

Preliminary communication

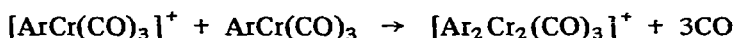
A Hammett correlation in the ion-molecule reactions of arenechromium tricarbonyl derivatives

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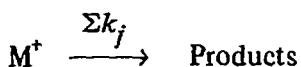
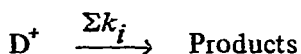
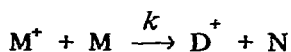
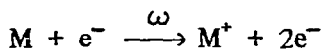
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Recent work has demonstrated that bimolecular ion-molecule reactions occur readily in a mass spectrometer with many organometallic compounds¹⁻⁴. We have studied the substituent effects on such reactions using the arenechromium tricarbonyl system:



Generalising the above reaction such that the parent arenechromium tricarbonyl is represented by M, the dinuclear cation by D⁺ and a neutral fragment by N we may, neglecting losses due to instrumental factors, write the following equations:



Applying the stationary state approximation to both M⁺ and D⁺ yields the equation:

$$[\text{D}^+] = \frac{k \Sigma k_j}{\omega \Sigma k_i} [\text{M}^+]^2 = k' [\text{M}^+]^2$$

Assuming that the substituent has a negligible effect on the overall decomposition

of M^+ and $D^+{}^5$ at 50 eV a plot of the squared intensity of M^+ against the intensity of D^+ yields a composite rate constant, k' , including terms related to the ionisation cross-section of M .

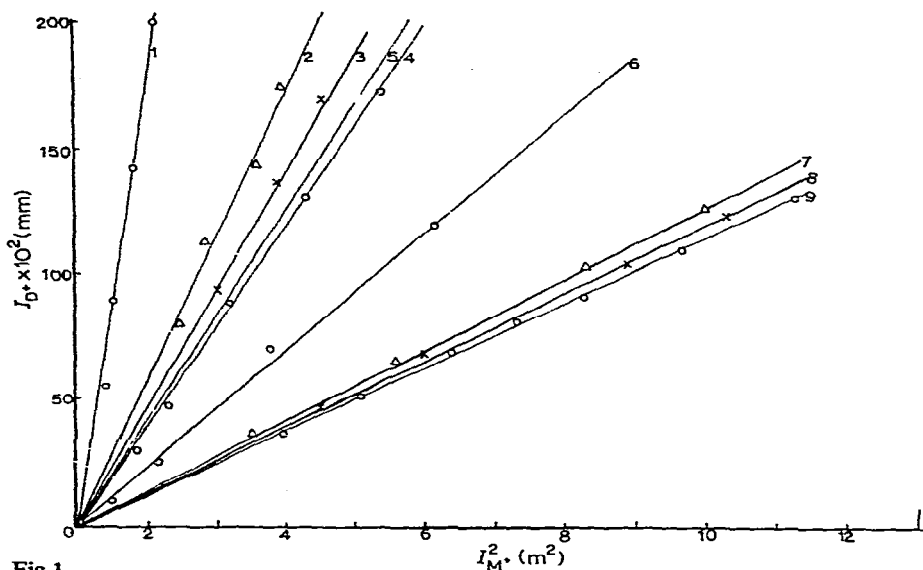


Fig.1.

Figure 1 shows these measured intensities of the two ions plotted for a series of compounds at varying pressure. Figure 2 demonstrates the excellent correlation obtained by applying the Hammett treatment to these results and plotting $\log(k'/k'_0)$ against the σ_p value for the ring substituent*.

Since this is the first reported correlation between the rate of a bimolecular reaction and substituent effects in mass spectrometry, caution must be employed in the interpretation of the results. If, however, comparison exists with solution kinetics, then the fact that the ρ value for the reaction is both negative and reasonably large in magnitude strongly suggests that the reaction is facilitated by electron donation at the site of attack by the cation and is sensitive to the electrical effects of the substituent. It should be noted, however, that both the ion and the neutral molecule are susceptible to substituent effects, and that, furthermore, the stabilisations of the initial, transition and final states almost certainly involve participation by the substituent.

Further work is currently in progress to clarify this correlation in terms of a more definite rate constant and to eliminate the factors mentioned above.

* Where more than one substituent is present in the benzene ring the σ_p value is calculated on the additivity principle.

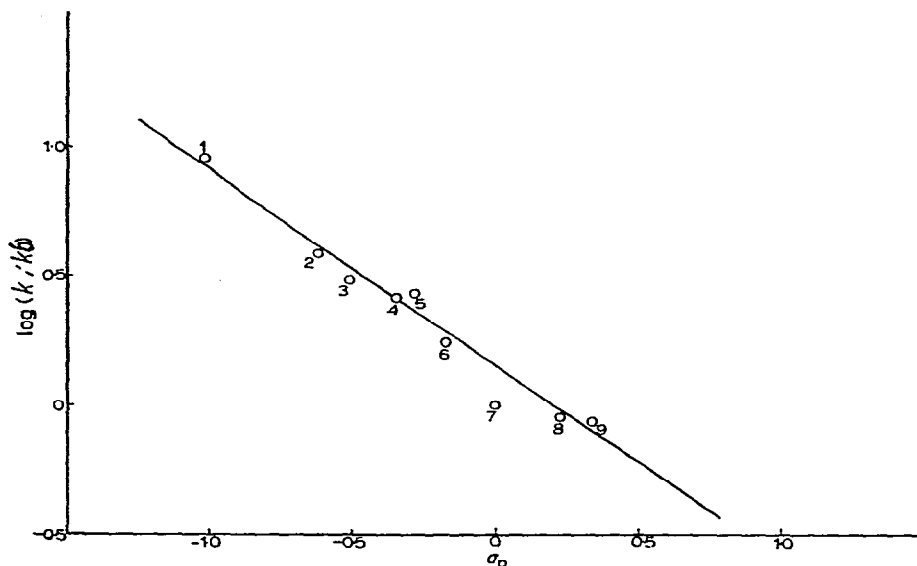


Fig. 2. Hammett plot of $\log(k/k_0)$ vs. σ_p .

EXPERIMENTAL

The mass spectra were measured with an AEI MS 12 instrument with an ionising potential of 50 eV, a trap current of 100 μ A. and an ion-accelerating voltage of 8 kV. The samples were introduced into the mass spectrometer by means of a direct insertion probe at an ion chamber temperature of 120°.

REFERENCES

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