

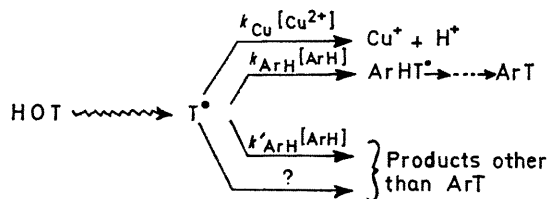
Substituent Effects on the Rate of Reaction of Aqueous Hydrogen (Tritium) Atoms with Aromatic Compounds

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Summary Relative rate constants for the reaction $\text{ArH} + \text{T}^{\bullet} \rightarrow \text{ArHT}^{\bullet}$ with a series of aromatic compounds are deduced from the effectiveness of the inhibition of β -radiation-induced aromatic tritium exchange in degassed aqueous solution by cupric ions.

ADSETTS and GOLD¹ have shown that the β -radiation-induced tritium isotope exchange between water and the nuclear hydrogen atoms of an aromatic solute (benzene² or mesitylene³) is initiated by the attack of aqueous tritium atoms on the solute. The exchange reaction can be inhibited by the addition of a copper(II) salt,¹ the cupric ions of which compete with the aromatic compound for tritium atoms, as in the Scheme.



It was established for mesitylene¹ that the cyclohexadienyl radical ArHT^{\bullet} goes predominantly to ArT . A leaving-group isotope effect in this conversion (either by direct hydrogen atom abstraction or by oxidation of the radical to the cyclohexadienyl cation, followed by proton abstraction) is expected strongly to favour this reaction over the alternative regeneration of ArH by tritium loss.

By measuring and comparing the effect of copper(II) sulphate on the β -radiation-induced exchange of a series of aromatic compounds in de-gassed aqueous solution, we have now deduced the relative reactivities of these aromatic compounds (ArH) towards tritium atoms with formation of ArHT^{\bullet} . These results are listed in the second column of the Table. It is considered that these values represent the relative reactivities of the aromatic compounds towards the sterically least demanding free radical, the hydrogen atom.

The internal consistency and interpretation of the experimental results is confirmed by several cross-checks (see footnotes c—f). We also find that the ratio of the reactivity of cupric ion to that of benzene (0.36), as deduced from their relative effects in the inhibition of mesitylene exchange, is consistent with the somewhat more discordant pulse-radiolysis data reported for the reaction of hydrogen atoms with cupric ion³ and with benzene.⁴

The results evaluated from the present study, with degassed solutions, are virtually identical with those of the earlier study^{1,3} in which the solutions were aerated. The chief difference between the observations of the two

investigations occurs at very low cupric ion concentrations. It is tentatively ascribed to the function of oxygen as an electron and radical scavenger, which becomes masked in the presence of higher concentration of cupric ion.

Relative reactivities of aromatic compounds ArH towards radical R^{\bullet} ($k_{\text{PhX}}/k_{\text{Benzene}}$)

Substrate	$\text{R}^{\bullet} =$	
	$\text{T}^{\bullet\text{a}}$	$\text{Ph}^{\bullet\text{b}}$
Mesitylene	8.5 ^c	
Toluene	2.2 ^d	1.23
Anisole	2.7	2.01
Fluorobenzene ..	1.0	1.03
Chlorobenzene ..	1.1 ^e	1.06
Bromobenzene ..	1.1	1.29
Benzonitrile ..	0.9 ^f	3.7

^a Reaction $\text{Ar-H} + \text{T}^{\bullet} \rightarrow \text{ArHT}^{\bullet}$.

^b D. H. Hey, *Adv. Free-Radical Chem.*, 1967, **2**, 47; G. H. Williams, in "Essays on Free-Radical Chemistry," *Chem. Soc. Special Publ. No. 24*, p. 25 (1970).

^c The same value (8.5 ± 0.5) was found by Adsetts and Gold² by competition between benzene and mesitylene in aerated solutions. Such competition experiments in de-gassed solutions (this work) gave a ratio 6.9.

^d Pulse-radiolysis experiments give the value 2.4 for the reaction of hydrogen (protium) atoms (M. H. Studier and E. J. Hart, *J. Amer. Chem. Soc.*, 1969, **91**, 4068).

^e From inhibition of chlorobenzene exchange by mesitylene (this work) the value 1.0 is obtained.

^f From inhibition of benzonitrile exchange by toluene (this work) the value 0.7 is obtained.

The reactivity ratios are numerically similar to results reported for free-radical phenylation of the corresponding compounds.⁵ Benzonitrile forms one exception: two independent reactivity comparisons for tritium atoms indicate that this compound is less reactive than benzene whereas, according to the phenylation results,⁶ it is the most reactive member of our group. The generally low selectivity of tritium atoms is consistent with the large specific rates of the reactions although, by comparison, the *ca.* 10^6 times less reactive⁷ phenyl radical is remarkable in being equally or even more unselective.

Because the leaving-atom isotope effect favours the formation of ArT from ArHT^{\bullet} , it is reasonable to assume that slight variations in the leaving-atom isotope effect with substrate reactivity, as are known to exist in heterolytic aromatic substitution,⁸ are unlikely to introduce a significant error into the reactivity ratios based on the exchange experiments. However, when the leaving group of the substrate is replaced by deuterium, the basic assumption is no longer valid and some loss of tritium from the intermediate or intermediates may occur. It is in this way that we interpret our observation that $[1,3,5\text{-}^2\text{H}_3]$ mesitylene is apparently 1.5 ± 0.2 times less "reactive" towards exchange than ordinary mesitylene. On the assumption that there are no secondary isotope effects due to isotopic

replacement at the site of tritium atom attachment, this finding is compatible [by use of the formula⁹ $(k_H/k_D)^{1.442} = k_H/k_T$] with leaving-atom isotope effects (k_H/k_T) in the region of 10.

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³ M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493; J. H. Baxendale, R. S. Dixon, and D. A. Stott, *Trans. Faraday Soc.*, 1968, **64**, 2398; cf. G. C. Barker and P. Fowles, *ibid.*, 1970, **66**, 1661.

⁴ M. C. Sauer, jun., and B. Ward, *J. Phys. Chem.*, 1967, **71**, 3971; B. D. Michael and E. J. Hart, *ibid.*, 1970, **74**, 2878.

⁵ For results and references, see D. H. Hey, *Adv. Free-Radical Chem.*, 1967, **2**, 47, G. H. Williams, "Essays on Free-Radical Chemistry," *Chem. Soc. Special Publ. No. 24*, p. 25 (1970).

⁶ R. L. Dannley and E. C. Gregg, *J. Amer. Chem. Soc.*, 1954, **76**, 2997.

⁷ D. F. DeTar, *J. Amer. Chem. Soc.*, 1967, **89**, 4058.

⁸ L. Melander and S. Olsson, *Acta Chem. Scand.*, 1956, **10**, 879; B. Östman and S. Olsson, *Arkiv Kem.*, 1960, **15**, 275; L. Melander in "The Transition State," *Chem. Soc. Special Publ. No. 16*, p. 77 (1962); see also S. Olsson, *Arkiv. Kem.*, 1970, **32**, 105, and papers cited therein.

⁹ C. G. Swain, E. C. Stivers, J. F. Reuwer, and L. J. Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5888.