

We thank the Science Research Council for support of these and related studies.

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### Reactivity of Aromatic Compounds towards Hydrogen Atoms

THE reactivity of aromatic compounds toward hydrated electrons and hydroxyl radicals has been the subject of various recent investigations<sup>1,2</sup>. The effects of substituents on the reactivities of benzene and benzoate ion were correlated with the substituent constant ( $\sigma$ ) of Hammett's equation. It has been shown that the mechanism of attack of hydroxyl radicals on aromatic compounds is analogous to electrophilic aromatic substitution<sup>2</sup>. On the other hand, the reactions of hydrated electrons followed a pattern analogous to nucleophilic substitution. The reactivity of aromatic compounds toward hydrogen atoms was investigated in order to study the nature of the  $\text{PhX} + \text{H}$  reaction.

The specific rate constants of substituted benzenes with hydrogen atoms were determined by competition kinetics, using isopropanol as the competing compound. De-aerated solutions containing  $5 \times 10^{-2}$  M isopropanol,  $1 \times 10^{-3}$  M acetone (as  $e_{aq}^-$  scavenger in order to avoid the  $e_{aq}^- + \text{PhX}$  reactions) and different concentrations of  $\text{PhX}$  at pH 8–9, were irradiated in a cobalt-60  $\gamma$ -source ( $4 \times 10^{17}$  eV  $\text{g}^{-1}$   $\text{min}^{-1}$ ). The doses of irradiation were  $8\text{--}40 \times 10^{17}$  eV  $\text{g}^{-1}$ . The yield of hydrogen was determined by gas chromatography (on a column of 'molecular sieves' 5 Å). Each experiment was repeated at least eight times and the coefficient of variation was  $\pm 10$  per cent.

Under the experimental conditions the hydrated electrons react with acetone, whereas the hydroxyl radicals react with isopropanol. Hydrogen atoms may react with isopropanol to form hydrogen, or with  $\text{PhX}$  to form  $\text{PhXH}$  radicals, which do not yield hydrogen<sup>3</sup>. The experimental yield of hydrogen is therefore the sum of the 'molecular' yield  $G_{\text{H}_2}$  and of  $G(\text{H} + \text{isopropanol})$ .  $G_{\text{H}_2}$  was determined under similar conditions using a solution of  $1 \times 10^{-3}$  M potassium bromide. The sum of  $G_{\text{H}}$  and  $G_{\text{H}_2}$  the total yield of hydrogen atoms, was determined using a solution of  $5 \times 10^{-2}$  M isopropanol +  $1 \times 10^{-3}$  M acetone. Using these values and the known value of the specific rate constant for the reaction of hydrogen atoms with isopropanol,  $k_{\text{H} + \text{isopropanol}} = 5.0 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$  (ref. 4), the rate constant of the reaction  $\text{H} + \text{PhX}$  was calculated:

$$\frac{k_{\text{H} + \text{PhX}}}{k_{\text{H} + \text{isopropanol}}} = \frac{[G_{\text{H}} - G(\text{H} + \text{isopropanol})][\text{isopropanol}]}{G(\text{H} + \text{isopropanol})[\text{PhX}]}$$

The results are summarized in Table 1. The order of reactivity is  $\text{PhSO}_3^- < \text{PhCN} < \text{PhNHCOCH}_3 < \text{PhCH}_2\text{COO}^- < \text{PhCOO}^- < \text{PhCOCH}_3 < \text{PhNO}_2 < \text{PhNH}_2 < \text{PhOH}$ . This order is in fair agreement with the order of reactivity of these compounds toward electrophilic aromatic substitution, with one exception: the reactivity of nitrobenzene is much higher than would be expected from the general behaviour of aromatic substitution. This

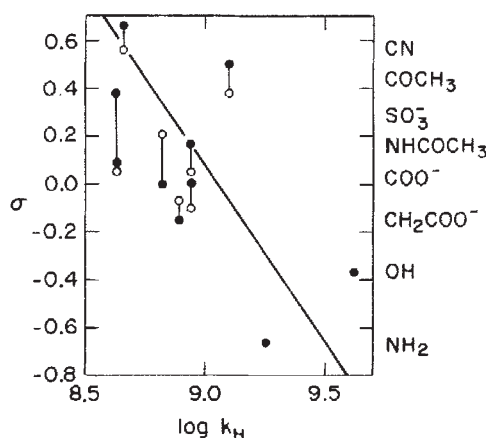


Fig. 1. Plot of  $\log k_{\text{H} + \text{PhX}}$  against  $\sigma$

is most probably due to a direct attack by hydrogen atoms on the  $\text{NO}_2$  group, as may be inferred from their fast reaction rates with  $\text{NO}_2^-$  ion<sup>5,6</sup> and  $\text{C}(\text{NO}_2)_4$  (ref. 7).

Table 1. REACTIVITY OF AROMATIC COMPOUNDS TOWARDS HYDROGEN ATOMS

Compound	Rate constant ( $\text{M}^{-1} \text{ sec}^{-1}$ )
$\text{C}_6\text{H}_5\text{SO}_3\text{Na}$	$4.80 \times 10^8$
$\text{C}_6\text{H}_5\text{CN}$	$4.53 \times 10^8$
$\text{C}_6\text{H}_5\text{NHCOCH}_3$	$6.70 \times 10^8$
$\text{C}_6\text{H}_5\text{CH}_2\text{COONa}$	$7.70 \times 10^8$
$\text{C}_6\text{H}_5\text{COONa}$	$8.70 \times 10^8$
$\text{C}_6\text{H}_5\text{COCH}_3$	$1.26 \times 10^9$
$\text{C}_6\text{H}_5\text{NO}_2$	$1.68 \times 10^9$
$\text{C}_6\text{H}_5\text{NH}_2$	$1.76 \times 10^9$
$\text{C}_6\text{H}_5\text{OH}$	$4.20 \times 10^9$

A quantitative treatment of the results is shown in Fig. 1, where  $\log k_{\text{H} + \text{PhX}}$  is plotted against Hammett's  $\sigma$  values (taken from refs. 8 and 9). Both  $\sigma_m$  and  $\sigma_p$  values were taken for substituents having a deactivating effect, but only the  $\sigma_p$  values were taken for the other substituents. (The attack by hydrogen atoms on aromatic compounds is electrophilic in nature, thus their attack on the *meta* position of aromatic compounds carrying *ortho-para* directing substituents can be neglected.) A  $\sigma$  value similar to that of  $\text{CH}_2\text{CH}_3$  and  $\text{CH}_2\text{CH}_2\text{COO}^-$  groups was taken for the  $\text{CH}_2\text{COO}^-$  group. Neglecting the value for nitrobenzene, which is unexpectedly high, as explained before, a straight line could be drawn with a slope =  $-0.7$ , which demonstrates the electrophilic nature of the attack of hydrogen atoms on aromatic compounds. The absolute value of  $\rho = -0.7$  is higher than that observed for the reaction of hydroxyl radicals ( $\rho = -0.41$ ) (ref. 2). This is in accordance with the relatively lower reactivity of hydrogen atoms, which makes them more selective.

The electrophilic behaviour of hydrogen atoms in the  $\text{H} + \text{PhX}$  reaction is not surprising, since a higher electron density on the aromatic ring promotes the formation of the new C—H bond and stabilizes the  $\text{PhXH}$  radical formed.

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