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Chemometric analysis of disubstituent effects on the ^{13}C chemical shifts of the carboxyl carbons (δ_{CO}) of benzoic acids. A comparative study of the substituent effects on the strength of benzoic acids in apolar aprotic media

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The results of measurements of substituent induced chemical shifts of carboxyl carbons (δ_{CO}) of dichloro- and difluorobenzoic acids, including the monosubstituted ones with substituents at *meta-* and/or *ortho-*positions, in chloroform-d and strengths of these acids (log K) in chlorobenzene show an anomalous reverse trend between δ_{CO} and log K, while the electron density at carboxyl carbons should influence similarly both δ_{CO} and log K. A detailed *chemometric analysis* of comparison of disubstituent effects between δ_{CO} and log K on the basis of Fujita–Nishioka's multiparameter approach and assumption of additivity of substituent effects shows a dominance of the localized π-polarization mechanism relative to simple electrostatic effects upon δ_{CO}. Further, steric factors play a significant role in determining δ_{CO} whereas with respect to log K they were insignificant. The overall anomaly has been rationalized keeping in mind that, while log K is a gross measure of energy differences between the ionized and unionized forms of the acids, δ_{CO} is a very sensitive probe for determining changes in electron density at the carboxyl carbon of the unionized acid. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: ^{13}C substituent induced chemical shift; disubstituent effects; benzoic acid strength in apolar aprotic solvents; Fujita–Nishioka methodology; reverse inductive effect; localized π-polarization

INTRODUCTION

The electron density at the carboxyl carbon in a substituted benzoic acid molecule is the prime factor in determining its acid strength as well as its ^{13}C chemical shift (δ_{CO}). A comparative study of substituent effects together with a *chemometric analysis* of the data is of potential interest. The preferred medium for such an investigation is an apolar aprotic solvent ($\varepsilon_r < 15$, $\mu < 8.3 \times 10^{-30}$ Cm and E_N^T *ca* 0.0–0.3 as defined by Reichardt[1]) in which specific solute–solvent interactions due to solvent's own acidity/basicity are reduced to a minimum if not eliminated. Despite this, there have been no detailed reports of chemometric analysis of substituent effects on δ_{CO} of benzoic acid in an apolar aprotic solvent, although a few reports on studies evaluating the acid strength in toluene and benzene[2–4] have appeared. On the contrary, there are several reports of substituent effect analysis of δ_{CO} of benzoic acid measured in the dipolar electron-pair donor solvent DMSO-d_6 or its mixture with water containing varying amounts of HCl or NaOH.[5–7] Comparisons between mono- and disubstituent effects on δ_{CO} (DMSO-d_6) and acid strength (DMSO and H_2O) have been made.[6–8] An interesting revelation of these studies is the apparent 'reverse substituent effect' on δ_{CO} which was explained by localized π-polarization of carboxyl π-electrons. Acid strength and δ_{CO} values for substituted benzoic acids when measured in an apolar aprotic solvent would obviously be more intrinsic compared to those reported in DMSO or DMSO/H_2O. Recently the strengths of a series of difluoro- and dichlorobenzoic acids with the substituents at the *ortho-* and/or *meta-*positions, as well as the monosubstituted benzoic acids, in chlorobenzene ($\varepsilon_r = 5.62$, $\mu = 5.4 \times 10^{-30}$ Cm and $E_N^T = 0.188$),[1] an apolar aprotic solvent, have been measured in reference to the carbinol base of crystal violet dye, and disubstituent effects on the strengths of benzoic acids have been analyzed *chemometrically*.[9] In this article we wish to critically discuss our *chemometric results* of a comparison of disubstituent effects on the strength of benzoic acids in chlorobenzene and on its δ_{CO} measured in chloroform-d ($\varepsilon_r = 4.81$, $\mu = 3.8 \times 10^{-30}$ cm and $E_N^T = 0.259$),[1] another apolar aprotic solvent like chlorobenzene.

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