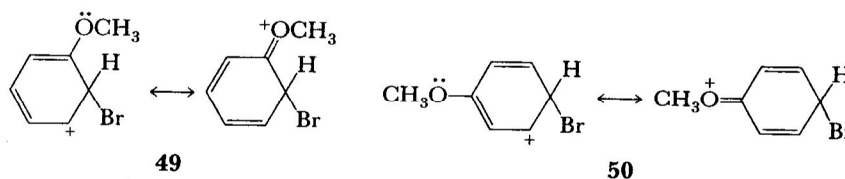


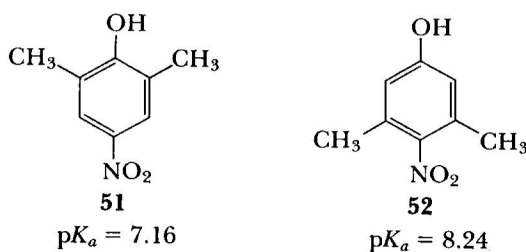
**Figure 2.7** Bromination of monosubstituted benzenes in acetic acid. In (a) data are plotted against  $\sigma$ ; in (b) against  $\sigma^+$ . Reprinted with permission from Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979. Copyright 1958 American Chemical Society.

Figure 2.7, in which  $\sigma$  constants are plotted against  $\log k/k_0$  for the bromination of monosubstituted benzenes, shows an example of the usefulness of these new parameters. As can be seen from Structures 49 and 50—which are representations of the intermediates in the ortho and para bromination of anisole—substituents electron-donating by resonance ortho or para to the entering bromine can stabilize the positive charge in the intermediate and therefore also in the transition state by through-resonance.



In Figure 2.7(a), in which Hammett  $\sigma$  constants are plotted, there is a scatter of points; but in Figure 2.7(b)  $\sigma^+$  parameters are used and a straight line is obtained.

Sometimes substituents that are able to undergo through-resonance with a reaction site are prohibited from doing so by steric effects. For example, 51 is a stronger acid than 52 because in 52 the methyl groups force the  $\text{NO}_2$  group out of the plane of the benzene ring and thus, although still allowing an inductive effect cut down on the resonance effect. This phenomenon is called *steric inhibition of resonance*.<sup>42</sup>



<sup>42</sup>Wheland, G. W. "The Theory of Resonance"; Wiley: New York, 1944, p. 195.