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LIGHT-INDUCED TRITIATION OF AROMATIC COMPOUNDS WITH PROPANETHIOL[S^3H]

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The aromatic tritiation induced by irradiation of mixtures of aromatic compounds and propanethiol[S^3H] was studied with respect to the tritium distribution in the nucleus and the relative rate of tritiation. A mechanism involving a reaction of an excited aromatic molecule with the thiol is proposed.

A recent report on the aromatic substitution by tritium atoms generated by photolysis of thiophenol[S^3H]1) prompted us to communicate our results of the light-induced hydrogen-tritium exchange between aromatic compounds and propanethiol[S^3H].2)

A mixture of propanethiol[S^3H] (0.033 mole, 3.4×10^{11} dpm/mole), benzene (0.165 mole), and a monosubstituted benzene (0.165 mole) was placed in a Pyrex tube (25 mm × 205 mm), degassed by the usual chill and thaw cycles, and irradiated for 40 hr at 4–12° with a 400 W high pressure mercury arc lamp. After removal of the thiol by washing the mixture with 10% aqueous potassium hydroxide, the aromatic compounds were recovered by fractional distillation. A portion of each fraction, benzene and a monosubstituted benzene, was purified by gas chromatography and submitted to tritium assay. The remainder of the monosubstituted benzene was degraded by the known procedures3) in order to determine the tritium distribution.

Table 1 shows the intramolecular tritium distribution and the relative rates of tritiation of monosubstituted benzene (per C-H bond). The order of reactivity among the nuclear positions is o>m>p with aromatic compounds bearing an electron-donating group, while it is p>>o>m in compounds with an electron-withdrawing group. All substituents examined activate the nucleus towards the tritiation irrespective of their polar character. Extremely high rates are shown by benzonitrile and methyl benzoate. These observations provide a striking contrast with the results

Table 1. Tritiation of Substituted Benzene PhX with Propanethiol[S^3H]

X	Tritium distribution (%)			k_{rel}*
	Ortho	Meta	Para	
CH_3	49.0	34.6	16.5	3.61
NH_2	90.4	7.6	2.0	3.36
CN	17.4	2.0	80.8	254
CO_2CH_3	16.6	1.0	82.4	421
NO_2	52.2	0.6	47.6	1.49

* Rate (per C-H bond) of nuclear tritiation relative to benzene.

of electrophilic (D^+)4) and radical ($T\cdot$)1,5) substitutions, and it would therefore seem probable that the tritiation takes place under the present conditions by the reaction of aromatic molecules in an excited state with the thiol in the ground state, at least in the case of benzonitrile and methyl benzoate.

This view is further supported by the following experiments. When a mixture of benzene, benzonitrile, and the thiol was irradiated by light with a 400 W high pressure mercury arc lamp filtered through a layer of benzonitrile 1 cm in thickness, the relative rate of the tritiation was decreased considerably (k_{rel} being 79.1), whereas the tritium distribution was hardly affected, being 12.1% ortho, 2.3% mata, and 85.5% para. This finding is readily explained by supposing that the excitation of benzonitrile was suppressed by the benzonitrile filter much more strongly than that of benzene. If a reaction between benzonitrile and tritium atoms generated by photolysis of the thiol had contributed effectively to the nuclear tritiation besides the reaction between excited benzonitrile and the thiol in the ground state, the suppression of excitation of benzonitrile might have brought about some change in the tritium distribution. The fact that such a possibility was not the case shows that it is highly unlikely that tritium atoms should play an important role in the tritiation.

Irradiation of a mixture of benzonitrile and tritium-labelled acetic acid[O^3H] was also found to cause the tritiation of the nucleus with a similar distribution (12.4% ortho, 1.0% meta, and 86.7% para), and the participation of similar intermediates is accordingly suspected in the distribution determining step in acetic acid as well as in propanethiol. However, the fact that the rate of tritium incorporation into benzonitrile is smaller in tritiated acetic acid than in the thiol by a factor of about 10^{-3} in spite of the higher acidity of acetic acid suggests that the tritiation does not proceed by an ionic mechanism involving tritons (T^+), but by a homolytic or a concerted mechanism involving a molecule of a tritium donor in the rate determining step. The difference in the rate should be attributed to the difference in the bond dissociation energy between the S-H (88 kcal/mole) and O-H (112 kcal/mole) bonds.6)

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