

Crampton M R. Meisenheimer complexes.
Advan. Phys. Organ. Chem. 7:211-57, 1969.
[Department of Chemistry, University of Durham, England]

The article reviews the chemistry of σ -adducts formed by the covalent addition of bases and anionic nucleophiles to aromatic molecules activated by electron-withdrawing groups. Spectroscopic evidence, mainly ^1H nuclear magnetic resonance, for the structures of the adducts is presented, and the results of equilibrium and kinetic studies are discussed. [The *SCI*® indicates that this paper has been cited in over 255 publications.]

M.R. Crampton
Department of Chemistry
University of Durham
Durham DH1 3LE
England

May 10, 1988

The intense colours produced by the addition of bases to solutions of strongly activated aromatic compounds had fascinated chemists since the nineteenth century. Likely modes of interaction were thought to include electron transfer, proton abstraction (of either ring or side-chain protons), and covalent addition of base at a ring-carbon atom. An excellent method for differentiating these possibilities, namely, nuclear magnetic resonance (NMR) spectroscopy, became available in the 1960s. My research in the area started when I was a post-graduate student at King's College, London, working with Victor Gold. A postdoctoral worker had constructed an NMR spectrometer (28 MHz), and I spent much of my time in the basement, where the instrument was located, struggling to obtain spectra. It was rumoured that a peak appeared whenever an underground train arrived at the nearby Aldwych station! Obtaining sufficient solubility was a problem, and a big step forward was made when I found that dimethyl sulphoxide was an effective solvent for studying the interactions.

Later, at the University of Durham, access to a commercial NMR spectrometer made the determination of the structures more routine, and my work accelerated. I also became interested in the effects of structure on the kinetics and equilibria of adduct formation, and the emphasis shifted in this direction.

By 1969 there was enough information from my work and that of others for a review. The spectroscopic studies had shown several interesting phenomena including isomeric addition. For example, methoxide attack on 2,4,6-trinitroanisole resulted in kinetically controlled reaction at the 3-position followed by isomerisation to the thermodynamically preferred 1,1-dimethoxy adduct. It had also been shown that reactions of 2,4,6-trinitroaniline and its *N*-substituted derivatives may result in base addition of the 3-position in competition with transfer of an amino-proton. There were also some interesting solvent effects. Addition of dipolar aprotic solvents to hydroxylic solvents greatly enhanced the stabilities of 1:1 adducts. However, in water multicharged adducts were common, resulting from addition of two or more anionic nucleophiles to one molecule of the aromatic compound. A good example here was the 1:2 picrate:sulphate adduct, which carries five negative charges and demonstrates the effectiveness of water at solvating localised negative charge.

This was the first review of an area that was expanding rapidly, hence the high citation rate. There subsequently have been hundreds of reports of adducts formed from both aromatic and heteroaromatic molecules.¹⁻⁵ The subject is also relevant to nucleophilic aromatic substitution where reaction by the $S_{\text{N}}\text{Ar}$ mechanism involves σ -bonded intermediates, which expel a nucleofuge. The first steps in the $S_{\text{N}}(\text{ANRORC})$ mechanism involve adduct formation and ring cleavage. σ -Adducts are also formed as intermediates during "vicarious substitution" of hydrogen by carbanions. A common feature here, which may explain the formation of unexpected products, is that nucleophilic attack at ring-carbons carrying hydrogen is often faster than at substituted ring positions.

1. Bunce E, Crampton M R, Strauss M J & Terrier F. *Electron deficient aromatic- and heteroaromatic-base interactions: the chemistry of anionic σ -complexes*. Amsterdam, The Netherlands: Elsevier, 1984. 499 p. (Cited 20 times.)
2. Cox J P L, Crampton M R & Wight P. Comparison of the intrinsic reactivities of carbon and oxygen nucleophiles at the 1,3,5-trinitro-substituted aromatic ring. *J. Chem. Soc. Perkin Trans. II* (1):25-9, 1988.
3. Illuminati G & Stegel F. The formation of anionic σ -adducts from heteroaromatic compounds: structures, rates and equilibria. *Advan. Heterocycl. Chem.* 34:305-444, 1983. (Cited 85 times.)
4. Terrier F. Rate and equilibrium studies in Jackson-Meisenheimer complexes. *Chem. Rev.* 82:77-152, 1982. (Cited 90 times.)
5. Artamkina G A, Egorov M P & Beletskaya I P. Some aspects of anionic σ -complexes. *Chem. Rev.* 82:427-59, 1982. (Cited 45 times.)

15-2