Aryl Rearrangements in Ions and the Hammett Function

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THE recent increased interest[1] in the study of aryl migration in ions by correlation of the effects of substituents with the Hammett (σ) or Brown (σ^+) function has centred mainly on the use of a relationship developed by McLafferty,[2] in which the intensities of ions at low electron-beam voltages are compared. This method has given some encouraging linear correlations, although others are very poor.[1] A recent publication by Williams[3] has drawn attention to at least one potentially serious source of error in McLafferty's method which, being somewhat subjective, is also open to interpretative errors. For some time we have used a basic principle of kinetic work that, knowing the activation energy of a reaction, a quantitative correlation with σ may be sought. Although accurate measurement of these energies is not at present particularly easy we suggest that they should be measured before Hammett-type correlations are attempted. Some workers[4] have correlated ionisation or appearance potentials with σ or σ^+, but few measurements of the difference between these potentials (a measure of the energy of activation for a reaction) have appeared.[5] The correlation of ionisation potentials with σ is in accordance with the removal of an electron from the upper occupied molecular orbital of the π-system; since the substituents in the phenyl ring will affect the energy of the upper orbital in proportion to their degree of interaction with the ring (measured by σ) such a correlation should be observed. In fact there is an equally good correlation for simple benzene compounds between u.v. absorption maxima and σ.[6]

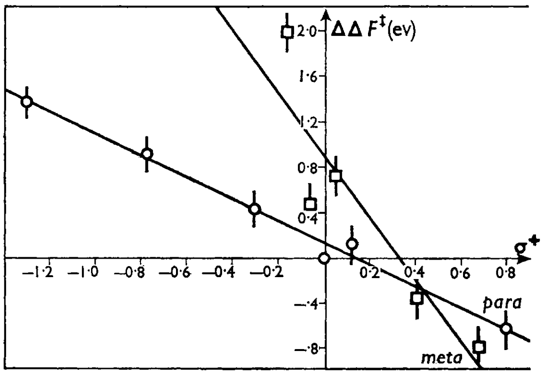
The slope of the σ or σ^+ functions can give information on the nature of the reaction occurring. Reactions involving a highly-charged centre may be expected to have a large slope (ρ) while those at a radical, or slightly-charged centre, much smaller slopes, generally about unity.[7] The correlations with σ or σ^+ generally have small positive slopes, as for example with the butyrophenones (I)[1] which show a good linear correlation (ρ *ca.* 1·3). As the McLafferty rearrangement is characterised by reaction though a radical centre, the small value of ρ is in accordance with the generally accepted mechanism,[8] especially in the absence of solvation.

Remarkably, most of the published Hammett correlations generally include *para*-substituents and, where *meta*-substituents are included, there is often poor linear correlation. This property is a characteristic of excited-state reactions of benzenoid compounds in which good correlations are observed with *para*-substituents while *meta*-substituents tend to fall on a separate line, due to increased resonance participation in the excited state.[9]

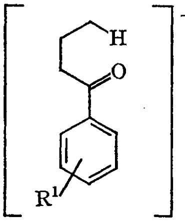
TABLE

m-Substituent	Me	Cl	NO_2	OMe	NH_2
σ_R (ref. 10)	$-0·05$	$+0·47$	$+0·63$	$+0·23$	$+0·10$
α^* (ref. 11)	1·0	0·5	0·6	0·9	1·3

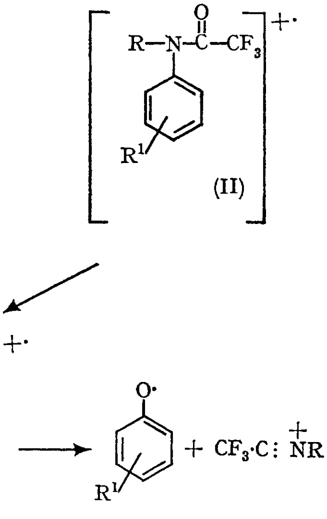
We have measured the energy of activation for the rearrangement of trifluoroamides (II) to the trifluoroiminoethers (III); the rearrangement product requires little energy (*ca.* 0·05 eV as measured) to fragment. The results were correlated with σ^+ (Figure) and show a good linear plot for the *para*- but not the *meta*-substituents which fall on a different line. The two slopes (16·90 and 27·9) derived from the free-energy plot are large and in keeping with reaction at a charged centre, as suggested earlier.[10] Separate plots of the ionisation potentials of the amides (II) and the appearance potentials of the fragment ion showed similar linear correlations with σ^+, the *meta*- and *para*-substituents falling on different lines. A plot of $\log (Z/Z_0)^1$ against σ or σ^+ showed no correlation whatsoever. Using a Taft treatment[11] to separate inductive and resonance effects, and assuming the *para*-substituents give a reasonable estimate of the ground-state reaction, the enhanced resonance effect (α^*) of the *meta*- compared to the *para*-substituents can be calculated (Table). The results show enhanced participation of the *meta*-substituents as would be observed for an electronically excited-state process, with electron-donating substituents increasing the activation energy and electron-withdrawing ones decreasing it, with respect to the σ correlation. We suggest therefore that this reaction proceeds through an electronically-excited state and, further, that where good Hammett correlations are found for *para*- but not *meta*-substituents, those reactions may proceed also through an excited state.



FIGURE



(I)



(II)

(III)

Measurements of the energy of activation for reactions involving aryl rings may, therefore, give good correlations with the σ or σ^+ function and, from the slopes of these lines, information may be obtained on both the reaction centre and the electronic state.

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