

CRYPTATE ACIDITY SCALES. SOLVENT POLARITY EFFECT ON ION-PAIR AND FREE ION ACIDITY OF ORGANIC COMPOUNDS

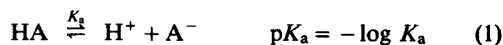
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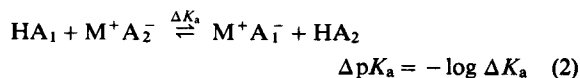
[2.1.1] Cryptated lithium salts of a wide range of CH-acids were studied spectrophotometrically and conductimetrically in solvents of low polarity. Such salts exist in media of different dielectric constants in the form of cryptand-separated ion pairs which are identical in their spectral and conductance properties with common solvent-separated ion pairs. No formation of higher ionic clusters was observed for the studied ions at concentrations below 10^{-3} mol^{-1} even in the benzene. The relative equilibrium acidities in benzene, *N*-methylmorpholine and tetrahydrofuran for a number of CH-acids are reported. Solvent polarity does not influence the cryptate ion-pair acidity of the investigated compounds. The relative free ion acidities were calculated for some of the studied acids in different solvents by combination of the ion-pair acidity values with the conductimetric data on dissociation constants of the cryptate ion pairs. A linear relationship between the free ion acidity and the reciprocal of the dielectric constant was found. An extrapolation method is suggested for the calculation of gas-phase acidity from the data obtained in solution.

INTRODUCTION

Since the pioneering work of Hammett¹ until the mid-1960s, acidity measurements on organic compounds were limited to relatively strong acids in aqueous or mixed media. The direct measurement of the Brønsted equilibria constant gives the acidity value:



Such systems have been widely and rigorously studied.² However, the wide use of non-aqueous solvents and carbanionic reactions in synthesis soon demanded the study of weak acids in low dielectric constant solvents. In such media, direct measurements of the equilibrium (1) constants is impossible so only the relative acidity values may be obtained by the indicator method:



The alkali metals were usually used as M in this reaction. The first steps made by McEwen³ and Conant

and Wheland⁴ to the establishment of a quantitative scale of carbon acidity in non-polar solvents were both decisive and discouraging. They indicated that not only electronic effects influence the acidity, but also the nature of the acid, cation, and solvent.

Existing acidity scales in different solvents are unsuitable for quantitative analysis of the influence of the medium on acidity. The main causes are the inconstancy of the type of ionic particles in solution and specific intermolecular interactions.

It is well known that alkali metal salts of organic compounds exist in non-aqueous solvents as species of different tightness.⁵ With decrease in solvating ability of the media they pass through in the order free ions, solvent-separated ion pairs (SSIP), contact ion pairs (CIP), ion triplets and finally clusters of ions and ion pairs of indefinite size. The type of species may change not only from solvent to solvent but even in a single solvent for different anions or for one anion with different cations. Such changes dramatically influence the acidity values and make any quantitative comparisons speculative. On another hand, the specific interactions of cations with acid anions or the interactions of the solvent with the particles present in the solution may also seriously hinder the determination of the real value of the acidity.

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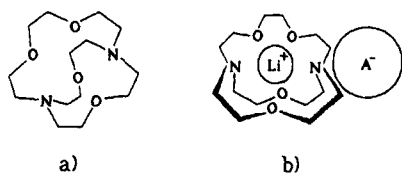


Figure 1. (a) [2.1.1]Cryptand and (b) cryptated ion pair

Two approaches are usually used to bypass this hindrance. Some researchers adhere mainly to a single solvent,⁶ others decrease the range of acids studied to make them more uniform,⁷ but in both cases no wide comparison of scales can be made. The gas-phase values of 'intrinsic' acidity commonly also correlate very poorly with the scales in most solvents.

We have suggested another solution to the problem,⁸ namely the replacement of the traditionally used alkali metal cations in reaction (2) with the large 'organic skin'-coated lithium [2.1.1]cryptate ion. The interaction of the lithium salts of the organic compounds with [2.1.1]cryptand, a macrobicyclic ligand [Figure 1(a)], leads to the formation of the cryptated ion pair [Figure 1(b)]. Such ion pairs possess unique properties. First, the large size of the cryptate cation ($R = 0.5 \text{ nm}$)⁹ diminishes its electrostatic interactions with the anion. In addition, the cryptand fully coordinates the lithium cation and the cryptate does not interact specifically with either the anion or the solvent.

Taking into account the extremely high stability of the inclusion complex of the lithium cation and [2.1.1]cryptand (the formation constant is up to 10^{12} , depending on the solvent¹⁰), one may consider the cryptated ion pair in two ways. On the one hand, such an ion pair may be regarded as the contact ion pair of the acid anion and the huge complex cation. One may also consider it as the ion pair of the lithium cation and the acid anion separated by cryptand molecule in a

similar manner to solvent molecules in the common SSIP. To avoid terminological uncertainty, we shall henceforth call such ion pairs the cryptand-separated ion pairs or the cryptate ion pairs (CrIP), and the acidity measured using such salts will be called the cryptate acidity.

RESULTS AND DISCUSSION

Spectrophotometric investigation of the cryptated ion pairs of the carbanions in solvents of different dielectric constant showed that their electronic spectra are similar to those of the corresponding SSIPs. As an example, in Table 1 the spectra of fluorenyllithium and [2.1.1]cryptated fluorenyllithium in the different solvents are presented. The spectral characteristics of the fluorenyllithium ion pairs have been thoroughly studied.⁵ In non-polar solvents it forms CIPs with an absorption maximum at 346 nm. In intermediate polarity media such as THF the CIPs are neighbouring the SSIPs, which have an absorption maximum at 373 nm and three additional waves in the range 450–520 nm. In polar solvents the CIPs and the corresponding maxima disappear. The spectra of the free anions are similar to those of the SSIPs. The spectroscopic data for the cryptated fluorenyl lithium salt presented on the right in Table 1 indicate that even in the least polar solvents no CIPs form, i.e. the cryptand effectively separates the lithium cation and anion. Similar behaviour is also characteristic of other carbanions. In Figure 2 the absorption maximum wavelengths of a wide range of cryptated carbanion salts in the least polar solvent studied, benzene, are plotted against the corresponding values for the lithium salts in DMSO, where they are believed to dissociate into free ions. Figure 2 suggests that the spectral characteristics of the anions are identical in both solvents. The same picture is also observed with the cryptates in *N*-methylmorpholine and THF as solvents.

Table 1. Dependence of spectral behaviour of 9-fluorenyl carbanion on the counter ion and solvent nature (25 °C)

Solvent	$\lambda_{\text{max}}(\text{nm})^{\text{a}}$	
	Lithium salt	[Li ⁺ c 2.1.1] salt
Hexane	346	375
Benzene	346	375, 456, 484, 517
<i>N</i> -Methylmorpholine	350	375, 456, 486, 521
Cyclohexylamine	367	374, 457, 486, 521
Tetrahydrofuran	349, 373, 455, 484, 516	374, 456, 486, 521
Morpholine	368, 454, 479, 511	373, 456, 485, 519
Ethylenediamine	374, 458, 486, 521	374, 458, 487, 520
Dimethyl sulphoxide	373, 456, 486, 516	373, 458, 486, 518

^a $\pm 1 \text{ nm}$.

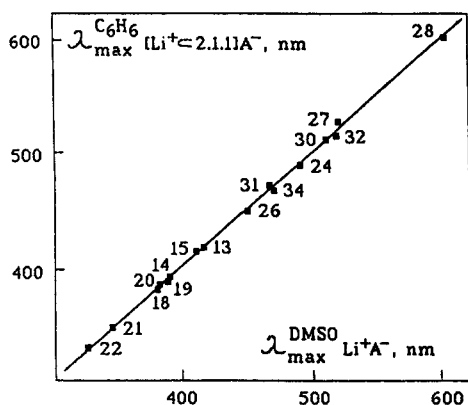


Figure 2. Plot of maximum light absorbance wavelengths of cryptated carbanion salts in benzene vs corresponding values for lithium salts in DMSO. Numbers of compounds correspond to those in Table 4

We also studied the cryptated lithium salts conductimetrically in non-aqueous solvents of low dielectric constant, i.e. benzene, *N*-methylmorpholine (NMM) and tetrahydrofuran (THF). Since the dissociation constant depends strongly on the solvent polarity, different approaches were used for the data treatment. In THF the dissociation constant of the cryptated ion pairs were calculated according to the Fuoss–Kraus equation:¹¹

$$F(z)/\Lambda = (1/\Lambda_0) + (c f_{\pm}^2 \Lambda / F(z) K_d \Lambda_0^2) \quad (3)$$

where $F(z)$ = Fuoss function, c = salt concentration and f_{\pm} = activity coefficient of ions determined according to the Debye–Hückel equation. First, from the dependence of Λ on $c^{1/2}$ the approximate value of the electroconductance at infinite dilution (Λ_0) was determined and for each experimental point the correction factor $F(z)$ was evaluated. Then, from equation (3) corrected Λ_0 and dissociation constant K_d values were determined. Using the corrected Λ_0 , the procedure was repeated until consecutive values differed by less than $0.1 \Omega^{-1} \text{cm}^{-1}$.

In less polar solvents, *N*-methylmorpholine and benzene, the equivalent conductance of the cryptated salts is too low for equation (3) to be used, so the Ostwald dilution law equation¹² was used in this case:

$$1/\Lambda = (1/\Lambda_0) + (\Delta c / K_d \Lambda_0^2) \quad (4)$$

The slope of the plot of $1/\Lambda$ vs Δc gives $1/K_d \Lambda_0^2$ values. Λ_0 in *N*-methylmorpholine and benzene was calculated from the experimental Λ_0 values in THF according to the Walden rule, $\Lambda_0 \eta = \text{constant}$ (η = solvent viscosity). This rule was proved to be true for the electrolytes which do not interact with the solvent specifically.¹³ The absence of linearity of the above plot indicates, according to Fuoss and Accacina,¹¹ the formation of ionic triplets. In this case the ion-pairs dissociation

constants were calculated from the $\Lambda c^{1/2}$ vs c dependence:¹¹

$$\Lambda c^{1/2} = \Lambda_0 K_d^{1/2} + \Lambda_0^2 K_d^{1/2} K_{as}^1 c \quad (5)$$

(Λ_0^1 and K_{as}^1 = equivalent conductance at infinite dilution and association constant of ion triplets, respectively), or from the minimum of the Λ vs c plot according to the equation:¹¹

$$K_d = c_{\min} \Lambda_{\min}^2 / 4 \Lambda_0^2 \quad (6)$$

where c_{\min} and Λ_{\min} are the concentration and the equivalent electroconductance at the minimum point, respectively.

The value of c_{\min} (which usually ranges from 10^{-5} to $10^{-4} \text{mol l}^{-1}$) allows the evaluation of the association constant of the ion pairs in ion triplets (assuming symmetric triplets) according to the equation $K_{as}^1 = 3/c_{\min}$.¹¹ Since K_d of the studied ion pairs is below $10^{-14} \text{mol l}^{-1}$ and K_{as}^1 ranges from 10^4 to 10^5l mol^{-1} , the relative share of the ion triplets is no more than $10^{-3}\%$ of the overall salt concentration. Hence the monomeric ion pairs are the main type of particles at working concentrations even for the anions most likely to undergo aggregation and even in benzene.

The conductimetric data obtained are summarized in Table 2. The ΔG_d values for the cryptates calculated as $\Delta G_d = -RT \ln K_d$ correlate well with the reciprocal of the dielectric constant of the solvent, ϵ^{-1} , (Figure 3) according to the Fuoss electrostatic model of ion pairs:¹⁴

$$K_d = 3000 e^b / 4 \pi N a^3 \quad (7)$$

$$b = -e^2 / a \epsilon K T$$

The value of a in this equation is the effective interionic distance of direct contact of the ions in the ion pair. This value may be calculated from the slope (β) of the correlations presented in Figure 3:

$$a = N e^2 / \beta \quad (8)$$

The calculated values of the interionic distance for the ion pairs of some cryptates are presented in Table 3. One can see that the interionic distances change remarkably little and are nearly equal to the sum of the ionic radii of the carbanion (0.2–0.3 nm) and the cryptated lithium cation (0.5 nm). This indicates the existence of the cryptated lithium organic salts in cryptand-separated form. In addition, the linear dependence of the dissociation free energies (ΔG_d) on ϵ^{-1} confirms the constancy of the type of ion pairs in studied solvents.

It was found that the K_d values are independent of the relative excess of the cryptand (2–100-fold). In addition, linearity of $\log K_d$ vs $1/T$ plots over a wide range of temperatures (-20 to 40°C) was observed. These results indicate the absence of ion pairs other than cryptand separated ion pairs (e.g. those externally solvated by cryptand).

Table 2. Ion pair dissociation constants, K_d ($\pm 20\%$, mol l⁻¹, 25 °C) of cryptated lithium salts of carbon acids in three solvents

Acid	THF ($K_d \times 10^6$)	<i>N</i> -methylmorpholine ($K_d \times 10^{11}$)	Benzene ($K_d \times 10^{15}$)
Fluoradene	5.1	—	76
1,1-(<i>o</i> -Biphenylene)- 3,3-diphenylprop-1-ene	2.0	—	—
9-Phenylfluorene	2.0	—	—
11-Phenylbenzo[<i>a</i>] fluorene	7.8	—	—
Diphenylacetonitrile	1.3	—	—
2-Phenylindene	3.7	—	—
Cyclopentadiene	0.89	6.0	0.18
Indene	1.9	8.2	0.6
9-Benzylfluorene	1.0	30	23
Fluorene	2.3	85	8.0
Phenylacetonitrile	5.5	120	22
2-(<i>N,N</i> -Dimethylamino)fluorene	2.5	—	—
1,1,3-Triphenyl-2- azaprop-1-ene	2.0	—	—
1,1,3-Triphenylprop-1-ene	3.8	—	150
9-Phenylxanthene	1.4	—	—
<i>p</i> -Biphenyldiphenylmethane	3.4	—	—
Xanthene	2.3	—	—
9,10-Dihydroanthracene	1.0	—	—
Triphenylmethane	4.0	170	53
Diphenylmethane	2.0	—	15

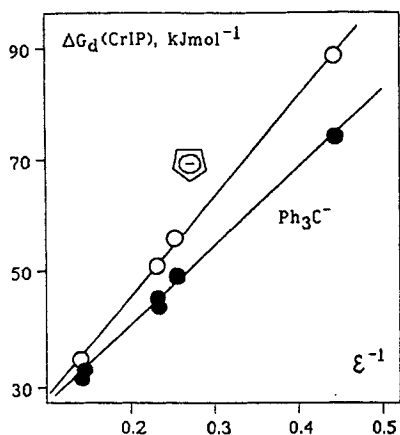


Figure 3. Plot of dissociation free energies of some cryptate ion pairs in different solvents vs reciprocal of dielectric constant of the solvent

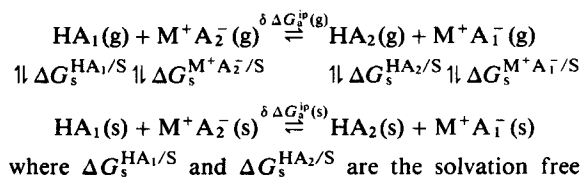
Hence the conductimetric and spectrophotometric study suggests that the [2.1.1]cryptated lithium salts of the studied CH-acids exist in media of different polarity as monomeric cryptand-separated ion pairs. No formation of higher ionic clusters is observed for most of the anions studied at concentrations below 10⁻³ mol l⁻¹ even in the least polar solvent, benzene. These ion pairs

Table 3. Effective distances of maximum approach of ions in the ion pairs of [2.1.1]cryptated lithium salts of some carbon acids

Acid	<i>a</i> (nm)
Triphenylmethane	9.8 ± 0.3
Cyclopentadiene	7.7 ± 0.3
Indene	8.0 ± 0.5
Fluorene	8.9 ± 0.3
Benzylfluorene	9.9 ± 0.7
Phenylacetonitrile	9.0 ± 0.4

are identical in their spectral and conductance properties with the common SSIPs. Such uniformity allows us to establish acidity scales which may be used for the study of the solvent effect on acidity.

The analysis of the influence of the media on the ion-pair acidity may be carried out using the following Born-Haber cycle:



energies of the acids HA₁ and HA₂ and $\Delta G_s^{M^+A_2^-/S}$ and $\Delta G_s^{M^+A_1^-/S}$ the solvation free energies of their salts' ion pairs in the solvent S.

Hence the relative ion-pair acidity, $\delta \Delta G_a^{ip}(s)$, in the solvent S may be expressed by the following equation:

$$\delta \Delta G_a^{ip}(s) = \delta \Delta G_a^{ip}(g) - (\Delta G_s^{HA_1} - \Delta G_s^{HA_2}) + (\Delta G_s^{M^+A_1^-} - \Delta G_s^{M^+A_2^-}) \quad (9)$$

where $\delta \Delta G_a^{ip}(g)$ is the relative ion-pair acidity of the compounds HA₁ and HA₂ in the gas phase. The two terms in parentheses represent the difference in the solvation energies of the acids and their salts' ion pairs. They will determine solvent effects on the relative acidity.

The solvation free energy of a compound A_i in the solvent S may be considered as the sum of the energies of dispersion, electrostatic and specific interactions of the solute with the solvent:

$$\Delta G_s^{A_i/S} = \Delta G_s^{A_i/S}(\text{disp}) + \Delta G_{\text{int}}^{A_i/S}(\text{elect.}) + \Delta G_{\text{int}}^{A_i/S}(\text{spec.}) \quad (10)$$

Hence for the prediction of the influence of the media on the ion-pair acidity it is necessary to evaluate the contribution of each of these interactions in the thermodynamics of reaction (2), i.e. the change in the dispersion solvation energy:

$$\delta \Delta G_s(\text{disp.}) = [\Delta G_s^{M^+A_1^-}(\text{disp.}) - \Delta G_s^{M^+A_2^-}(\text{disp.})] - [\Delta G_s^{HA_1}(\text{disp.}) - \Delta G_s^{HA_2}(\text{disp.})] \quad (11)$$

the electrostatic interactions of the reacting particles with the solvent:

$$\delta \Delta G_s(\text{elect.}) = [\Delta G_{\text{int}}^{M^+A_1^-}(\text{elect.}) - \Delta G_{\text{int}}^{M^+A_2^-}(\text{elect.})] - [\Delta G_{\text{int}}^{HA_1}(\text{elect.}) - \Delta G_{\text{int}}^{HA_2}(\text{elect.})] \quad (12)$$

and their specific interactions with the solvent:

$$\delta \Delta G_s(\text{spec.}) = [\Delta G_{\text{int}}^{M^+A_1^-}(\text{spec.}) - \Delta G_{\text{int}}^{M^+A_2^-}(\text{spec.})] - [\Delta G_{\text{int}}^{HA_1}(\text{spec.}) - \Delta G_{\text{int}}^{HA_2}(\text{spec.})] \quad (13)$$

As shown earlier,^{15,16} the non-specific dispersion solvation energy of the organic compounds depends linearly on their molecular refraction. For reaction (2) the sums of the molecular refractions of the compounds in the left- and right-hand parts do not differ significantly, so the following equation must be true:

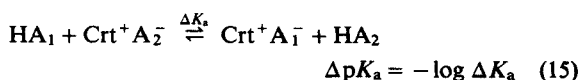
$$\Delta G_s^{HA_1/S}(\text{disp.}) + \Delta G_s^{M^+A_2^-/S}(\text{disp.}) = \Delta G_s^{HA_2/S}(\text{disp.}) + \Delta G_s^{M^+A_1^-/S}(\text{disp.}) \quad (14)$$

The combination of equations (14) and (11) results in $\delta \Delta G(\text{disp.}) = 0$, i.e. the dispersion interactions do not influence the relative ion-pair acidity.

Another type of solvation interactions are the electrostatic interactions. For the study of their influence on the relative acidities three solvents were chosen: benzene ($\epsilon = 2.2$), *N*-methylmorpholine ($\epsilon = 4.3$) and THF ($\epsilon = 7.4$). According to theoretical concepts, the

energy of the solute-solvent electrostatic interactions is proportional to the reciprocal of the dielectric constant (ϵ^{-1}), to the Kirkwood function ($\epsilon - 1/2\epsilon + 1$) or to a similar function.¹⁷ It is remarkable that the values of such functions change most significantly in solvents of low dielectric constant ($\epsilon = 2-10$). In addition, these solvents are aprotic so in most cases they do not interact specifically either with the acids or with their anions.

The relative acidities were determined in these three solvents according to the equilibrium



where Crt⁺ is the lithium [2.1.1]cryptate cation. Absolute acidity values are assigned on the basis of a reference pK_a value for 9-phenylfluorene taken as 17.9.⁶ The data obtained are summarized in Table 4.

Comparison of the relative cryptate ion-pair acidity scales in benzene, *N*-methylmorpholine and THF shows the remarkably well fitting correlations with a slope of unity and a zero intercept. The correlation equations are as follows:

$$\Delta pK_a(N\text{-methylmorpholine}) = (1.00 \pm 0.01) \Delta pK_a(\text{THF}) - (0.22 \pm 0.17)$$

$$n = 20, \sigma = 0.14, r = 0.999$$

(n = number of points; σ = standard deviation; r = correlation coefficient);

$$\Delta pK_a(\text{benzene}) = (1.01 \pm 0.01) \Delta pK_a(\text{THF}) - (0.23 \pm 0.13)$$

$$n = 29, \sigma = 0.19, r = 0.999$$

The unit slope of the correlations indicates the absence of an influence of the solvent's dielectric constant on the relative acidity values. Hence solute-solvent electrostatic interactions have a negligible effect on the ion-pair acidity.

Such correlations were found earlier by Streitwieser and co-workers¹⁸ for the caesium acidity scales in THF, cyclohexylamine and 1,2-dimethoxyethane. However, they were correct only for the few hydrocarbon acids that form highly delocalized carbanions. The state of the other acids' salts in these solvents varies strongly and no correlation is observed.

It is also interesting to compare the cryptate scales with known scales in other solvents. The plot of the cryptate relative acidity values in THF and Bordwell's acidities in DMSO (see Table 4) reveals a good correlation for most compounds (Figure 4). The correlation equation is

$$\Delta pK_a(\text{DMSO}) = (1.02 \pm 0.02) \Delta pK_a(\text{THF}) - (0.52 \pm 0.53)$$

$$n = 27, \sigma = 0.36, r = 0.998$$

However, some CH-acids exhibit anomalous behaviour, being more acidic in DMSO than would be

Table 4. Equilibrium cryptate ion-pair acidities of some CH-acids in non-aqueous solvents and free ion acidities in DMSO and THF (± 0.1 p*K*_a, 25 °C)

No.	CH-acid	THF	NMM ^a	Benzene	DMSO ^b	THF ^c
1	Fluoradene	10.6	—	10.7	10.5	10.2
2	1,1,3,3-Bis(<i>o</i> -biphenylene)propene	11.7	—	11.6	—	—
3	Dicyanomethane	12.0	—	10.8	11.1	—
4	4-Nitrophenylacetonitrile	13.0	—	12.6	12.5	—
5	1,2,3,4-Tetraphenylcyclopentadiene	14.2	—	14.2	13.7	—
6	Ethyl cyanoacetate	14.8	—	13.7	13.1	—
7	2,4-Dinitrotoluene	15.5	—	15.4	15.6	—
8	Ethyl 4-nitrophenylacetate	15.6	—	15.6	14.5	—
9	9-(4-Methylphenylthio)fluorene	15.9	—	15.9	15.9	—
10	Diethyl malonate	16.5	—	—	16.4	—
11	Nitromethane	17.0	—	—	17.2	—
12	1,1-(<i>o</i> -Biphenylene)- 3,3-diphenylprop-1-ene	17.7	17.5	17.7	—	17.7
13	9-Phenylfluorene ^d	17.9	17.9	17.9	17.9	17.9 (17.6)
14	11-Phenylbenzo [α] fluorene	18.0	17.8	18.1	17.9	17.4
15	Diphenylacetonitrile	18.2	17.9	18.1	17.5	18.4
16	2-Phenylindene	19.6	19.5	20.0	19.4	19.3
17	Cyclopentadiene	20.7	20.6	20.7	18.0	21.0
18	Indene	21.1	20.8	21.1	20.1	21.1
19	9-Benzylfluorene	21.4	21.0	21.3	21.4	21.7 (21.3)
20	Fluorene	22.3	22.4	22.1	22.6	22.2 (22.9)
21	Phenylacetonitrile	22.6	22.5	22.3	21.9	22.2
22	Ethyl phenylacetate	23.5	23.4	23.5	22.7	—
23	2-(<i>N,N</i> -Dimethylamino)fluorene	23.9	23.8	23.8	24.2	23.8
24	1,1,3-Triphenyl-2-azaprop-1-ene	24.4	24.3	24.4	24.3	24.5
25	1,1,3-Triphenylprop-1-ene	25.8	25.6	26.0	25.9	25.5
26	Benzhydryl phenylsulphide	26.9	26.8	27.1	26.7	—
27	9-Phenylxanthene	27.7	27.7	28.0	27.7	27.9
28	<i>p</i> -Biphenylyldiphenylmethane	29.3	29.4	29.6	29.4	29.1
29	Phenyl methylsulphone	29.4	—	—	29.0	—
30	Xanthene	29.7	—	29.7	30.0	29.6
31	9,10-Dihydroanthracene	29.8	29.6	29.8	30.1	30.1
32	Triphenylmethane	30.8	30.8	31.4	30.6	30.5 (30.4)
33	Phenylacetylene	31.1	—	31.0	28.7	—
34	Diphenylmethane	32.4	32.0	32.4	32.3	32.4

^a *N*-Methylmorpholine.^b Bordwells free ion acidity.⁶^c Free ion acidities in THF calculated according to equation (16); values in parentheses are from Ref. 22.^d Reference acid.

expected from the common correlation. These are hydrocarbons that form highly localized carbanions (cyclopentadiene, phenylacetylene, indene) and CH-acids that form ambident anions susceptible to chelation. We propose that it may be ascribed to ion pairing of potassium cation and such anions in DMSO.

For the latter group the ion association is not so unexpected, since for the β -di- and β -tricarboxyl carbon acids such pairing in DMSO is well known¹⁹ and the Bordwell's acidities for such compounds are corrected to account for its acidifying effect. These corrected values (e.g. for diethylmalonate) do not deviate from the correlation in Figure 4. It is obvious that for some reason the ion pairing of potassium with anions of

such compounds as CH₂(CN)₂ and NCCH₂COOEt in DMSO was not detected by previous investigators, so the acidity values were left uncorrected, i.e. exaggerated.

However, more unexpected is the deviation from the correlation line of hydrocarbons such as cyclopentadiene and phenylacetylene. The ion pairing of anions of β -dicarbonyl compounds is attributed to strong chelation of the potassium cation. In the case of the above hydrocarbons, the specific interactions are negligible and the association may be due to the electrostatic interaction between the cation and anion. The cyclopentadienyl anion has a small ring and hence the charge density is relatively high, whereas in phenylacetylide

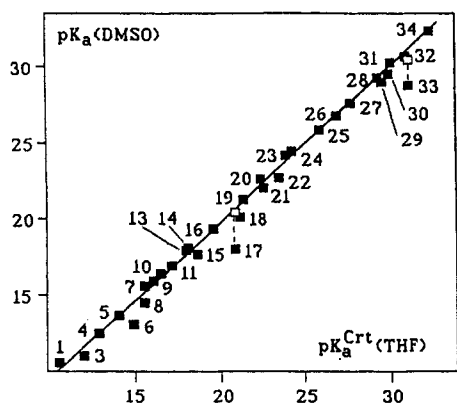


Figure 4. Plot of free ion Bordwell's acidities in DMSO vs cryptate acidities in THF. Numbers of compounds correspond to those in Table 4

anion the charge is almost completely localized on the terminal carbon atom. The high charge density causes very strong electrostatic interactions with the cation.

To confirm the suggestion about the ion pairing of cyclopentadienyl and phenylacetylide anions with potassium cations in DMSO, the acidity values of their conjugated acids in the same solvent using the cryptate cation instead of potassium ion were determined. These values (20.5 for cyclopentadiene and 30.7 for phenylacetylene) obey exactly the correlation in Figure 4 (shown by the open symbols), i.e. the deviations are actually due to the association in ion pairs, while the use of the cryptate ions precludes their formation and gives the correct acidity values. Hence the comparison with cryptate acidity provides a simple semi-quantitative method of testing for ion association.

The case of phenylacetylene, the anion of which is known to be likely to associate and aggregate with cations, is worth special discussion. The conductimetric study of the [2.1.1]cryptated lithium salt of phenylacetylene was impossible owing to its instability at low concentrations. However, indirect evidence for the mainly monomeric state of its ion pairs in the concentration range used can be obtained from the acidity data. The differences between the Bordwell's and cryptate acidities are fairly close for cyclopentadiene and phenylacetylene, 2.7 and 2.3 pK_a units, respectively. Hence the tendency of their anions to undergo association does not differ much in DMSO and obviously in other solvents. As was shown above for the cyclopentadienyl anion, the share of the ion triplets in the studied solvents is negligible. Hence the same may be assumed for phenylacetylide also. Another piece of evidence for the absence of aggregation with [2.1.1]cryptated lithium phenylacetylide is the good adherence of the phenylacetylene acidity to the correlations between cryptate

acidity scales in solvents of different polarity. In the opposite case the extent of aggregation and hence the acidity values would vary from solvent to solvent. The influence of ion aggregation on the relative acidity in THF was shown earlier.²⁰

A logically following step in our investigation was the study of the influence of the solvent on ionic acidities. As mentioned above, the most significant changes in the electrostatic solvation interactions energy must be observed in solvents of low dielectric constant. However, in such solvents the direct measurement of the free ion acidity is impossible.

By combining the ion pair acidity values with the dissociation constants of the corresponding ion pairs, it is possible to calculate the relative free ion acidities according to the equation

$$\Delta pK_a^{fi}(s) = \Delta pK_a^{ip}(s) - [\log K_d(M^+A_1^-) - \log K_d(M^+A_2^-)] \quad (16)$$

where $\Delta pK_a^{fi}(s)$ and $\Delta pK_a^{ip}(s)$ are the free ion and the ion pair relative acidities of the compounds HA_1 and HA_2 , respectively.

The conductimetric K_d measurements of salts with cations other than lithium cryptate in media of low dielectric constant are complicated owing to strong ion aggregation. Therefore, the free ion acidity values are available only for solvents which have relatively high dielectric constants (1,2-dimethoxyethane,²¹ THF,²² DMSO⁶).

We established a scale of relative free ion acidities in THF using the K_d data for cryptated ion pairs in THF and the cryptate ion-pair acidities of corresponding CH-acids. The values of free ion acidities in THF are presented in the last column of Table 4. These are fairly close to corresponding values obtained by Streitwieser and co-workers²² (given in parentheses, relative to fluorene pK_a taken as 22.9). The free ion acidities in THF do not differ significantly from the ion-pair values. This is not unexpected since the range of dissociation constants for the studied cryptate ion pairs is remarkably small (see Table 2), especially taking into account the considerable structural and size variations of the anions.

We also determined relative free ion acidities for some compounds in benzene and *N*-methylmorpholine in order to examine the influence of solvent dielectric constant on ionic acidity. Free ion acidities in solvents of different dielectric constant are compared in Table 5, and also their gas-phase acidities.²³ The acidity values are expressed relative to cyclopentadiene as the reference acid. In contrast to the ion-pair acidities, the free ion acidities depend significantly on the dielectric constant of the media. Moreover, the anion electrostatic solvation was found to reverse the order of free ion acidity. For example, 9-benzylfluorene, fluorene and phenylacetonitrile are less acidic than cyclopentadiene

Table 5. Relative equilibrium free ion acidities of some CH-acids in non-aqueous solvents and in the gas phase (± 0.1 p*K*_a, 25 °C)

Acid	Medium (ϵ_{25})					
	DMSO ^a (46.6)	THF (7.39)	NMM (4.03)	Benzene (2.27)	G.P. ^b (1)	Extrapolated G.P. ^c
Fluoradene	-10.0	-10.8	-	-12.2	-16.6	-15.1
Cyclopentadiene ^{d,c}	0	0	0	0	0	0
Indene ^c	0.6	0.1	0.1	0.1	-	-0.6
9-Benzylfluorene	0.9	0.7	-0.2	-0.5	-	-4.8
Fluorene	2.1	1.2	0.7	-0.2	-3.2	-3.3
Phenylacetonitrile ^c	2.2	1.2	0.7	-0.3	-2.6	-3.6
1,1,3-Triphenylprop-1-ene	5.4	4.4	-	2.5	-	-1.3
Triphenylmethane	10.1	9.5	8.8	8.4	-	6.0
Diphenylmethane	11.8	11.4	-	10.3	6.7	8.3

^a Based on Ref. 6.^b Gas-phase acidities.²³^c Gas-phase acidities extrapolated according to correlation equations $\Delta pK_a^{fi}(s) = ae^{-1} + b$.^d Reference acid.^e Values in DMSO, this work.

and indene in DMSO and THF. In *N*-methylmorpholine the difference is levelled and in benzene indene and cyclopentadiene become less acidic than the first three acids.

The free ion acidities correlate linearly with the reciprocal of the dielectric constants of the solvents. It is important that the gas-phase acidity values also obey these correlations well. Correlation equations for some of the acids studied are as follows:

Fluoradene:

$$\Delta pK_a^{fi}(s) = -6.68e^{-1} - 9.73$$

$$n = 4, \sigma = 0.39, r = 0.994$$

Fluorene:

$$\Delta pK_a^{fi}(s) = -5.27e^{-1} + 2.07$$

$$n = 5, \sigma = 0.13, r = 0.998$$

Phenylacetonitrile:

$$\Delta pK_a^{fi}(s) = -4.70e^{-1} + 1.98$$

$$n = 5, \sigma = 0.25, r = 0.993$$

Diphenylmethane:

$$\Delta pK_a^{fi}(s) = -5.25e^{-1} + 12.15$$

$$n = 4, \sigma = 0.40, r = 0.990$$

These correlations suggest that the influence of the media on the free ion acidity is due mainly to the ion-dipole solvation interactions.

The linear relationship between ΔpK_a^{fi} and e^{-1} (from the highly polar solvents to the gas phase) may be used for the prediction of ionic acidity in any non-hydrogen-bonding media. Most remarkable is the possibility of evaluation of the gas-phase acidity from solution

acidity data by extrapolation of the ΔpK_a^{fi} vs e^{-1} dependence to the gas phase ($e^{-1} = 1$). The extrapolated values are presented in the last column of Table 5. They are fairly close to the experimental values. Not less significant is also the interpolation of the ionic acidity values in solvents with known dielectric constants in cases when the direct experimental measurement is complicated.

EXPERIMENTAL

Some CH-acids were commercially available and the others were synthesized according to known methods.⁸ The liquid compounds were distilled twice over calcium hydride. The purity was monitored by gas-phase chromatography (GPC) on a CHROM-5 chromatograph. For all compounds the content of the main substance was above 99%. The solid substances were recrystallized twice from a suitable solvent and then sublimed under vacuum. The purity was monitored by GPC for sufficiently volatile substances. The melting points of the solids agreed with the literature values.

[2.1.1]Cryptand was partially synthesized according to the slightly modified Lehn method²⁴ and was partially a commercial product from Merck. No difference was observed in parallel experiments using the commercial and synthesized cryptand. The cryptand was distilled under vacuum (b.p. 120 °C at 10⁻³ Torr). The distilled cryptand unexpectedly proved to be a solid substance with m.p. 31.6 ± 0.2 °C (the commercial compound was a viscous oil).

Halide-free butyllithium was synthesized according to a special method²⁵ in an evacuated apparatus in benzene solution.

All the samples of acids, cryptand and butyllithium were sealed in thin spherical glass ampoules (*ca* 15 mm diameter) after evacuating to a residual pressure below 10^{-4} Torr. The solid acids and cryptand were placed in the preweighed ampoules, evacuated, degassed by heating to 100°C and sealed. The volatile liquid acids were degassed under vacuum, dried over the calcium hydride and distilled via a special manifold into the preweighed ampoules. The contents were then frozen by liquid nitrogen and the ampoules were sealed. Butyllithium was dropped into the ampoules via a special evacuated glassware manifold system to avoid contact with the air, and the solvent was removed under vacuum to a liquid nitrogen trap. The weights of the samples were corrected to take account of the weight of evacuated air. The samples of acids and cryptand ranged from 10 to 50 mg and of butyllithium from 2 to 10 mg.

The reservoirs for conductance and acidity measurements consisted of several (2–4) vertical glass tubes (*ca* 2 cm diameter and 25 cm long) connected at their upper parts by horizontal tubes. One of the tubes was graduated for volume measurement. No joints, stoppers or stopcocks were used. All the connections and closures were one-piece, all-glass. A quartz spectroscopic cuvette (optical length 0.2 or 1.6 cm) and, if necessary, a conductimetric cell were attached. The coaxial cylindrical platinum electrodes of the conductimetric cells were welded to the molybdenum wires which extended through the reservoir's wall. The outlet of the reservoir was supplied with a standard joint for connection to the vacuum line and was also sealed after all preparation procedures had been completed. A piece of thin glass rod (for breaking the ampoules) and several ampoules containing the samples were placed in one of the tubes of the reservoir. For the conductimetric measurements samples of the acid, cryptand and, if necessary, butyllithium (one of each) were taken. For acidity measurements samples of two acids (3–4 of each), the sample of cryptand and, if necessary, butyllithium were taken.

The solvents were prepurified by refluxing over potassium for several days and distillation. Final solvent purification and the preparation of the initial cryptate solution were slightly different for THF and for *N*-methylmorpholine and benzene. For solvent purification a special manifold of two connected vertical tubes was attached to the vacuum line and the measurement reservoir was attached via a joint to the manifold. Into one tube of the manifold the solvent was poured (10–15 ml) and both contained a piece of potassium (100–200 mg) and indicator compound (50–100 mg) (anthracene for THF or triphenylmethane for *N*-methylmorpholine and benzene). The solvent was frozen by liquid nitrogen, the glassware system evacuated and the solvent repeatedly degassed by melting–freezing–evacuation cycles. After final evacuation, the piece of potassium was heated until sublimation

with the formation of a mirror. The solvent was melted and isothermally distilled on the mirror. The attainment of required solvent purity was indicated by a stable colour of the indicator anion: a violet colour of dihydroanthracene dianion in THF or a red colour of trityl anion in *N*-methylmorpholine and benzene. If necessary, the sublimation of potassium and redistillation of the solvent were repeated in the second tube of the manifold. The purified solvent was isothermally distilled into the measurement reservoir and frozen by liquid nitrogen. After sealing of the reservoir and melting of solvent, the volume of the latter was measured in the graduated tube of the reservoir.

In the case of THF, a piece of lithium (10–20 mg) and naphthalene (20–50 mg) were placed in advance in the measurement reservoir (a butyllithium sample was not needed in this case). After distilling the solvent and sealing the reservoir, the reaction between lithium and naphthalene began with the formation of green dihydronaphthalene lithium salt. After several hours the solution became dark green. The reservoir was washed with this solution and an excess of dihydronaphthalenyllithium together with a piece of lithium was sealed off. The ampoule with the sample of indicator acid was then broken by knocking the ampoule with the glass rod. The reaction of dihydronaphthalenyllithium with an excess of indicator acid yielded the lithium salt. Dihydronaphthalene is much less acidic than the weakest acid studied. Subsequently the sample of cryptand was introduced in the same manner and the spectrum of the cryptated salt was recorded. The molar absorptivity was calculated assuming that of lithium naphthalenide to be $2200\text{ l mol}^{-1}\text{ cm}^{-1}$ at 810 nm .²⁶ The concentration of salt was chosen so that resulting optical absorbance at λ_{max} would be in the range 0.8–1.5 to allow accurate measurements.

In the case of benzene and *N*-methylmorpholine the ampoules of indicator acid and butyllithium were broken after sealing the reservoir with solvent. The acid was always in excess over butyllithium. The excess of salt was sealed off from the reservoir in a tube. Introduction of cryptand yielded the starting cryptate solution for measurements. Knowing the amount of butyllithium, the molar absorptivities were calculated.

The starting solution was used for conductimetric or relative acidity measurements. The conductimetric study consisted in the determination of the concentration and temperature dependence of the salt's equivalent electroconductance. The starting solution was consequently diluted by pouring part of it (usually half) from the conductimetric cell into the reservoir itself, with further isothermal distillation of solvent into the cell. The concentration was monitored at each point spectrophotometrically. The resistance values were measured by a conductimeter at 1 kHz. The conductimeter was a standard Wien bridge.²⁷ The equivalent conductance was calculated according to the equation

Table 6. Concentration dependence of the equivalent electroconductance of [2.1.1]cryptated fluorenyllithium solution in THF (25°C, 1 kHz, cell constant $1.2 \times 10^{-2} \text{ cm}^{-1}$)

Point	$c \times 10^5 (\text{mol l}^{-1})$	$\Lambda (\text{cm}^2 \Omega^{-1} \text{ mol}^{-1})$
1	117	3.89
2	58.4	5.12
3	29	6.83
4	14	9.13
5	7.0	12.1
6	3.7	16.0

Table 7. Concentration dependence of the equivalent electroconductance of [2.1.1]cryptated cyclopentadienyllithium solution in *N*-methylmorpholine (25°C, 1 kHz, cell constant $1.2 \times 10^{-2} \text{ cm}^{-1}$)

Point	$c \times 10^6 (\text{mol l}^{-1})$	$\Lambda \times 10^2 (\text{cm}^2 \Omega^{-1} \text{ mol}^{-1})$
1	100	9.36
2	50	11.0
3	25	14.1
4	13	17.3
5	6.0	25.1

Table 8. Concentration dependence of the equivalent electroconductance of [2.1.1]cryptated indenyllithium solution in benzene (25°C, 1 kHz, cell constant $1.2 \times 10^{-2} \text{ cm}^{-1}$)

Point	$c \times 10^5 (\text{mol l}^{-1})$	$\Lambda \times 10^4 (\text{cm}^2 \Omega^{-1} \text{ mol}^{-1})$
1	40	13.4
2	23	10.5
3	12	11.1
4	6.2	9.86
5	3.7	8.82

$\Lambda = 1000k/Rc$ (k = cell constant, R = resistance of the solution, c = concentration). The cell constant was determined using tetramethylammonium iodide solution in DMSO²⁸ to be $1.2 \times 10^{-2} \text{ cm}^{-1}$. Typical runs are presented in Tables 6–8. Equations for data treatment in different cases were discussed above [equations (3)–(6)].

The acidity measurements consisted in equilibration of the starting cryptated salt of the indicator acid with another acid. Samples of each acid were alternately introduced one by one and the concentrations of anions were determined spectrophotometrically at each point. Generally equilibrium was reached immediately after

dissolving the acid in all the solvents studied. The attainment of equilibrium was checked by repeated measurement of the absorbance for 30–60 min after introduction of the acid sample. *p*-Biphenyl-diphenylmethane was the only acid for which slow establishment of equilibrium was observed. The equilibrium constants were calculated at each point, using the simplifying assumption that the ratio of activity for HA_1 and HA_2 and for their respective ion pairs is unity:

$$\Delta K_a = [\text{HA}_1][\text{A}_2^-]/[\text{HA}_2][\text{A}_1^-] \quad (17)$$

This assumption seems to be correct in view of the low concentrations employed. From the equilibrium constant and known $\text{p}K_a$ of one of the acids, the $\text{p}K_a$ of the other acid was calculated. The several $\text{p}K_a$ values obtained within a run usually varied by less than 0.05 unit, which was additional evidence for the establishment of equilibrium. The reproducibility between runs was generally better than 0.1 $\text{p}K_a$ unit. The concentrations of acids varied from 10^{-4} to $10^{-2} \text{ mol l}^{-1}$ and of salts from 10^{-5} to $10^{-4} \text{ mol l}^{-1}$.

The pairs of acids were chosen so that they were within 2 $\text{p}K_a$ units to allow accurate equilibrium measurements. In many cases both acids had coloured anions (double indicator measurement). The concentration ratio of the anions can be calculated for such systems as

$$\frac{[\text{A}_2^-]}{[\text{A}_1^-]} = \frac{\varepsilon_1(D_{\text{A}_2^-} - k_1 D_{\text{A}_1^-})}{\varepsilon_2(D_{\text{A}_1^-} - k_2 D_{\text{A}_2^-})} \quad (18)$$

where ε_1 and ε_2 here are the molar absorptivities of anions A_1^- and A_2^- at their λ_{max} , $k_1\varepsilon_1$ and $k_2\varepsilon_2$ are the molar absorptivity of A_1^- at the λ_{max} of A_2^- and that of A_2^- at the λ_{max} of A_1^- , respectively, and $D_{\text{A}_1^-}$ and $D_{\text{A}_2^-}$ are the absorbances at the λ_{max} of A_1^- and A_2^- , respectively.

In other cases the anion of the second acid was colourless (single indicator measurement). In this case the calculation of the above ratio is much simpler:

$$\frac{[\text{A}_2^-]}{[\text{A}_1^-]} = D/(D_0 - D) \quad (19)$$

where D_0 here is the initial absorbance of the starting solution at the indicator anion's λ_{max} and D is the actual absorbance in the presence of HA_1 .

The double indicator method is more complicated because the overlap of the spectra of the indicators must be accounted for, but more accurate as the concentrations of both anions can be controlled. The compounds with colourless anions were linked with not less than two other indicator acids. The reproducibility of the equilibrium constants within a run evidenced the absence of decomposition of the anions by impurities in single indicator measurements. Examples of runs for both double and single indicator measurements are presented in Tables 9 and 10, respectively.

Table 9. Relative equilibrium cryptate acidity of 4-phenyltriphenylmethane (HA₁) and 9,10-dihydroanthracene (HA₂) in THF 25 °C, cuvette optical length 0.2 cm)

Point	<i>D</i> ₄₆₂	<i>D</i> ₆₁₀	[A ²⁻]/[A ⁻] ^a	[HA ₁]/[HA ₂]	Δ <i>pK</i> _a
—	0.981 ^b	0.00	—	—	—
1	0.745	0.673	1.87	0.171	-0.49
2	0.733	0.374	3.53	0.0763	-0.57
3	0.750	0.241	5.78	0.0493	-0.54
4	0.585	0.426	2.39	0.118	-0.55
5	0.528	0.528	1.66	0.178	-0.53

$$^a [A^{2-}]/[A^{-}] = 44 \times 10^3 (D_{462} - 0.15D_{610}) / 22.5 \times 10^3 D_{610}.$$

^b Starting solution.

Table 10. Relative equilibrium cryptate acidity of phenylmethyl sulphone and 9,10-dihydroanthracene in THF (25 °C, cuvette optical length 0.2 cm)

Point	<i>D</i> ₄₆₂	[A ²⁻]/[A ⁻]	[HA ₁]/[HA ₂]	Δ <i>pK</i> _a
—	1.61 ^a	—	—	—
1	1.05	1.88	0.228	-0.37
2	0.752	0.877	0.483	-0.37
3	0.892	1.24	0.355	-0.36
4	0.664	0.704	0.588	-0.38
5	0.750	0.870	0.472	-0.39

^a Starting solution.

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