223. *Addition of Methyl Radicals to Substituted Benzenes.*

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Methyl affinities of some substituted benzenes were determined at 65°. It was found that the addition of methyl radicals to substituted benzenes is slightly accelerated by F, Cl, and Br atoms, and retarded by the OCH_3 group. Methyl affinities of *p*- and *m*-dichlorobenzenes are nearly identical and higher than that of the monochloro-derivative.

The rates of addition are also enhanced by CN, OAc, and CO_2Et groups. An exceptionally high reactivity of nitrosobenzene is probably due to the reaction of methyl radicals with the nitroso-group. One has to distinguish, therefore, between the effect of a substituent upon the reactivity of the benzene ring, and the effect due to the addition reaction involving a substituent (*e.g.*, the addition of a radical to styrene).

The results now reported are compared with Hey's results on the rate of phenylation. The trends in both reactions are very similar.

The work of Hey and his co-workers [1-3] on the effect of substituents upon the rate of phenylation of benzene derivatives induced us to study similar reactions involving, however, methyl instead of phenyl radicals. In the system studied by Hey, a compound, generating phenyl radicals by its decomposition, is dissolved in an equimolecular mixture of two aromatic solvents, say HA_1 and HA_2. Under the conditions of Hey's experiments, the decomposition yields eventually the phenylated solvent molecules, A_1Ph and A_2Ph, and it is the purpose of the experiment to determine their mole ratio.

In the interpretation of his results Hey assumes tacitly that the phenyl radicals, generated in his system, are added to the respective aromatic compounds according to equation (1):

$$Ph + A{\cdot}H \longrightarrow Ph{\cdot}A{\cdot}H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The radicals formed in reaction (1) are supposed to react rapidly with radicals R according to equation (2):

$$Ph{\cdot}A{\cdot}H{\cdot} + R \longrightarrow Ph{\cdot}A + RH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and thus to yield the final product of the reaction. If reaction (2) is much faster than reaction (1), *i.e.*, if reaction (1) is rate-determining in the overall phenylation process, and if radicals R participating in reaction (2) are different from Ph·A·H radicals, then the molar ratio $PhA_1 : PhA_2$ gives the ratio of the bimolecular rate constants of reactions (1) for A_1H and A_2H respectively.

This scheme seems to be plausible. It appears that the Ph·CO·O radicals are fulfilling the rôle of R radicals when benzoyl peroxide is used for generating phenyl radicals, since the equivalent amount of benzoic acid is formed in the process. Furthermore, Hey demonstrated [4] that the ratio $PhA_1 : PhA_2$ is approximately independent of the nature of the compound used for generating phenyl radicals. To complete the evidence in favour of the suggested scheme it would be desirable, however, to measure the ratio $PhA_1 : PhA_2$ for a varying ratio $HA_1 : HA_2$ and to show the proportionality of these two variables; but, even in the absence of this information, Hey's results seem to be well founded.

A method was developed in our laboratories [5, 6] which permits one to determine the

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[1] Augood, Hey, and Williams, *J.*, 1952, 2094; 1953, 44.
[2] Hey and Williams, *Discuss. Faraday Soc.*, 1953, **14**, 216.
[3] Cadogan, Hey, and Williams, *J.*, 1954, 794.
[4] Hey, Stirling, and Williams, *J.*, 1955, 3963.
[5] Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.
[6] Szwarc, *J. Polymer Sci.*, 1955, **16**, 367.

relative rates of addition of methyl radicals to aromatic or olefinic compounds. The addition reaction is similar to reaction (1), namely,

$$CH_3 + HA \longrightarrow H{\cdot}A{\cdot}CH_3 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The kinetic basis of our technique was thoroughly investigated, and the method seems to be particularly useful when applied to reactive substrates. It is inferior, however, to Hey's method if one desires to determine the point of attack by a radical. While this information is easily obtained in Hey's method, unfortunately it is not available in our measurements.

The application of our technique to substituted benzenes is somewhat difficult since these compounds belong to the class of not too reactive substrates. This forces us to work with very high mole-fractions of substrates, and consequently we have to change considerably the environment in which the reaction proceeds. The results are, therefore, not as good as desirable although the conclusions are very definite. We confirm the essential findings of Hey, namely, that the effect of a substituent on the rate of addition of radicals is small as compared with the enormous effects observed in reactions involving ionic intermediates. However, the addition of methyl radicals seems to be more affected by a substituent than the addition of phenyl radicals. We find also that fluorinated, chlorinated, and brominated benzenes are more reactive than benzene, which parallels Hey's findings on the rate of phenylation. Furthermore, nitrobenzene seems to be more reactive than benzene. However, the latter reactions show some pecularities which probably indicate the reversibility of the addition process, *e.g.*, $CH_3{\cdot}C_6H_5{\cdot}NO_2 \rightleftharpoons C_6H_5{\cdot}NO_2 + CH_3{\cdot}$. These results are omitted, therefore, from the present paper and will be discussed later. On the other hand, we found that anisole is less reactive than benzene. This result parallels that obtained in a series of quinones,[7] and we believe that it illustrates the general rule that electron-donating groups slow down the radical addition, while electron-withdrawing groups accelerate it.* However, the phenomenon is more complex if one deals with substituents which are themselves unsaturated. A possible explanation of these phenomena is given in a paper by Szwarc.[8] It is noteworthy that a deactivation effect of the *tert.*-butyl group was found by Cadogan, Hey, and Williams [8] and attributed to steric hindrance.

All the experimental results are listed in Table 1, while the relative rate constants of addition of methyl radicals to the substituted benzenes are listed in Table 2. The latter values are referred to as methyl affinities, and a value of unity has been arbitrarily chosen for the methyl affinity of benzene.

EXPERIMENTAL

The experimental technique has been described fully.[5, 6, 10] Methyl radicals were generated by thermal decomposition of dilute solutions of acetyl peroxide in 2-methylheptane. The amounts of methane and carbon dioxide formed were determined quantitatively. On addition of the desired amount of aromatic or olefinic compounds the amount of methane formed decreases, and it is assumed that the decrease is due to reaction (3). Hence, the relative rate constant of reaction (3) could be determined from the relative decrease in the amount of methane formed.

Commercial reagents were used, purified as usual if necessary. Their purity was checked by their b. p.s or m. p.s.

All the experiments were carried out at 65° in 2-methylheptane. The concentration of acetyl peroxide was of the order 3×10^{-2}M, and about 6% of the peroxide was decomposed in

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* This conclusion is based on some, as yet unpublished, results. The generalization should be taken cautiously since methyl or ethyl groups exhibit, sometimes, an effect contrary to their electron-donating power. See ref. 8 and Buckley and Szwarc, *J. Amer. Chem. Soc.*, 1956, **78**, 5696.

[7] Rembaum and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 4468.

[8] Szwarc, *J. Phys. Chem.*, in the press.

[9] Cadogan, Hey, and Williams, *J.*, 1954, 3352.

[10] Leavitt, Levy, Szwarc, and Stannett, *J. Amer. Chem. Soc.*, 1955, **77**, 5493.

each experiment. The second column of Table 1 gives the mole % of substrate in the solution; the next two columns give the amounts of carbon dioxide and methane formed in the reaction. These two values give the $CH_4 : CO_2$ ratio used in calculating k_3/k_i. The $CH_4 : CO_2$ ratio obtained in pure 2-methylheptane was determined to be 0·800. k_3 denotes the rate constant of the addition reaction (3), while k_i denotes the rate constant of hydrogen abstraction from 2-methylheptane. Finally, the last column in Table 1 gives the unimolecular rate constant of the decomposition of acetyl peroxide measured by the amount of carbon dioxide formed.

DISCUSSION

The k_3/k_i values for benzene had been determined by Levy and Szwarc.[5] The present results at 65° (0·22 and 0·24) compare well with theirs, namely 0·26, 0·33, and 0·29. However, in order to preserve the self-consistency of the present data we have chosen the average of our two determinations as our standard value used in the calculation of methyl affinities.

Table 1 shows that the relative rates of addition of methyl radicals are approximately independent of the concentration of the investigated substrates, although in the case of fluorobenzene and benzonitrile the data reveal a definite trend. The change in the molar ratio 2-methylheptane : substrate by a factor of 9 (from 3 to 1/3) changes the relative rate of methyl-radical addition to fluorobenzene by less than a factor of 2, a similar change in the ratio affects the rate of addition to benzonitrile by only 50%. Although we do not know the detailed reasons for such trends, we suspect that they are caused by a considerable

TABLE 1.

Compound	Mole %	$CO_2 \times 10^2$ (millimoles)	$CH_4 \times 10^2$ (millimoles)	k_3/k_i	$10^5 k_u$ (sec.$^{-1}$)
C_6H_6	50	0·480	0·315	0·22	0·89
,,	50	0·483	0·310	0·24	0·90
PhOMe	75	0·794	0·460	0·13	2·10
,,	75	0·818	0·430	0·18	2·16
PhF	25	0·415	0·275	0·62	1·02
,,	50	0·398	0·215	0·48	1·01
,,	50	0·433	0·230	0·51	1·10
,,	75	0·370	0·132	0·38	1·02
PhCl	25	0·382	0·230	0·98	0·96
,,	25	0·354	0·210	1·05	0·89
,,	50	0·351	0·150	0·87	0·89
,,	50	0·355	0·145	0·95	0·90
PhBr	50	0·355	0·153	0·86	0·90
,,	50	0·350	0·156	0·80	0·89
p-$C_6H_4Cl_2$	25	0·352	0·150	2·7	0·89
m-$C_6H_4Cl_2$	25	0·388	0·162	2·8	0·88
PhCN	10	0·398	0·260	2·0	0·82
,,	10	0·404	0·260	2·2	0·89
,,	25	0·459	0·190	2·8	0·95
,,	25	0·465	0·190	2·9	0·99
,,	50	0·515	0·088	3·7	1·08
,,	50	0·495	0·096	3·1	1·04
Ph·COMe	75	0·690	0·204	0·57	1·62
,,	75	0·665	0·204	0·54	1·58
Ph·CO_2Et	25	0·456	0·252	1·3	0·96
,,	25	0·445	0·250	1·3	0·93
,,	50	0·450	0·170	1·1	0·93

TABLE 2. *Methyl affinities of substituted benzenes at 65°.*

Compound	Methyl affinity	Compound	Methyl affinity
Benzene	1·0	Anisole	0·65 ± 0·15
Fluorobenzene	2·2 ± 0·2	Benzonitrile	12·2 ± 1·5
Chlorobenzene	4·2 ± 0·2	Acetophenone	2·4
Bromobenzene	3·6 ± 0·2	Ethyl benzoate	5·2
p-Dichlorobenzene	11·7	Nitrosobenzene	10^5
m-Dichlorobenzene	12·2		

change of the environment in which the reaction proceeds, which in turn leads to second-order effects in the kinetics. It is noteworthy that the increase in the concentration of substrates decreases the apparent reactivity of fluorobenzene but increases that of benzonitrile.

The last column of Table 1 gives the rate constant k_u of the decomposition of acetyl peroxide. It is important that this rate constant remains essentially unaffected by the presence of substrate,* indicating that the substrate does not react directly with the peroxide. The only exceptions are anisole and, to a smaller extent, acetophenone. While the rate of decomposition seems to be twice as high in 75 mole % of anisole as in pure 2-methylheptane solution, the increase in the rate amounts only to about 50% in the case of acetophenone. These effects are not surprising since it is known that ethers accelerate the rate of decomposition of peroxides.[11, 12]

The results obtained for chloro- or bromo-benzene might be vitiated by the abstraction reaction, *e.g.*, $C_6H_5Br + CH_3 \longrightarrow C_6H_5 + CH_3Br$. In our method of calculation of k_3/k_i such a reaction would increase the apparent value of k_3/k_i. Qualitative tests † seem to indicate, however, that methyl chloride is not formed in the reaction, and that the amount of methyl bromide formed is negligible.

Comparison of Hey's results with ours, summarised in Table 2, indicates a greater spread in the reactivities of substituted benzenes towards methyl radicals than towards phenyl radicals. Since our work was carried out at 65° while Hey's was at 80°, the difference in reactivities should be greater in our investigation. Moreover, one has to realise that the ratio of reactivities of various substrates depends not only on their nature but also on the nature of the attacking radical (see the discussion of intrinsic reactivities of radicals in refs. 4—7). Hey and Williams [2] discuss the relative reactivities in terms of changes in localization energies. They assume that the change in the latter is *equal* to the change in the activation energy of the process, while all that could be expected is a proportionality between the difference in activation energies and the difference in the respective localisation energies.

Finally, we discuss the reactivity of nitrosobenzene. Two experiments were carried out with this compound one with 0·1 mole % solution in 2-methylheptane, and the other with the same concentration of nitrosobenzene in ethyl methyl ketone: k_3/k_i was calculated from the first experiment at 29,000, while k_3/k_{EMK} was calculated from the second experiment at about 3000. Since, $k_{EMK} = 9k_i$ (see ref. 9), the result of the second experiment can be recalculated into the k_3/k_i scale to give a value of about 27,000. Thus, the agreement between these two results is satisfactory.

It is obvious that the high value of methyl affinity of nitrosobenzene does not result from the activation of the benzene ring, but it represents a reaction between a methyl radical and the nitroso-group. Hence, in discussing reactions of substituted benzene, one has to distinguish between the effect of a substituent upon the reactivity of the benzene ring and an effect resulting from a reaction taking place on the substituent. For example, the high methyl affinity of styrene is not caused by the activation of the benzene ring by the vinyl group but by the " activation " of a molecule of ethylene by the phenyl group.

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* The rate constant of the unimolecular decomposition of acetyl peroxide at 65° and in pure 2-methylheptane solution is $0{\cdot}95 \times 10^{-5}$ sec.$^{-1}$.

† These tests were performed by adding a few drops of the reacting solution to a methanolic solution of silver nitrate.

[11] Nozaki and Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686.

[12] Smid, Rembaum, and Szwarc, *ibid.*, 1956, **78**, 3315.