rate with 1-propanethiol could readily be accommodated in terms of a slight inclusion of tritium atoms generated by the photolysis of the thiol in the tritiation process, since tritium atoms add more easily to benzene than to benzonitrile.

The observed difference in results between tritiation with 1-propanethiol and that reported by Pryor[2] using benzenethiol requires some discussion. Benzenethiol would be photolyzed more easily than 1-propanethiol, because the former has a much smaller S–H bond strength (75 *versus* 88 kcal/mol).[9] In addition, the high pressure mercury arc lamp in a Pyrex immersion well was employed in this work, whereas Rayonette lamps (nominally 300 nm) were used in the earlier experiments,[2] in which hydrogen atoms could be produced more efficiently. In order to confirm this view the photolysis of benzenethiol[S$^3$H] in a mixture of benzonitrile and benzene was re-examined under the present conditions and the results are listed in Table 2. The tritium distribution takes intermediate values between those with 1-propanethiol and those reported by Pryor[2] with benzenethiol, and the relative rate is decreased to 21. These observations suggest that the tritiation by tritium atoms in the present study occurs moderately with benzenethiol, but not so seriously as in the photolysis using the Rayonette lamps. Thus, it is probable that the values of tritium distribution reported by Pryor are evaluated as the results for the hydrogen atom reactions.

TABLE 2. LIGHT INDUCED TRITIATION OF BENZONITRILE

| Triton donor | Tritium distribution (%)[a] | | | $k_{\mathrm{rel}}$[b] |
|---|---|---|---|---|
| | *Ortho* | *Meta* | *Para* | |
| Diethylamine[N$^3$H] | 18.9 | 1.4 | 79.7 | 1740 |
| Triethylamine and tritiated water | 10.0 | 0.2 | 89.8 | |
| 1-Propanethiol[S$^3$H][c] | 17.4 | 2.0 | 80.8 | 254 |
| Acetic acid[O$^3$H][c] | 12.4 | 1.0 | 86.7 | |
| Benzenethiol[S$^3$H] | 31.0 | 5.0 | 64.0 | 21 |
| Benzenethiol[S$^3$H][d] (Pryor *et al.*) | 42.0 | 45.2 | 12.8 | |

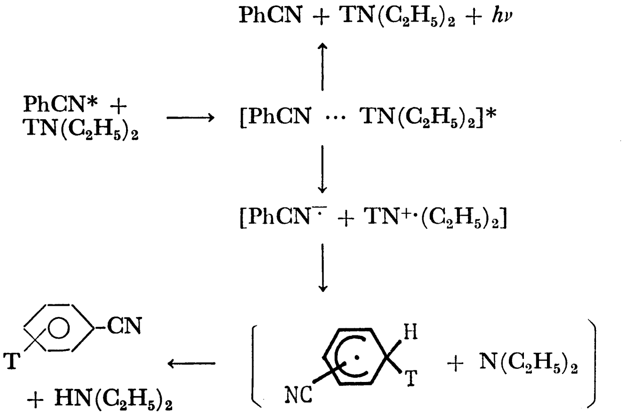
a) Average values of data obtained by duplicate runs. b) Rate (per C–H bond) of nuclear tritiation relative to benzene. c) Data taken from Ref. 3. d) Data taken from Ref. 2.

*Mechanism for Hydrogen Isotope Exchange.* In recent years light induced hydrogen isotope exchange of aromatic compounds has been investigated in acidic media.[10] The previous studies[10] showed that the excited states are much more basic than the ground states, and the exchange takes place through prototropic equlibria of the excited state. As to the multiplicity of the excited state,[10] the first excited singlet states were suggested to be responsible for the exchange from fluorescence quenching experiments, but in some cases a triplet state or a higher excited singlet state was demonstrated to participate in the reaction. Previously, we have shown that the rate of tritium incorporation into benzonitrile is lower in tritiated acetic acid than in tritiated 1-propanethiol by a factor of $10^{-3}$ in spite of the higher acidity of acetic acid.[3] This fact indicates that proton transfer is not involved in the rate determining step and the basicity of the excited states is irrelevant to the exchange.

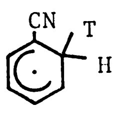
The UV spectra of benzonitrile–diethylamine and –triethylamine mixture in hexane were the sums of the absorption spectra of each component, indicating that charge-transfer interaction in the ground state is absent or very weak. Thus, a possible role of a charge-transfer complex in the ground state is ruled out.

As mentioned above, fluorescence of aromatic nitriles was quenched efficiently by the amines and the quenching of benzonitrile by triethylamine was accompanied by the appearance of a new exciplex emission (Fig. 1). In view of these findings the most plausible mechanism for the exchange reaction seems to involve an exciplex possessing charge-transfer nature between singlet excited benzonitrile and the amines.[11)]

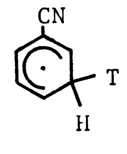
The exciplex either deactivates to each component in the ground state *via* exciplex emission or undergoes electron transfer from the quencher to the quenchee to give a radical cation and a radical anion, respectively. With diethylamine[$N^3H$], the radical cation contains an acidic triton and the triton transfer from the radical cation to the radical anion may occur to give a radical pair, which may disproportionate to result in the hydrogen exchange. On the other hand, the radical cation from triethylamine does not contain an acidic proton (triton) and tritiated water in the system functions as a triton donor to the anion radical.



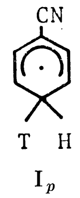
The suggested reaction pathway is compatible with the observation that the order of the tritiation among the nuclear positions is *para*≫*ortho*>*meta*. The triton transfer to the anion radical of benzonitrile occurs to the *ortho*- and *para*-positions to give cyclohexadienyl radicals, $I_o$ and $I_p$, in preference to the *meta*-positions to give $I_m$, because the greater electronic stabilization is achieved in $I_o$ and $I_p$ than $I_m$. This trend is kept in the subsequent disproportionation reactions to give the *ortho*- and *para*-tritiated benzonitrile in higher portion than the *meta*-substituted one.



$I_o$



$I_m$



$I_p$

Inspection of the tritium distribution pattern in Table 1 indicates that there is an overall similarity between 1-propanethiol, acetic acid, and the amines. It is, therefore, suggested that similar intermediates participate in the distribution determining step. The decrease in the rate of the tritiation with acetic acid and scarce quenching of benzonitrile fluorescence by acetic acid are rationalized as a reflection of the difference in ionization potential between acetic acid,[12)] 1-propanethiol,[13)] and the amines.[7)] The formation of the charge transfer exciplex and following electron transfer from quencher to aromatic substrate would be hard in quenchers having higher ionization potential such as acetic acid.

## Experimental

*Materials.* Benzene, diethylamine, triethylamine, and benzonitrile were purified by distillation or vacuum distillation. Terephthalonitrile was recrystallized three times from benzene. α-Naphthonitrile was purified by distillation under reduced pressure followed by twice recrystallizations from ligroin.

*Diethylamine*[$N^2H$]: Diethylamine was fractionally distilled from deuterated water. The distillation was repeated until no signal due to the amino proton was observed in the NMR spectrum.

*Diethylamine*[$N^3H$]: Diethylamine (15.0 ml) was mixed with tritiated water (0.1 ml, 5 Ci/ml), stirred for 30 min, dried over artificial zeolite, and purified by bulb to bulb distillation to give the tritiated amine (2.90 Ci/mol).

*Benzenethiol*[$S^3H$]: benzenethiol was tritiated in a way similar to the above and purified by distillation.

*Deuteration of Benzonitrile.* *(a) With Diethylamine*[$N^2H$]: A mixture of benzonitrile (19.4 mmol) and diethylamine-[$N^2H$] (58.4 mmol) was irradiated for 20 h under nitrogen atmosphere with a 1 kW high pressure mercury arc lamp (RIKO Rotary Photochemical Reactor, Model RH 400—10W). After irradiation, the deuterated benzonitrile was recovered by fractional distillation under reduced pressure. Irradiation of a solution of benzonitrile (9.7 mmol) and the amine (19.5 mmol) in 10 ml of acetonitrile was carried out under the same conditions and benzonitrile was recovered by distillation.

*(b) With Triethylamine and Deuterated Water*: A solution of benzonitrile (9.7 mmol), triethylamine (14.3 mmol), and deuterated water (100 mmol) in 10 ml of acetonitrile was irradiated for 15 h with the high pressure mercury arc lamp and the deuterated benzonitrile was fractionated.

The isotopic content was determined by mass spectral analysis using a Hitachi RMU-6 mass spectrometer.

*Tritiation of Benzonitrile with Diethylamine*[$N^3H$]. Tritiated diethylamine (42.0 mmol, $6.38\times10^{12}$ dpm/mol), benzonitrile (218 mmol), and benzene (218 mmol), all of which were degassed by the usual freeze-thaw cycles, were mixed in Pyrex tubes under nitrogen atmosphere. Irradiation was carried out for 20 h under nitrogen atmosphere with the 1 kW high pressure mercury arc lamp. The reaction mixture was washed with 1 M sulfuric acid and water to remove the amine and the aromatic compounds were recovered by distillation. Benzene was further purified by fractional distillation and submitted to tritium assay. Benzonitrile (17.5 g) recovered was hydrolyzed by refluxing with a solution of potassium hydroxide (14.5 g) in 68 ml of water for 5 h. After the usual work-up, the tritiated benzoic acid isolated was purified by recrystallization from water until reproducible specific activities were obtained and submitted to tritium assay.

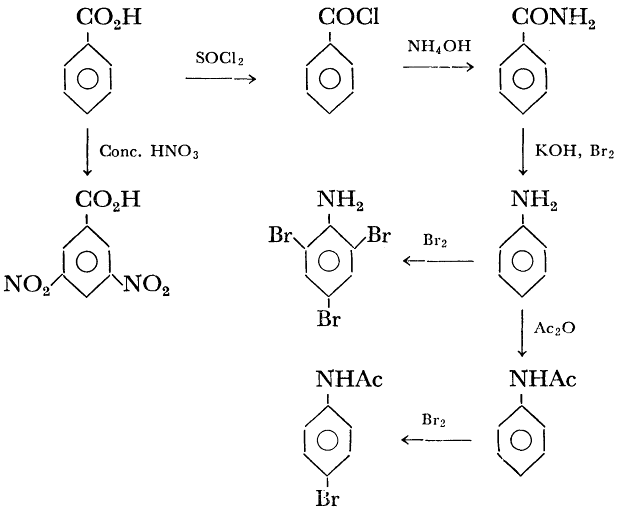
A reference solution, identical to the irradiated solution but stored in the dark for the corresponding period, was subjected to the same procedure and the incorporation of tritium in the substrate was confirmed to be negligible.

*Tritiation with Triethylamine and Tritiated Water.* A solution of benzonitrile (291 mmol), triethylamine (43 mmol), and tritiated water (6.0 ml, 3.61 mCi/ml) in 30 ml of acetonitrile was placed in Pyrex tubes, deoxygenated by purging with argon, and irradiated for 10 h with the 1 kW lamp.

After the irradiation, triethylamine and water were removed by distillation. The residue was washed with water and hydrolyzed as described above.

*Tritiation with Benzenethiol[$S^3H$].* A mixture of benzenethiol[$S^3H$] (99 mmol, $4.45\times10^{11}$ dpm/mol), toluene (501 mmol), and benzonitrile (486 mmol) was placed in Pyrex tubes, degassed by the usual freeze-thaw cycles, and irradiated for 6 h with the 1 kW lamp. After irradiation, benzenethiol was removed by washing with 10% NaOH and water, and the aromatic compounds were recovered by fractional distillation. Toluene was oxidized to benzoic acid by refluxing with aq. $KMnO_4$. Benzonitrile was converted to benzoic acid as described above.

The relative rate of nuclear tritiation of benzonitrile to toluene was determined as 5.9 from the specific activities of each benzoic acid derived from benzonitrile and toluene. The relative rate of benzonitrile to benzene (per C-H bond) was calculated to be 21 using the reported value of toluene (3.6),[3] which was obtained by competitive tritiation of toluene and benzene with 1-propanethiol[$S^3H$]. Since the relative rate of toluene to benzene for the addition of hydrogen atoms (1.7)[14] is small and photolysis of benzenethiol is supposed to generate much more amounts of hydrogen atoms than that of 1-propanethiol under the present condition, the relative rate of toluene would be diminished if it were determined with benzenethiol[$S^3H$]. Thus, the estimated value for benzonitrile would be larger than the value determined experimentally.



*Degradation.* The tritiated benzoic acid was diluted, if necessary, with inactive specimen for convenience in chemical manipulations, and then degraded in order to determine the tritium distribution according to the preceding schemes.[8]

The degradation products were purified by means of recrystallization until reproducible specific activities were obtained. Tritium activity was measured with a Packard Tri-Carb liquid scintillation spectrometer Model 3380. Each sample was counted for a period sufficient to reduce the randam error to 1% or less.

*Quenching studies.* Fluorescence measurements were made on a Hitachi fluorescence spectrophotometer MPF-2A.

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