Novel Method for the Determination of Acidities of Weak Carbon Acids

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Summary ^{13}C N.m.r. spin–lattice relaxation data obtained from solutions containing paramagnetic relaxation reagents, such as trisacetylacetonatochromium, can be used for the determination of hydrogen-bond donor acidities of weak carbon acids.

The thermodynamic, kinetic, as well as hydrogen-bond donor acidities of weak carbon acids are of great interest to organic chemists,[1–4] but these acidities are not as easily and precisely accessible as those of oxygen and nitrogen acids.[1–4]

This communication reports ^{13}C n.m.r. spin–lattice relaxation determination of the relative acid strengths of representative hydrocarbons in CCl_4 solutions *via* association with the paramagnetic relaxation reagent, tris(acetylacetonato)-chromium(III) [Cr(acac)$_3$]. It has been shown by ^{13}C n.m.r. spectroscopy, among other methods, that Cr(acac)$_3$ is a good proton acceptor for moderately acidic protons: *e.g.* acetylenic protons[5] and the OH protons in alcohols[5] and phenols.[6] This kind of interaction can be conveniently monitored by the measurement of ^{13}C n.m.r. electron–nuclear relaxation times, T_1^e values.[5] In a mixed solvent system, any preferential solvation by one component of the solution towards the paramagnetic chelate causes the T_1^e values for this component to shorten compared with the T_1^e values of the 'noninteracting' compound. Also, within the interacting molecule the T_1^e values of the carbon atoms closer to the site of complexation with Cr(acac)$_3$ (more acidic in our case) are shorter than the T_1^e values for the remote carbon atoms.

We show here that even a very weak hydrogen bond interaction between substrate and Cr(acac)$_3$ can be probed by spin–lattice relaxation measurements. The Table presents the relative electron–nuclear relaxation rates, $\alpha' = 1/T_1^e$, for the acidic carbon atoms of interest in the compounds studied with reference to the relaxation rates of the 'inert' standards hexadecane (average $1/T_1^e$ values over the 16 carbon atoms) and CCl_4 (α'_1 and α'_2, respectively) in 0·8 M solutions of the compounds in CCl_4 containing 1 M hexadecane and 0·05 M Cr(acac)$_3$.

The two α' scales are nearly proportional to one another with a linear regression coefficient $r = 0{\cdot}998$. These two α' indices are a measure of relative hydrogen-bond donor (HBD) acidities.[4] The only other factor which may contribute to the observed α' relaxation rates is the steric effect.[5] With the exception of phenylacetylene, the hydrocarbons studied here do not differ appreciably in structure.

In the Figure the logarithm of the relative HBD acidity strengths of hydrocarbons in CCl_4 (α'_1-scale) are compared with the pK_a values of the MSAD scale[1] of acidities.† It is

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† The data point for indene is excluded from the correlation. While in all other cases the anion derived from the hydrocarbon has the same number of carbon atoms for attachment of a proton as the number of carbon atoms with dissociable protons in the acid, the indenyl anion has twice as many points of attachments as there are 'dissociable' carbon atoms in indene. This influences the pK_a but not the α-indices. The point for indene should lie below the line in the Figure, as is indeed the case.

Table The α'-scale of hydrogen-bond donor acidities [a]

	Compound	α'_1	α'_2	pK_a (ref 1)
(1)	Phenylacetylene (CH)	3 59	2 46	18 5
(2)	Fluorene (CH_2)	2 45	1 79	23
(3)	Indene (CH_2)	2 13	1 53	20
(4)	Diphenylmethane (CH_2)	1 99	1 38	33
(5)	Toluene (CH_3)	1 65	1 16	35
(6)	Indane (α CH_2)	1 64	1 14	?
(7)	Benzene	1 55	1 09	37
(8)	Toluene (=CH)	1 54	1 09	?
(9)	Indane (β CH_2)	1 45	1 00	?
(10)	Cyclohexane	1 12	0 77	45
(11)	Hexadecane	1 00	0 69	?
(12)	Hexafluorobenzene	0 97	0 67	—

[a] $\alpha' = T_1^e$ (reference compd)/T_1^e (hydrocarbon) $1/T_1^e$ is the adjusted relaxation rate after separation of small diamagnetic component ($1/T_1{}^{dia}$) from the observed relaxation rate in the $Cr(acac)_3$ containing solutions 39 °C 22 63 MHz, Bruker CXP 100 IRFT for T_1's in the paramagentic solutions FIRFT for the degassed diamagnetic solutions Internal T_1 accuracy 2%

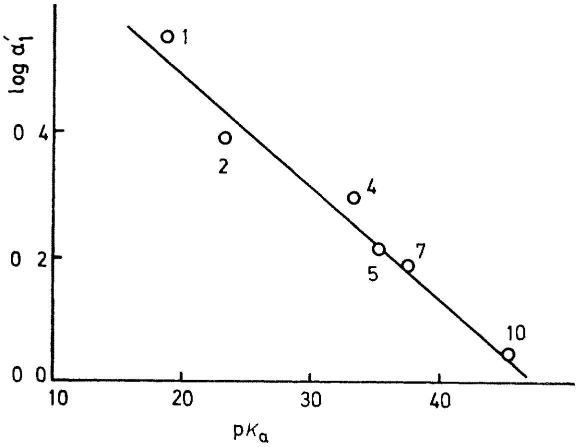

Figure Plot of the logarithm of α_1 indices against the pK_a values Numbering of the compounds as in the Table correlation coefficient, r 0 982

apparent that the HBD acidities of hydrocarbons, as measured by association with $Cr(acac)_3$ are satisfactorily correlated with the ionic dissociation constants, pK_a values [7] A similar correlation, with the exception of phenylacetylene, can be obtained for the absolute equilibrium acidities scale in dimethvl sulphoxide [3] The different behaviour of phenylacetylene in these two correlations is expected [3] In the MSAD scale steric association effects are reflected in the reported pK_a values (ion-pair CH acidities), whereas pK measurements in dimethyl sulphoxide are free from such problems

In conclusion, ^{13}C n m r spin–lattice relaxation data obtained from solutions containing the paramagnetic relaxation reagent [$Cr(acac)_3$] can be used for the determination of the HBD acidities of weak carbon acids, thus complementing the data obtained by other methods

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