Organolithium Chemistry. The Acidity of Weak Carbon Acids

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Summary A method for determining quantitatively the acidity of weak carbon acids has been developed: the acidities cover a range of approximately 24 pK_a units and the calculated values are generally in good agreement with those determined experimentally.

I REPORT a simple method for evaluating the acidities of weak carbon acids.[1,2] Since n.m.r. spectroscopy provides a measure of the electron density in the vicinity of a proton or group of protons,[3] it should be possible to determine pK_a's by this technique. It was found that the acidity of a hydrocarbon is related to the difference[3] in chemical shift between a compound of the type X–CH_2–Y (where X and/or Y are H, alkyl, or aryl) and its lithium salt, X–CHLi–Y. The following equation was derived on the basis of n.m.r. measurements of a variety of hydrocarbons and their organolithium derivatives (see Table, compounds I—VII).

$$pK_a = 3{\cdot}20\Delta + 35{\cdot}12$$

where Δ = [chemical shift (p.p.m.) of X–CH_2-Y] − [chemical shift (p.p.m.) of X–CHLi-Y] and pK_a's are on the MSAD scale.[1]

The relative standard deviation in pK_a is 3·57, based on a least-squares fit of data for compounds (I—VII). This deviation is approximately the same as the uncertainty in pK_a values on which the correlation is based. The fact that a correlation is obtained using values determined by several workers (often employing different experimental techniques) suggests that this correlation rests on some principle which is not clear at the moment. Support of the existence of such a principle is gained by the observation that there is no correlation of pK_a with either the chemical shift of the hydrocarbon (relative standard deviation = 42·5) or the lithium salt (relative standard deviation = 8·9) alone.

The pK_a of propane (primary hydrogen, compound VIII) has been determined by the n.m.r. method and found to be slightly less acidic than ethane, in accord with

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Correlation of pK_a *with Chemical Shift*

Compound	Shift[a] (p.p.m.)	Δ	pK_a[1]	pK_a[b]
Benzyl-lithium (I)	1·62[4]	+0·70	35·0	37·4
Toluene	2·32			
Diphenylmethyl-lithium (II)	4·22[4]	−0·33	34·1	34·1
Diphenylmethane	3·89			
Indenyl-lithium (III)	8·39[c]	−5·39	18	17·9
Indene	3·00			
Allyl-lithium (IV)	2·12[6]	−0·41	35·5	33·8
Propene	1·71			
Methyl-lithium (V)	−1·30[c,7]	+1·57	40	40·1
Methane	0·23			
Ethyl-lithium (VI)	−0·99[c,7]	+1·87	42	41·1
Ethane	0·18			
Cyclopentadienyl-lithium (VII)	9·10	−6·20	15	15·3
Cyclopentadiene	2·90			
n-Propyl-lithium (VIII)	−1·00[9]	+1·90	42·5[2]	41·2
Propane	0·90			
9-Lithio-9,10-dihydroanthracene (IX)	4·04[c]	−0·18	—	34·5
9,10-Dihydroanthracene	3·86[c]			
2-Lithiocyclohexanone (X)	4·16[10]	−1·91		29·0
Cyclohexanone (α-H)	2·25		[e]	

[a] Chemical shifts of the salts were obtained as dilute solutions in tetrahydrofuran (THF) or ether. Chemical shifts of the hydrocarbons were obtained as solutions in $CDCl_3$ and/or THF.

[b] Calculated from the equation given in the text.

[c] This work.

[d] In acetonitrile solvent.[8]

[e] Acetone has a pK_a of 27. Assuming the acetyl group adds a constant increment to the pK_a, extrapolation of the pK_a's [1,2] of acetone, acetylacetone, and acetylcyclohexanone leads to an estimated pK_a of 28 for cyclohexanone.

other estimates.[2] The calculated pK_a of 9,10-dihydroanthracene (IX) is similar to that of diphenylmethane (II), the open chain analogue.

Development of pK_a–Δ correlations for other types of compounds, *e.g.*, nitro-compounds,[1] is currently in progress.

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