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Light Induced Hydrogen Isotope Exchange between Terephthalonitrile and Thiols

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Synopsis. Interaction of an excited singlet state of terephthalonitrile with thiol is shown to be responsible for the title reaction on the basis of higher reactivity of terephthalonitrile relative to benzene and efficient quenching of fluorescene from terephthalonitrile by thiols.

We have shown that irradiation of mixtures of aromatic compounds and propanethiol tritiated at the S–H bond causes tritium uptake by the aromatic nucleus with distributions different from the results of substitutions by hydrogen ions and atoms.[1] In addition the rate of nuclear tritiation relative to benzene (k_{rel}) was found to be fairly high in benzonitrile and methyl benzoate (k_{rel}: 254 and 421, respectively). On the basis of these observations, the mechanism was proposed as involving a reaction of an excited aromatic molecule with propanethiol. The present paper describes the identification of light-induced hydrogen exchange reaction of terephthalonitrile with thiols and the determination of the excited state participating in the reaction.

When a solution of terephthalonitrile in benzene was irradiated with a high pressure mercury arc lamp under nitrogen atmosphere in the presence of *n*-pentanethiol-*d*, incorporation of deuterium occurs to an extent of 22% in the nucleus of terephthalonitrile recovered. With tritium labelled *n*-pentanethiol, tritiation took place in both the nuclei of terephthalonitrile and benzene, the relative rate of tritiation of terephthalonitrile (k_{rel}) being 3.8×10^3 and 4.1×10^3 (per C–H bond) in duplicate runs. The marked enhancement of the relative rate by introduction of one more cyano substituent into benzonitrile argues against that tritium atoms generated by photolysis of thiols contribute mainly to the exchange,[2] and involvement of an excited terephthalonitrile in the nuclear tritiation process is suspected. In this connection it is of interest to study on quenching of the excited singlet states of aromatic compounds by thiols.

TABLE 1. QUENCHING OF FLUORESCENCE FROM AROMATIC COMPOUNDS BY *n*-OCTANETHIOL IN AERATED BENZENE

Aromatic compound	$k_q\tau_s$, M^{-1}
Naphthalene	0.37
Anisole	9.38
Benzonitrile	36.7
Phthalonitrile	34.6
Isophthalonitrile	43.0
Terephthalonitrile	68.1

TABLE 2. QUENCHING OF TEREPHTHALONITRILE FLUORESCENCE BY THIOLS IN AERATED BENZENE

Thiol	$k_q\tau_s$, M^{-1}
n-Propanethiol	63.0
n-Pentanethiol	62.2
3-Methylbutanethiol	51.4
1-Methylbutanethiol	46.3
n-Octanethiol	68.1

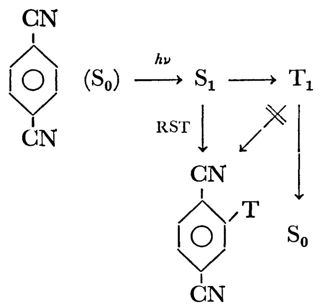
The fluorescence of aromatic compounds, such as benzonitrile and phthalonitriles, in benzene was quenched by the addition of *n*-octanethiol. Stern-Volmer plots of the reciprocal of relative fluorescence intensities against *n*-octanethiol concentrations were obtained for aromatic compounds; the slopes of these plots ($k_q\tau_s$) are presented in Table 1, where k_q is the rate constant for quenching of the excited singlet state of an aromatic compound by *n*-octanethiol and τ_s is the singlet lifetime of that aromatic compound. Similarly, the slopes ($k_q\tau_s$) obtained from the quenching of terephthalonitrile fluorescence by several thiols are given in Table 2.

It is notable, from Tables, that the slope ($k_q\tau_s$) is pronounced in benzonitrile and phthalonitriles in accord with their high rate of the tritiation reaction, while it is only slightly affected with respect to the structure of thiols. From the quenching of terephthalonitrile fluorescence by oxygen ($k_q\tau_s$: 289 M^{-1}) the terephthalonitrile singlet lifetime under air (τ_s) was obtained to be 1.3×10^{-8} s by assuming that the quenching rate by oxygen[3] is diffusion-controlled (1.5×10^{10} $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$).[4] As the observed slope ($k_q\tau_s$) for terephthalonitrile is 68.1 M^{-1}, this leads to an estimate for k_q of 5.2×10^9 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which is higher than k_q of naphthalene, 2×10^7 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, obtained from $k_q\tau_s$ of 0.37 M^{-1} and τ_s (aerated) of 1.5×10^{-8} s.[5] The result shows that *n*-octanethiol is an effective quencher of the excited singlet state of terephthalonitrile with the quenching rate constant near to the diffusion controlled one.

In order to examine a possibility that the triplet state of terephthalonitrile would interact with thiols, attempts have been made to observe the effect of *n*-pentanethiol on the triplet lifetime (τ_T) of terephthalonitrile. A convenient way of determining τ_T in solution at room temperature has often been to apply flash spectroscopy, but such a method was not applicable due to a failure in observing T-T absorption of the triplet state in the case of terephthalonitrile. A rewarding approach results from the measurement of the terephthalonitrile phosphorescence lifetime in EPA at 77 K, in which τ_T (1.6 s) is unaffected in the presence of high concentration of *n*-pentanethiol (1.1 M).

Thus, the tritiation from the triplet state appears to be improbable.

From all these results it is conceivable that interaction of the singlet excited terephthalonitrile with the ground state thiol is responsible to induce the hydrogen isotope exchange.



Experimental

Deuterium Exchange with Terephthalonitrile. A mixture of terephthalonitrile (1.57 mmol) and *n*-pentanethiol-*d* (16.5 mmol) in 30 ml of benzene was irradiated under nitrogen atomosphere for 20 hr with a 400 W high pressure mercury arc lamp. After removal of benzene and the thiol under reduced pressure, the residue was subjected to dry chromatography on silica gel. Elution with benzene gave 20 mg of the dinitrile. Deuterium included in the dinitrile was determined from its NMR spectrum in $CDCl_3$ using 1,4-dimethoxybenzene as an internal standard, reference being made to that of the authentic sample.

Tritium Exchange with Terephthalonitrile. A mixture of tritiated *n*-pentanethiol (0.992 mmol, 2.35×10^{12} dpm/mmol) and terephthalonitrile (0.499 mmol) in 10 ml of benzene was placed in a Pyrex tube, degassed by the usual chill and thaw cycles, and irradiated for 10 hr with a 1 kW high pressure mercury arc lamp using a merry-go-round photochemical reactor (RIKO Rotary Photochemical Reactor, Model RH 400-10W). After the irradiation, *n*-pentanethiol was removed by washing with aqueous sodium hydroxide and water. The amount of the dinitrile in the mixture (95 and 85% of the starting dinitrile for duplicate runs) was estimated by vpc on a 2 m column containing 10% XF 1150 on Chromosorb P at 200 °C. Benzene was recovered from the mixture by fractional distillation. To the residue 500 mg of the non-radioactive dinitrile was added and the combined dinitrile was purified by means of recrystallization until reproducible specific activities were obtained. The benzene distillate was washed further with aqueous basic hydrogen peroxide to remove traces of the radioactive thiol and submitted to tritium assay. 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 and phosphorescence spectra were recorded on a Hitachi fluorescence spectrophotometer MPF-2A.

References

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5) *Idem, ibid.*, p. 330.