

ON THE "NON-ADDITIVITY" OF pK VALUES OF POLINITROMETHANES

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Abstract—The effect of nitro and cyano substituents on the acidity of methane is dissected into intrinsic and solvation components with the CNDO/2 molecular orbital method.

The thermodynamic acidity of a C-H bond in methane is substantially enhanced by replacement of the other H atoms by nitro groups. The increase in acidity, as measured by pK values in various solvent systems, is not proportional to the number of nitro groups present, a dampening effect being observed upon substitution. Cyano substituents also increase the acidity of methane, but do so in a roughly proportional manner. As a consequence of these facts, even though nitromethane is more acidic in water than methyl nitrile by 14 pK units, nitroform is less acidic than cyanoform by some 5 pK units.¹ This has been attributed to the fact that while cyanoform anion is in the crystalline state planar or very nearly planar,² the NO₂ groups of nitroform anion do not share a common plane.^{3,4} It has been suggested that the nitro groups of some dinitromethyl anions do not share a common plane.⁵

It is of interest however to assess the relative importance of intrinsic effects within both hydrocarbons and anions as well as of solvation effects. To this purpose, a molecular orbital study of the acidity of nitro and cyano methanes both in the gas phase and in aqueous solution has been undertaken.

Methods and models

We have employed in these studies the CNDO/2 method⁶ with geometry optimization⁷ since it has been applied with success to carbanions.^{8,9} In addition, in the case of nitromethanes the CNDO/2 method has been shown¹⁰ to compare favourably with the more sophisticated *ab initio* method employing an STO-3G basis set.¹¹ We have assumed these correlations to apply as well as to cyanomethanes.

Solvation has been studied by considering super-

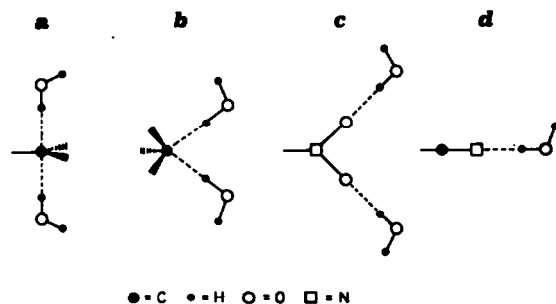


Fig. 1. Models of solvation of (a) a planar carbanionic center, (b) a pyramidal carbanionic center, (c) a nitro substituent, and (d) a cyano substituent.

molecules composed of an organic moiety and a varying number of H₂O molecules H-bonded to it at suitable places.^{8,12,13} The results may be directly compared with experiment since the compounds considered are acidic enough to be studied in aqueous solutions.

The models used for solvated species are depicted in Fig. 1 and are similar to those used in previous work on acidities of substituted methanes.⁸ The solvation energy of species X, E_s, is given by eqn (4) of the following thermodynamic cycle:



The energy difference E₁ is directly obtained with the MO method and E₃ may be identified with the experimentally available heat of evaporation of H₂O (10.5 kcal/mol).¹⁴ E₂ is difficult to assess but is in principle of opposite sign and same order of magnitude of E₃ since it involves mainly solvation of H₂O molecules. Since E₁ > E₃, we have taken E_t = E₁.

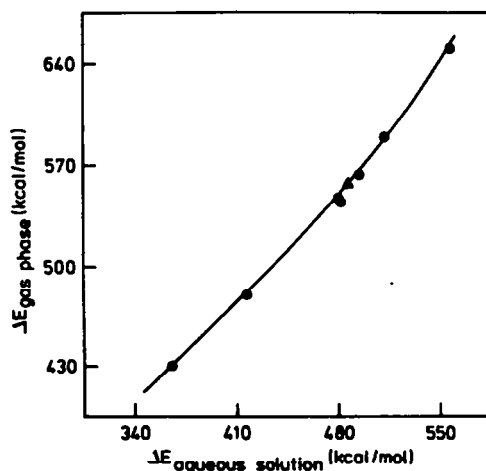


Fig. 2. Calculated acidities in the gas phase and in aqueous solution. The triangle represents the values of CH₂CHO, taken from Ref. 8.

RESULTS AND DISCUSSION

The reliability of the data calculated may be assessed by comparison with experimental acidity values. In the absence of sufficient gas phase measurements the values calculated for isolated species may be compared with pK values determined in DMSO solutions. These latter have been shown to refer to ionized carbanions¹⁵ and they parallel in some instances gas phase measurements within families of related compounds.¹⁶ The values calculated for solvated species may be compared directly with pK values determined in aqueous solution. The data in Table 1 show that for each series the calculated acidities parallel the experimental ones.

Gas phase acidities have been compared with solution acidities.²²⁻²⁶ In some cases linear correlations are found within a series of similar acids,²²⁻²⁴ while in others inversion of acidity orders are encountered.^{22,25,26} Figure 2 compares acidity values calculated for isolated species and for solvated ones. The result is a shallow curve† whose slope decreases with increasing acidity. This behaviour reflects the fact that when the charge in the anions is intrinsically better stabilized by additional substituents, the benefits of solvation in them decrease and become closer to the values in the parent hydrocarbons. As a corollary, solvation effects tend to compress the acidity scale at the higher end of it, the well-known levelling effect of polar solvents.

†Within a narrow range, this curve may be approximated by a straight line.⁹

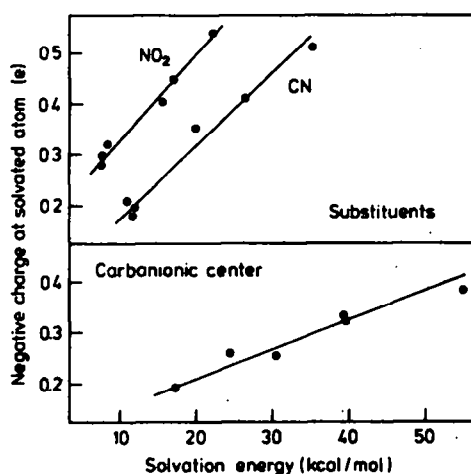


Fig. 3. Charges and solvation energies at different centers.

Solvation energies are larger for anions than for hydrocarbons (Table 2) and are found to correlate with the charge on the atom being solvated (Fig. 3). It is interesting to note that the points in Fig. 3 fall on three different lines which correspond to the three different atoms being solvated. For a given charge, solvation follows the order $C > N > O$. This order is also found in the gas phase basicities of compounds possessing these atoms as basic centers.²⁷

Table 1. Calculated and experimental acidities of nitro and cyano methanes

Compound	E(gas phase)†	pK(DMSO)	E(H ₂ O)‡	pK(H ₂ O)
CH ₄	649.5§	—	558.2§	—
CH ₃ NO ₂	547.4	16.95¶, 17.2¶	480.5	10.24¶
CH ₂ (NO ₂) ₂	479.8	7.14††	418.5	3.57¶¶
CH(NO ₂) ₃	4 ^{***} .0	-1.0‡‡	365.2	0.17¶¶¶
CH ₃ CN	590.2	31.3‡	511.9	25 ^{§§}
CH ₂ (CN) ₂	563.3	11.1	495.0	12 ^{¶¶}
CH(CN) ₃	544.8	—	480.8	-5 ^{¶¶}

†E(R⁻)-E(RH), in kcal/mol.

‡E(R⁻·nH₂O)-E(RH·[n-2]H₂O)-2E(H₂O), in kcal/mol. See text for details.

§Ref. 8.

¶Ref. 17.

¶¶Ref. 18.

††Extrapolated from the value for 1,1-dinitroethane based on the effect of methyl substitution upon nitromethane.¹⁷

‡‡This value was determined in Ref. 17 as <-1.0. However, judging from the differences in pK values in DMSO and in DMFA reported¹⁷ it can safely be assumed to lie close to -1.0.

§§Ref. 19.

¶¶¶Ref. 20.

¶¶¶Ref. 21.

Table 2. Solvation data†

Substituents	Hydrocarbon	Anion	
	At substituent‡	At substituent‡	At central carbon
NO ₂	16.9	44.5	39.3
(NO ₂) ₂	15.7	34.2	24.3
(NO ₂) ₃	15.6	31.8	17.3
CN	11.8	35.3	54.8
(CN) ₂	11.9	26.3	39.4
(CN) ₃	10.8	22.0	30.4

†In kcal/mol.

‡Values "per substituent".

As the number of substituents in the anions increases the solvation energy per substituent becomes smaller and also solvation at the substituent becomes progressively more important relative to solvation at the carbanionic center. These are consequences of the flux of charge away from the central C atom towards the substituents as these latter increase in number. The large contribution of solvation at the central C atom still present in the trisubstituted methanes reflects the larger contribution of field (or inductive) over resonance effects in nitro and cyano groups.²⁸⁻³⁰

The data on the effect of successive substitution on methane has been collected in Table 3. Several trends may be noted.

Deviations from additivity are present in the energies of hydrocarbons. These effects have been noted in cyanomethanes and have been rationalized by comparison of the hyperconjugative interaction of a C-H relative to a C-CN bond with the π system of other cyano groups in the molecules.^{31,32} The non additive effects in nitromethanes may be rationalized in the same way since nitro groups have qualitatively similar σ and π electron withdrawing properties than cyano groups.

Deviations in anions are more pronounced due to the larger interaction between the substituents. They may be rationalized in terms of O-O repulsions between neighbouring nitro groups. Thus, the Coulomb interactions between the closest O atoms on adjacent nitro groups (taken as point charges of the magnitude given by the CNDO/2 calculation) accounts for more than half the deviation from additivity† and also correlates with it satisfactorily (Fig. 4). At zero Coulomb interaction (i.e. only one nitro group present), the deviation from additivity extrapolates to a number not far from zero, in consistency with the assumptions of the model.

Solvent effects on the hydrocarbons are almost additive, presumably because the substituents are to a large extent independent (see above however) and form H-bonds of similar strengths with solvent. This is not the case in anions where strong and varying π interactions prevail. Overall, solvation effects are roughly half as important as intrinsic effects on accounting for non-additive behaviour of acidities (columns ΣG and ΣS).

The last column in Table 3 shows that the sum of

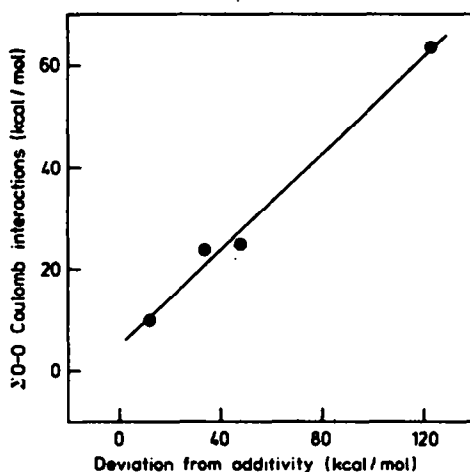


Fig. 4. Test of the model for deviations from additivity in nitro compounds.

intrinsic and solvent effects on non-additive behaviour of acidities is substantially larger for nitro than for cyano compounds, in agreement with experimental data.

CONCLUSIONS

CNDO/2 calculations have been shown to account for the non-additive behaviour of acidities of nitromethanes and for the additive behaviour of acidities of cyanomethanes. In the former case, non-additivity may be attributed to an extent of about two thirds to intrinsic effects and one third to solvation effects; deviations are more marked in the anions where O-O repulsions between adjacent nitro groups play a dominant role in the isolated species. In the latter case, intrinsic and solvation effects are comparatively small and also more marked in the anions.

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Table 3. Deviations from additivity†

Change in substitution		Intrinsic effects			Solvation effects			Total $\Sigma G + S$
		G_{RH}	G_{R^-}	ΣG	S_{RH}	S_{R^-}	ΣS	
Nitro groups	0-1‡	0	0	0	0	0	0	0
	1-2	12.0	47.5	35.5	-2.5	16.3	18.8	54.3
	2-3	21.4	75.2	53.8	-1.3	27.6	28.9	82.7
Cyano groups	0-1‡	0	0	0	0	0	0	0
	1-2	17.6	14.8	-2.8	0.1	3.1	3.0	0.2
	2-3	12.4	28.4	15.0	-3.1	5.6	8.7	23.7

†Values in kcal/mol. A positive number implies that the additional substituent decreases the energy of the system by that amount less than that expected on the basis of the first substitution. G refers to gas phase, S to solution. RH to hydrocarbons and R^- to anions.

‡The effect of the first substitution is taken as reference for each series.

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