Reactions of Alkyl Radicals. Part III.[1] Relative Rates of Methylation and Hydrogen Abstraction by Methyl Radicals

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Relative rates of reaction of several aromatic substrates towards attack by methyl radicals formed by photolysis of methylmercuric iodide (' methyl affinities ', benzene = 1) are reported.

REACTIONS of methyl radicals formed by the photolysis of methylmercuric iodide with aromatic compounds have previously been described.[1-3] With benzene and halogenobenzenes about half the available methyl radicals occur in the products as methane, while similar yields of products of monomethylation of the substrates are formed. Thus, the σ complex MeArH· formed by addition of a methyl radical to the substrate may be dehydrogenated either directly by a second methyl radical to give the observed yields of products, or by reaction (1*d*). Mechanism (1) was considered[1] to be the more likely, and also leads to the observed stoicheiometry, and we have now confirmed directly that (1*e*)

$$\begin{aligned} &(a)\ \mathrm{MeHgI} \xrightarrow{h\nu} \mathrm{Me}\cdot + \mathrm{HgI}\cdot \\ &(b)\ \mathrm{HgI}\cdot \longrightarrow \mathrm{Hg} + \mathrm{I}\cdot \\ &(c)\ \mathrm{Me}\cdot + \mathrm{ArH} \longrightarrow \mathrm{MeArH}\cdot \qquad (1) \\ &(d)\ \mathrm{MeArH}\cdot + \mathrm{I}\cdot \longrightarrow \mathrm{MeAr} + \mathrm{HI} \\ &(e)\ \mathrm{HI} + \mathrm{MeHgI} \longrightarrow \mathrm{MeH} + \mathrm{HgI_2} \end{aligned}$$

occurs rapidly and quantitatively. We have also confirmed the earlier conclusions by measuring methane yields for the reactions in benzene, fluorobenzene, chlorobenzene, bromobenzene, and t-butylbenzene, using two distinct experimental techniques, under the standard conditions also used for competitive experiments. With t-butylbenzene nuclear methylation products were also identified.

Isopropylbenzene reacts only at the side chain[1] giving, as we now find, 0·96—0·99 mole of methane per mole of isopropylbenzene, and bicumyl, but no products of nuclear methylation. No α-methylstyrene, which might arise by disproportionation of α-cumyl radicals, was formed at the relatively low temperature of the experiments now described (85°), in agreement with previous results.[1,3,4]

Toluene gives 0·84—0·86 mole of methane, together with bibenzyl and isomeric xylenes. It has previously been shown[1] that with toluene almost all the methyl radicals not accounted for as methane are consumed in the formation of xylenes. For all these solvents, therefore, the stoicheiometry of the reaction is established, and the relative reactivities of the various nuclei can be measured by measurement of yields of methane formed in competitive experiments. With ethylbenzene, methane (96—97%), was formed together with *meso*- and racemic 2,3-diphenylbutane and small quantities of 2-, 3-, and 4-ethyltoluene, and the reaction therefore apparently follows an analogous path. For the halogenobenzenes and t-butylbenzene, therefore, which react with methyl radicals only at nuclear positions, the competing solvent used was cumene, which reacts only at the side chain, whereas for toluene and ethylbenzene, the competing solvent was benzene. From the complete decomposition of methylmercuric iodide in biphenyl and in diphenyl ether, methane yields of 8—11 and 9—11% respectively were obtained. Small quantities of the isomeric methylation products together with high boiling residues were formed in both cases, and the low yields of methane are therefore probably due to the more ready dimerisation of σ complexes with these substrates, leading to involatile tetranuclear hydroaromatic products. With this assumption, the relative rates of reaction of these solvents can be calculated.

Competitive experiments by both techniques were conducted for the various solvent pairs, and the results (except for ethylbenzene) obtained by the two methods are in sufficiently good agreement for them to be combined. Mean values with 95% confidence limits, calculated from standard deviations, are given in the Table. For ethylbenzene, because $\not>5\%$ of the total reaction is at the nucleus, there is a large uncertainty in the derived methyl affinity. Our results, however, indicate with 95% confidence that any activation of the nucleus by the ethyl group towards attack by methyl radicals is by a factor $\not>2$. The methyl affinity of t-butylbenzene has not previously been reported, but the deactivation revealed by our result has previously been observed for homolytic phenylation[5] and cyclohexylation[6] of this substrate, and has been attributed

Methyl affinities of aromatic compounds (benzene = 1)

Substrate	Temp. (°C)	Number of determinations	Methyl affinity with 95% confidence
Fluorobenzene	80	7	1·51 ± 0·23
Chlorobenzene	85	11	2·11 ± 0·32
Bromobenzene	85	10	3·87 ± 0·55
Toluene[a]	85	9	1·46 ± 0·16
t-Butylbenzene	85	7	0·68 ± 0·10
Biphenyl	85	6	7·47 ± 1·35
Diphenyl ether	85	8	4·89 ± 0·69

[a] For reaction at nuclear positions.

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to steric hindrance to attack at the otherwise reactive 2-positions. Clearly this is still important even with the smaller methyl radical. The increase in activation of the nuclei of the halogenobenzenes in the order $\mathrm{PhF} < \mathrm{PhCl} < \mathrm{PhBr}$ has also been observed for phenylation of these compounds.[7-9] The methyl affinities for the halogenobenzenes and toluene now reported, may be compared with those given by Heilman *et al.*[10,11] Our results for the halogenobenzenes differ from the previous values, which, however, in marked contrast to ours, were obtained from reactions of unknown stoicheiometry, and on the basis of stoicheiometric assumptions which may, or may not have been correct. Previous workers reported the methyl affinity of biphenyl as 5 [12,13] and that of diphenyl ether as 2·5.[12] These substrates would be expected to be fairly reactive to free radicals because of the conjugation of biphenyl and the presence of the oxygen function in diphenyl ether.

As compared with relative rates of phenylation [8,14] the methyl affinities show a greater spread, and this greater selectivity of methyl than of phenyl radicals may be attributed to the lower reactivity of the former species.[12]

EXPERIMENTAL

Solvents, reagents and reference compounds were prepared or purified by methods already in the literature and their purity was checked by g.l.c. and i.r. spectroscopy.

Photolyses.—Method I. Approximately M/20 solutions of methylmercuric iodide were irradiated (at $85 \pm 0{\cdot}1^{\circ}$ unless otherwise stated) as described,[2] and the evolved gas was collected over saturated brine in a water-jacketted gas burette.

Method II. The reaction vessels were two-necked Pyrex flasks (50 ml) equipped with magnetic stirrers and magnetically operated break seals in one neck. Degassed solutions (0·05 mol l^{-1}; 20 ml) were introduced into these vessels through the other neck, which was then sealed, and the contents were immersed in the thermostat and irradiated for a time such that in control experiments, decomposition of methylmercuric iodide had been complete. After removal from the thermostat the flasks were cooled in liquid air and attached *via* the break seal to a standard vacuum line for analysis. After evacuation to 10^{-5} Torr the break seal was opened and the contents of the flask outgassed by successive freeze–pump–thaw cycles. Control experiments had shown that this procedure, in which a mercury diffusion pump and a Toepler pump were used together, allowed the gas to be transferred quantitatively from the reaction vessel and solvent to a storage section. The volume, temperature, and pressure of the gas were measured before it was transferred to a gas chromatograph (2 m silica gel column; flame ionisation detector [15]) for analysis.

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