The Correlation of the Thermodynamic Carbon Acidity of Trisubstituted Methanes by σ_R^-

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Summary The correlation of the thermodynamic acidities of 1-substituted 3,3-dinitropropenes by the σ_R^- parameter indicates that the conjugate bases of these carbon acids exist in a planar conformation in solution.

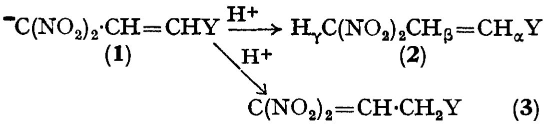
THE inability to correlate the kinetic or thermodynamic acidity of carbon acids bearing multiple conjugating electron-withdrawing substituents with linear free energy parameters has been often stated in the literature.[1–5] The failure of these attempts has generally been attributed to steric inhibition of the resonance interaction of the substituents.

We report the first correlation of the thermodynamic acidity of a series of carbon acids bearing three conjugating substituents by the Hammett σ_R^- parameter. Thus, the pK_a's of the conjugate acids of the 2-Y-vinyldinitromethide ion (**1**; Y = CO_2Me, CN, SO_2Me, and NO_2) yield an excellent correlation with the expanded Hammett equation

$$\log K = \sigma_I\rho_I + \sigma_R^-\rho_R + \log K_0 \qquad (1)$$

where σ_R^- is the parameter commonly used for electron-rich reaction sites.

The carbanions (**1**) have two sites for protonation; C-3 which produces the 1-Y-3,3-dinitropropene, (**2**) or C-1 to yield a 3-Y-1,1-dinitropropene, (**3**). Protonation of the carbanions (**1**) in chloroform, benzene, or dioxan with dry hydrogen chloride yields the conjugate acid whose n.m.r. spectrum is either an ABC or an ABX type exhibiting



$$\begin{tikzcd} \underset{(\mathbf{1})}{{}^{-}C(NO_2)_2\cdot CH{=}CHY} \arrow[r, "H^+"] \arrow[dr, "H^+"] & \underset{(\mathbf{2})}{H_\gamma C(NO_2)_2CH_\beta{=}CH_\alpha Y} \\ & C(NO_2)_2{=}CH\cdot CH_2Y \quad (\mathbf{3}) \end{tikzcd}$$

in chloroform, for example, a doublet for H_γ in the range δ 6·60—6·90 p.p.m., $J_{\beta\gamma}$ 9·0—9·5 Hz and for H_α in the range δ 6·13—7·60 p.p.m., $J_{\alpha\beta}$ 13·5—16·2 Hz. A four-line multiplet in the range δ 6·98—7·60 p.p.m. was observed for H_β. On the basis of these spectra, we have selected (**2**), the *trans*-1-Y-3,3-dinitropropene, as the structure of the conjugate acids of the carbanions (**1**). Deuteriation of (**1**) under identical conditions afforded the γ-D derivative (**2**). The n.m.r. spectra of the γ-D derivatives offered no evidence for α,γ-H,D exchange. Therefore, equilibrium between (**2**) and (**3**) can be ruled out.

The conjugate acids (**2**) readily added methanol to the double bond to form a β-methoxy-derivative. Therefore, pK_a's were calculated from extrapolated zero-time values of the carbanion concentration obtained from pseudo-first-order rate plots of the log of the carbanion concentration against time for the reaction with methanol at various methyloxonium chloride concentrations. The pK_a's are given in the Table together with the values of σ_I and σ_R^-[6,7] used in the correlation. A least-squares fit of the data in the Table to equation 1 gave $\rho_I = 1{\cdot}66$, $\rho_R = 7{\cdot}95$, and log $K_0 = -6{\cdot}22$. These parameters reproduced the values of log K in the Table with an average deviation of $\pm 0{\cdot}04$ pK_a units.

*p*K$_a$*'s of* 1-Y-3,3-*dinitropropene in methanol at* 15°, $\mu = 0{\cdot}1$

Y	pK_a	σ_I	σ_R^-
CO_2Me	3·14 ± 0·01	0·32	0·32
SO_2Me	1·65 ± 0·04	0·59	0·46
CN	1·93 ± 0·02	0·59	0·41
NO_2	0·07 ± 0·08	0·63	0·64

The ability of a linear free energy equation utilizing the σ_R^- parameter to correlate the pK_a's of the 2-Y-vinyldinitromethanes indicates that the conjugate bases exist in a planar conformation in solution with the charge *on* the carbanion delocalized by all three substituents. This conclusion is further supported by the following observations. These carbanions are extremely poor nucleophiles and do not add to $\alpha\beta$-unsaturated systems as does trinitromethide ion. Trinitromethane is 2000 times weaker an acid than the vinylogue (**2**; Y = NO_2). In the solid state, crystal-structure measurements have shown 2-carbamylvinyldinitromethide ion to be planar.[8] Finally, the value of $\rho_R = 7{\cdot}95$ found in this correlation is about one-fourth that of ρ_R (*ca.* 30) for the acidity of methanes with one conjugating substituent.[2] The much smaller ρ_R value for this correlation would be expected if the resonance effect of YCH=CH– upon the stability of the carbanions (**1**) is damped by a constant amount of charge delocalization by planar α-nitro-substituents in these substituted dinitromethide ions.

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