The Relative Reactivity of Benzene and Mesitylene towards Tritium Atoms

By J. R. ADSETTS and V. GOLD*
(*University of London, King's College, Strand, London, W.C.2*)

RECENT experiments have shown that the reaction between an aromatic hydrocarbon and tritium atoms can be studied by observing radiation-induced aromatic tritium exchange in aqueous solution.[1] Since the hydrogen atom is the simplest free radical, it seemed of interest to see whether the relative reactivities of different hydrocarbons could be determined by this technique. Such measurements are now reported. They also throw light on the basic question whether aromatic hydrocarbons react with tritium atoms to form products other than those arising from tritium addition to the aromatic ring.

We have examined the inhibition by added benzene, in low concentration, of the β-radiation-induced tritium uptake by mesitylene.

According to our model of the reaction, the velocity of exchange (v_M) in mesitylene (M) is related to the rate (v) of production of tritium atoms by the approximate equation (1)

$$v_M = v \times k_M[M]/\Sigma k_X[X] \quad (1)$$

where the denominator denotes a sum over all possible reactions of tritium atoms in this system; *e.g.* in the presence of benzene (B) it will contain the terms $(k_M + k'_M)[M] + (k_B + k'_B)[B] + \ldots$ where k_M and k_B are rate constants for tritium-scavenging reactions leading to labelled mesitylene and benzene, respectively, and k'_M and k'_B are rate constants for other tritium-scavenging reactions by the two hydrocarbons. If under our conditions the addition of cupric ion, benzene, or mesitylene has a negligibly small effect on the tritium-scavenging action of other species, then it follows from equation (1) that the study of mesitylene exchange as a function of concentration of these substances allows certain ratios of rate constants to be evaluated. We thus find

$$k(Cu^{2+}) : (k_B + k'_B) : (k_M + k'_M) = 0{\cdot}3 : 1 : 9$$

These ratios measure *total* scavenging reactivity of the substances towards tritium atoms.

As a second step, we have measured the tritium content of the benzene, which was present as inhibitor during the mesitylene exchange, and have compared this activity with that of mesitylene isolated from the same reaction mixture. In this experiment, the observed competition is between the two aromatic exchange reactions only, and hence we find that the value of the ratio k_M/k_B is 8·5. It thus follows that

$$(k_M + k'_M)/k_B + k'_B) \approx k_M/k_B$$

which means *either* that $k'_M/k'_B = k_M/k_B$ or else that $k_M \gg k'_M$ and $k_B \gg k'_B$. In view of the different possibilities for reactions with T•, other than addition, presented by mesitylene and benzene, the first of these assumptions seems less probable. Accordingly, we conclude that the most important reaction of tritium atoms with mesitylene (or benzene) is that leading to the tritium-labelled hydrocarbon. In particular, hydrogen abstraction by tritium atoms from the hydrocarbons seems to be less important than addition leading to substitution. These conclusions agree with earlier work on the reaction of hydrogen atoms with benzene.[2,3]

The measured reactivity ratio (*ca.* 9) thus represents very nearly the ratio for attachment of tritium atoms to the two compounds. It is a large ratio, in-view of the fact that the two second-order rate constants are approximately 10^9 and 10^{10} sec.$^{-1}$ M^{-1}. It is consistent with the ratio 2·5 : 1 found for the addition of hydrogen atoms to toluene and benzene by a different technique.[2]

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[1] J. R. Adsett and V. Gold, *Chem. Comm.*, 1968, 915.
[2] M. C. Sauer, jun., and B. Ward, *J. Phys. Chem.*, 1967, **71**, 3971.
[3] P. V. Phung and M. Burton, *Radiation Res.*, 1957, **7**, 199.