

Hammett-type relationship for the cleavage of radical anions of aromatic chlorides and bromides

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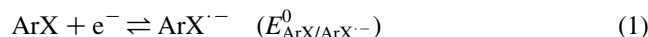
Abstract—A Hammett-type correlation pertaining to the cleavage of radical anions of aromatic halides has been formulated. The expression has been verified using the reaction series of aromatic chlorides and bromides. The correlation reveals the sensitive nature of the carbon–chlorine bond to the polar effects of the substituents in comparison to the carbon–bromine bond. The cleavage rate constants of radical anions of some aromatic chlorides and bromides have been deduced using the correlation. The standard potentials for formation of radical anions of aromatic chlorides and bromides have been estimated based on the correlation.

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1. Introduction

In the past few decades, the data collected on rates and equilibria of reactions have resulted in the formulation of a number of empirical relationships. The introduction of a substituent may alter the reactivity of a compound, for example, toluene is nitrated more rapidly than benzene and less rapidly than nitrobenzene. The structure–reactivity correlations are influenced by a number of factors, of which the polar effect is important. In this context, the Hammett equation¹ describes a linear correlation between the logarithms of rate or equilibrium constants of one reaction series with those of another reaction series which has been subjected to the same variations of substrate structure.

Aromatic molecules with a suitable leaving group (ArX) undergo electron transfer at the electrode surface and are capable of hosting transitorily the incoming electron in their π^* orbitals leading to the radical anions ($\text{ArX}^{\cdot-}$, reaction 1)



The radical anion $\text{ArX}^{\cdot-}$ readily undergoes decomposition to yield neutral radical Ar^{\cdot} and anion X^- (reaction 2) and the cleavage rate constant varies significantly with the nature of Ar and X. Reaction 1 is simply an outer-sphere

electron transfer where no bonds are broken or formed and the kinetics of the reaction can be analyzed using the Marcus–Hush theory of outer-sphere electron transfer.² Semi-empirical quantum mechanical calculations suggest that the cleavage of radical anion may be viewed as an intramolecular concerted electron transfer–bond breaking process.³ When the breaking bond begins stretching, the unpaired electron present in the π^* orbital of the ring is transferred to the σ^* orbital of the stretching bond simultaneous with its cleavage. The activation–driving force relationship for the intramolecular concerted electron transfer–bond breaking reactions is described by a relationship similar to the activation–driving force relationship of the Marcus–Hush model of outer-sphere electron transfer.⁴

The purpose of this paper is to report the formulation of a Hammett-type relationship for the reaction 2 and illustrate the correlation using the cleavage of radical anions of aromatic chlorides and bromides for which the first order cleavage rate constant data are available. As an application of the correlation, the cleavage rate constants of radical anions of some aromatic chlorides and bromides have been predicted. The standard potentials for formation of radical anions of aromatic chlorides and bromides, which are difficult (or impossible) to estimate in the case of irreversible voltammetric reductions, have also been deduced based on the correlation in conjunction with a previous report.⁴

2. Formulation of the relationship

The reduction of a large number of aromatic molecules

Keywords: Hammett equation; Aromatic halides; Reductive cleavage; Radical anion; Reaction constant; Cleavage rate constant; Standard potential.

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involving the cleavage of an aromatic carbon–heteroatom σ -bond leads to the formation of radical anions and the widely investigated family of compounds in this connection are aromatic halides. In the reductive cleavage reactions of aromatic halides, electron transfer and bond breaking are two distinct steps and the dissociation of radical anions may be viewed as an intramolecular dissociative electron transfer. According to the nature of the halogen and of the aromatic moiety, the life time of the radical anions spans between several minutes and nanoseconds.³ The polar effects of the substituents on the cleavage rate constant of the carbon–halogen bond should be equal for two different series of molecules having the same aromatic moieties but different halogens. Hence it follows that, the polar effects of the substituents on the cleavage of radical anions of aromatic halides can be studied, more suitably, using a Hammett-type relationship. Considering a reaction series of cleavage of radical anions of aromatic halides ($k_{\text{ArX}^-}^i$ as the first order cleavage rate constant of the i th radical anion) and another series with different halogen ($k_{\text{ArX}'^-}^i$ as the first order cleavage rate constant of the i th radical anion), a linear relationship between the logarithms of cleavage rate constants of the two series can be postulated as shown in Eq. 3.

$$\log k_{\text{ArX}^-}^i = \rho \log k_{\text{ArX}'^-}^i + c \quad (3)$$

where ρ is the slope and c , the intercept. For a special case where there is no substituent (i.e., hydrogen as the substituent) Eq. 3 may be rewritten as Eq. 4.

$$\log k_{\text{ArX}^-}^0 = \rho \log k_{\text{ArX}'^-}^0 + c \quad (4)$$

The constant c in the Eq. 3 can be eliminated by subtracting Eq. 4 from Eq. 3, to yield Eq. 5.

$$\log \frac{k_{\text{ArX}^-}^i}{k_{\text{ArX}^-}^0} = \rho \log \frac{k_{\text{ArX}'^-}^i}{k_{\text{ArX}'^-}^0} \quad (5)$$

Eq. 5 can be employed for any pair of series of aromatic halides. It is possible to relate any two series by correlating them to a standard series, for example to that of ArX'^- . Denoting $\log(k_{\text{ArX}'^-}^i/k_{\text{ArX}'^-}^0)$ values as σ , Eq. 5 becomes Eq. 6.

$$\log \frac{k_{\text{ArX}^-}^i}{k_{\text{ArX}^-}^0} = \rho \sigma \quad (6)$$

Eq. 6 is the Hammett-type relationship pertaining to the cleavage of radical anions of aromatic halides with ρ as the reaction constant and σ as the substituent constant. The reaction constant ρ is dependent on the carbon–halogen bond being cleaved and on the nature of the solvent, since the cleavage of ArX^- was found to be sensitive to the polarity of the solvent.⁶ The substituent constant σ represents a quantitative measure of the polar effects of the substituents relative to hydrogen.

For a given reaction series, the driving force of the cleavage of radical anions (reaction 2) is influenced by (a) the strength of the bond being cleaved, viz. the bond dissociation energy and (b) the standard potential of the radical anion ($E_{\text{ArX}^-}^0$). A linear relationship between the standard potential of the radical anions (which are a measure of the π^* orbital energy of the aromatic rings⁷) and

$\log k_{\text{ArX}^-}$ was reported and was rationalized invoking a linearized version of activation–driving force relationship which requires, for a given halogen, the assumption that the bond dissociation energy does not vary much with the aromatic moiety.⁴ Relationship 3, however, is more general and does not require the bond dissociation energy to be constant for each series. The influence of variation in bond dissociation energy on $\log k_{\text{ArX}^-}^i$ (lhs of Eq. 3) is proportionately compensated by the influence of variation in bond dissociation energy on $\log k_{\text{ArX}'^-}^i$ (rhs of Eq. 3), hence the polar effects of the substituents (which govern the π^* energy level of the ring where the unpaired electron is located) are reflected in the cleavage rate constants with high fidelity.

3. Cleavage of radical anions of aromatic chlorides and bromides

Aromatic chlorides and bromides follow a stepwise mechanism for reductive cleavage.⁸ Experimentally, direct and indirect electrochemical methods are used to determine the cleavage rate constants of radical anions, which span more than 10 orders of magnitude.³ For example, in the 10^{-1} – 10^7 s^{-1} range of k_{ArX^-} , direct electrochemical methods, viz. cyclic voltammetry or double potential step chronoamperometry is used. In the 10^6 – 10^9 s^{-1} range, redox catalysis which is an indirect electrochemical method, is used to estimate k_{ArX^-} . The rate constant data for the cleavage of radical anions of aromatic chlorides and bromides are available^{4,9} and can be employed to verify Eq. 6. Chlorobenzene and bromobenzene have been selected as the unsubstituted compounds of the respective series. The reaction series of chlorides and bromides have phenyl, 4-nitrophenyl, 4-benzoylphenyl, 3-acetylphenyl, 4-acetylphenyl, 1-naphthyl and 9-anthracenyl moieties. The cleavage rate constants of the chlorobenzene and bromobenzene were obtained using the respective standard potentials⁸ ($E_{\text{ArX}^-}^0$) and the linear variation of $\log k_{\text{ArX}^-}$ versus $E_{\text{ArX}^-}^0$ plots for the aromatic chlorides and

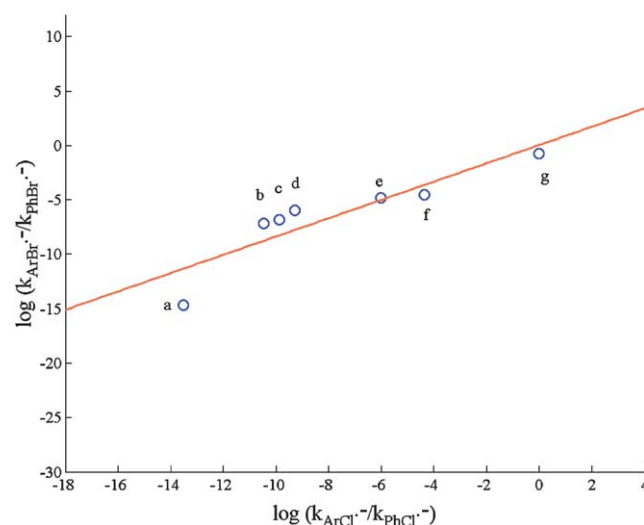


Figure 1. Correlation between $\log(k_{\text{ArBr}^-}/k_{\text{PhBr}^-})$ and $\log(k_{\text{ArCl}^-}/k_{\text{PhCl}^-})$ values for the aromatic moieties (a) 4-nitrophenyl, (b) 4-benzoylphenyl, (c) 9-anthracenyl, (d) 4-acetylphenyl, (e) 3-acetylphenyl, (f) 1-naphthyl and (g) phenyl.

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