# The order of lithium ion affinities for the 20 common α-amino acids. Calculation of energy-well depth of ion-bound dimers

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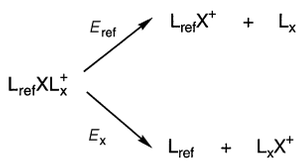
**In an earlier publication it was shown that the kinetic method for determination of proton affinities can be satisfactorily explained when the critical energies for decomposition of the proton-bound dimers are calculated from the Marcus equation. In this work it is shown that the critical energies for decomposition of alkali metal ion-bound dimers also seem to follow the Marcus equation. This supports the application of the kinetic method for measurements of alkali metal-ion affinities of organic molecules. Based on unimolecular decompositions of $Li^+$-bound dimers, the order of lithium ion affinity of the common α-amino acids has been established as: Arg > His > Gln > Asn > Lys > Trp > Glu > Asp > Tyr > Met > Phe > Thr > Pro > Ser > Ile > Leu > Val > Cys > Ala > Gly.**

## Introduction and theory

### The kinetic method

The present work is concerned with the lithium ion affinity (LIA) of the 20 common α-amino acids and is a continuation of studies of the proton and sodium ion affinities of α-amino acids.[1]

The method we have used is the kinetic method.[2] This method is based on competitive unimolecular decompositions of a series of ion-bound dimers which for positive ions have the general structure $L_{ref}XL_x^+$. One of the ligands $L_{ref}$ varies whereas the other $L_x$ is fixed. The ion-bound dimers decompose according to Scheme 1. $X^+$ can be a proton or some other ion




**Scheme 1**

and $L_{ref}$ and $L_x$ are ligands with similar structures. $L_{ref}$ is a series of reference compounds with known affinities for $X^+$ and $L_x$ is a compound whose affinity for $X^+$ is to be determined. From metastable or collision induced decompositions of $L_{ref}XL_x^+$ the relative abundance $L_{ref}X^+$ and $L_xX^+$ can be determined. Their relative order gives directly the order of the affinities of $L_{ref}$ and $L_x$ for $X^+$. With access to a set of reference compounds with closely spaced affinities the unknown affinity can be quite accurately determined. When the fragmentation of a number of ion-bound dimers is examined it is observed that there is a linear relationship between the logarithm to the ratio of the abundances of the fragment ions and the difference for $X^+$ of $L_{ref}$ and $L_x$. This is shown in eqn. (1) where $I_{LrefX^+}$ and $I_{LxX^+}$ refer to the abundance of the ions $L_{ref}X^+$ and $L_xX^+$ and $E_{XIA(L)}$ refer to the X-ion affinity of the ligand L.

$$\ln \frac{I_{LrefX^+}}{I_{LxX^+}} = [E_{XIA(L_{ref})} - E_{XIA(L_x)}]C \qquad (1)$$

### Linear energy relationships in the gas phase

The competitive reactions in Scheme 1 take place across the same internal energy profile as the exchange reaction [eqn. (2)].

$$L_{ref}X^+ + L_x \rightleftharpoons L_{ref}XL_x^+ \rightleftharpoons L_{ref} + L_xX^+ \qquad (2)$$

In solution the ion-bound dimer $L_{ref}XL_x^+$ is unstable compared to both the reactants and the products whereas in the gas phase it is the most stable structure.

For the calculations of the activation energy $\Delta E_M^‡$ for an exchange reaction: $L_{ref}X^+ + L_x \longrightarrow L_{ref} + L_xX^+$ the Marcus equation has the following form [eqn. (3)].[3] $\Delta E_0^‡$ is the average

$$\Delta E_M^‡ = \Delta E_0^‡ + \frac{\Delta E}{2} + (\Delta E)^2/16\Delta E_0^‡ \qquad (3)$$

of the critical energies $E^i_{ref}$ and $E^i_x$ for the identity reactions $L_{ref}X^+ + L_{ref} \longrightarrow L_{ref} + L_{ref}X^+$ and $L_xX^+ + L_x \longrightarrow L_x + L_xX^+$ and $\Delta E$ is the difference in energy between the products and the reactants. The Marcus equation has successfully been used to calculate rate–equilibrium relationships for exchange reactions taking place in solution as well as in the gas phase.[4] It can be derived by regarding energy differences arising from structural changes removed from the reacting atoms as linear perturbations of the energies. This is a procedure which in principle is similar to that developed by Benson and Buss[5] for calculations of thermochemical values.

It has been shown by Murdoch[6] that the Marcus equation is a special example of a more general analysis. For proton exchange reactions between amines in the gas-phase it has been shown by Murdoch and Magnoli[7] that the energy well-depth for the formation of the monomers from the dimers can be calculated in exactly the same way. In that case $\Delta E_M^‡$ in eqn. (3) refers to the depth of the energy-well. The thermodynamic cycle is illustrated in Fig. 1. The critical energy $E_{ref}$, for the formation of $L_{ref}X^+$ from the dimer, is equal to $-\Delta E_M^‡$, when the reaction is written as in eqn. (2), and the critical energy $E_x$ for the formation of $L_x$ is equal to $-\Delta E_M^‡$, for the reverse reaction. $\Delta E_0^‡$ equals $-(E^i_{ref} + E^i_x)/2$, and when $E_{ref}$ and $E_x$ are the critical energies for the formation of $L_{ref}X^+$ and $L_xX$ from the dimer (Scheme 1); they can be calculated from eqn. (4).

$$E_{ref} = \frac{E^i_{ref} + E^i_x}{2} - \frac{E_{XIA(L_{ref})} - E_{XIA(L_x)}}{2} + \frac{[E_{XIA(L_{ref})} - E_{XIA(L_x)}]^2}{8(E^i_{ref} + E^i_x)} \qquad (4a)$$

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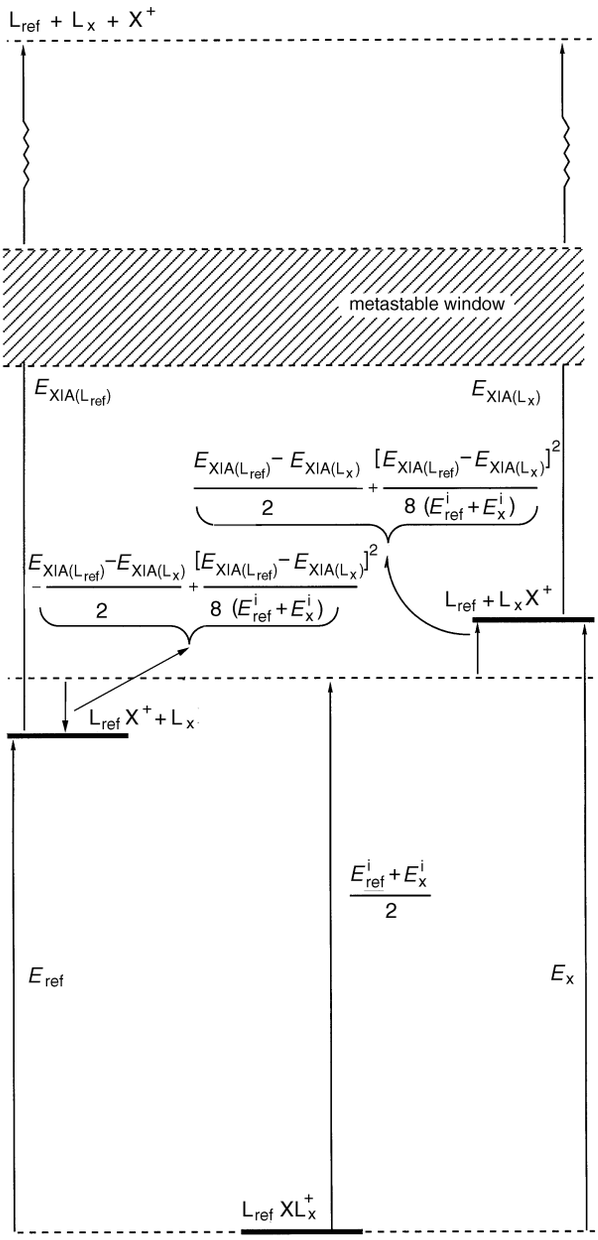


**Fig. 1** Illustration of how the Marcus equation is used to calculate the critical energies for decomposition of ion-bound dimers. The energy differences are not drawn to scale. The metastable window refer to the range of internal energies which the ion-bound dimers must have in order to react at rates which enable the detection of the fragments formed in the chosen field free region.

$$E_x = \frac{E^i_{ref} + E^i_x}{2} + \frac{E_{XIA(L_{ref})} - E_{XIA(L_x)}}{2} + \frac{[E_{XIA(L_{ref})} - E_{XIA(L_x)}]^2}{8(E^i_{ref} + E^i_x)} \quad (4b)$$

From these equations it is clear that $E_x - E_{ref}$ is equal to $E_{XIA(L_{ref})} - E_{XIA(L_x)}$, *i.e.* that the difference between the critical energies for the two competing reactions in Scheme 1 is equal to the reaction enthalpy for the exchange reaction [eqn. (2)]. When the reaction enthalpy is small compared to the well depth, as is the case for small amines, eqns. (4*a*) and (4*b*) reduce to the simple additivity scheme used earlier.[1d]

Rate–equilibrium relationships as analysed by Marcus and by Murdoch and Magnoli imply that the reacting species are in thermal equilibrium. This is not the case for unimolecular reactions observed within a given time window in a mass spectrometer either when the reactions involve metastable ions or when they are induced by collisions with an inert gas. In these cases the observed macroscopic rates and ion abundances must be expressed in terms of microscopic rate constants and internal energy distributions.

However, the observed relationship expressed by eqn. (1) is formally similar to a linear free energy relationship (LFER). The important differences are that it includes ion abundances instead of reaction rates and reaction enthalpies instead of free energies. It has previously been shown that when the critical energies for the decomposition of proton-bound amine dimers are calculated from a simple additivity scheme, this leads to a linear relationship as expressed in eqn. (1).[1d] The particular value of this rationalization of the kinetic method is that it avoids the introduction of common temperature. For the decomposition of metastable ions, it appears that the internal energy distribution cannot be very important as long as it does not change rapidly within fractions of a kJ $mol^{-1}$.

For protonated dimers, particularly amines, there are a number of measurements that enable a direct comparison between reaction enthalpies calculated by the Marcus equation and experimentally determined values. This provided the basis for Magnoli and Murdoch's work.[7] For other ion-bound species including alkali metal ions much fewer experimental values are available.[8]

Table 1 compares reaction enthalpies for the decomposition of mixed dimers with $Na^+$ and $K^+$ as the central ions. For these alkali metal ions the agreement between the calculated and experimental values is very satisfactory and this data set, albeit very limited, suggests that the Marcus equation may also be valid for calculations of reaction enthalpies for the decomposition of alkali metal ion-bound dimers.

## Experimental

A Kratos MS 50RF mass spectrometer with forward geometry was used for the linked scan (B/E) measurements. The datasystem was calibrated on a mixture of LiI and CsI. Fast atom bombardment was carried out with Xe (Messer-Griesheim, Germany) at *ca*. 9 kV from a saddle-field gun (Ion-Tech, UK). The post acceleration detector was operated at 15 kV. Fragment ions from metastable decompositions in the first field free region were detected by a linked scan (B/E) at 10 s/dec and 'raw data' acquisition. Typically, 15 scans were added for each measurement. The L-α-amino acids (Sigma) were typically dissolved in an aqueous solution of LiI (0.2 mol $dm^{-3}$) and trichloroacetic acid (5 mol $dm^{-3}$) in a mixture of dithiothreitol and dithioerythritol (1:1). On the four-sector instrument (Kratos Concept II HH) the precursor ions were selected by MS1 and collisionally activated (4 kV) in the region between the two mass spectrometers.

## Results

The order of lithium ion affinity we have obtained is shown in Table 2. All the cluster ions were analysed by a linked scan (B/E) on a two-sector instrument. In most of the scans only two fragment ions which could be assigned to the $Li^+$-bound amino acids were observed. However, the decomposition of some of the cluster gave rise to interference peaks the origin of which required analyses on a four-sector instrument. One such example is shown in Fig. 2(*a*). This shows the fragment ion spectrum of Glu-$Li^+$-Asp. The peaks at *m/z* 154.1 and *m/z* 140.1 can be assigned to $GluLi^+$ and $AspLi^+$ but the presence of a peak at *m/z* 134.1 which much be assigned to $AspH^+$, suggests a potential third competing fragmentation of the parent. A third fragmentation pathway, in addition to the two competing reactions shown in Scheme 1, would mean that the order of LIAs of Glu and Asp could not be determined from the intensities of the peaks at *m/z* 154.1 and 140.1. Similar peaks, corresponding to protonated monomers, were observed in the linked scans recorded from a number of $Li^+$-bound amino acid dimers. In order to determine the origin of these peaks, MS–MS

**Table 1** Comparison of measured reaction enthalpies for decomposition of mixed cluster ions and reaction enthapies calculated from the Marcus equation

| | | | | | | Reaction enthalpies for decomposition of dimers | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Ligands | | Affinities | | Identity reactions | | Measured | | Calculated from eqn. (4) | |
| | | $L_1$ | $L_2$ | $E_{XIA(L_1)}$ | $E_{XIA(L_2)}$ | $E^i(L_1)$ | $E^i(L_2)$ | $E(L_1)$ | $E(L_2)$ | $E_M(L_1)$ | $E_M(L_2)$ |
| | $Na^+$ | $H_2O$ | $SO_2$ | 24.0 | 18.9 | 19.8 | 16.6 | 20.2 | 16.9[a] | 20.8 | 15.6 |
| | $Na^+$ | $H_2O$ | $CO_2$ | 24.0 | 15.9 | 19.8 | 11.0 | 20.7 | 12.6[b] | 19.7 | 11.1 |
| | $K^+$ | $H_2O$ | $C_6H_6$ | 19.2 | 17.9 | 16.1 | 18.8 | 18.1 | 16.8[c] | 18.1 | 16.8 |

[a] From ref. 8(*b*). [b] From ref. 8(*c*). [c] From ref. 8(*a*).

**Table 2** Order of lithium ion affinity for α-amino acids[a]

| | Gly | Ala | Cys | Val | [Leu | Ile][b] | Ser | Pro | Thr | Phe | Met | Tyr | Asp | Glu | Trp | Lys | Asn | Gln | His |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Arg | | | | | | | | | | | | | | | | | | Arg | Arg |
| His | | | | | | | | | | | | | | | | | | His | |
| Gln | | | | | | | | | | Gln | | Gln | Gln | | Gln | | Gln | | |
| Asn | | | | | | | | | | Asn | Asn | Asn | | Asn | Asn | Asn | | | |
| Ly | | | | | | | | | | | | Lys | Lys | | Lys | | | | |
| Trp | | | | | | | | | | | | Trp | Trp | Trp | | | | | |
| Glu | | | | | | | | | | Glu | Glu | Glu | Glu | | | | | | |
| Asp | | | | | | | | | | Asp | Asp | Asp | | | | | | | |
| Tyr | | | | | | | | | Tyr | Tyr | Tyr | | | | | | | | |
| Met | | | | | | Met | | | Met | Met | | | | | | | | | |
| Phe | | | | | Phe | Phe | Phe | Phe | Phe | | | | | | | | | | |
| Thr | | | | | | Thr | Thr | Thr | | | | | | | | | | | |
| Pro | | | | | | Pro | Pro | | | | | | | | | | | | |
| Ser | Ser | Ser | Ser | Ser | Ser | Ser | | | | | | | | | | | | | |
| [Ile Leu][b] | | | Ile Leu | Ile Leu | | | | | | | | | | | | | | | |
| Val | Val | Val | Val | | | | | | | | | | | | | | | | |
| Cys | Cys | Cys | | | | | | | | | | | | | | | | | |
| Ala | Ala | | | | | | | | | | | | | | | | | | |

[a] Each amino acid indicated to the right of the first column can be assigned to the most abundant ion in the daughter ion spectrum of the ion-bound dimer which consists of the amino acid at the top of the column combined with that to the left in the row, *e.g.* decomposition of the lithium ion-bound dimer with the composition $AlaSerLi^+$ yields primarily $SerLi^+$ and consequently serine has a higher lithium ion affinity than alanine. [b] Isoleucine and leucine have the same exact mass and the order of their affinities is undetermined.

spectra of a selection of $Li^+$-bound amino acid dimers ($AspLysLi^+$, $AspGlnLi^+$, $AspGluLi^+$, $AsnTrpLi^+$, $GlnTrpLi^+$ and $LysTrpLi^+$) were recorded on a four-sector instrument. No ions corresponding to protonated amino acids were observed under these conditions, and the order of the abundances of the $Li^+$-bound monomers was the same as seen in the spectra obtained by the linked scan technique [Fig. 2(*b*)] so the additional peaks in the linked scans must be artefacts. The occurrence of interference peaks in linked scans has been analysed by Lacey and MacDonald.[9] The FAB ionization by which the $Li^+$-bound dimers were generated also produced abundant protonated dimers, and generally the protonated dimers were more abundant than the lithium ion bound dimers. The protonated dimers will fragment in the same manner as the $Li^+$-bound dimers. Thus, the reactions $Glu\text{-}H^+\text{-}Asp \longrightarrow AspH^+$ and $Asp_2H^+ \longrightarrow AspH^+$ will produce $AspH^+$ ions, some of which will have a kinetic energy that enables them to pass through the electric analyser and be detected at their correct *m/z* ratio. The spectrum shown in Fig. 1 was recorded without an energy resolving slit (β- slit) between the electric and the magnetic analyser. In later measurements, with a β- slit in place, this type of interference peak was not observed. The poor resolution in the selection of the parent ion under linked scans also meant that we observed some interference from decomposition of $^6Li^+$-bound dimers although the more abundant $^7Li^+$-bound ions were selected as the parent ion.

## Discussion

### Order of lithium ion affinity

The kinetic method has been used to estimate alkali ion affinities for a variety of compounds.[10] Affinities of organic compounds for other singly charged metal ions have also been studied by this method.[11]

For an order of ion affinities to be correctly determined by the kinetic method, the order of the rate constants for the competing reactions in Scheme 1 should be the same as the order of the critical energies. This means that analysis of metastable precursors, such as used in this work, is more likely to give the correct order of affinities than analysis of collisionally activated ions which on average will have more internal energy. Experimental support for this assumption is provided by the results of Grützmacher and Caltapanides[12] on the proton affinities of benzamides. In this work the proton affinities were determined in exchange experiments in an FT-ICR cell and compared with results from analyses of the reactions of metastable and collisionally activated proton-bound dimers. The order obtained from the analysis of metastable ions gave the same order as that obtained from the exchange experiments whereas the experiments with collisionally activated ions gave a different result.

The present results were obtained from analysis of metastable ions and this, together with the consistency of the results, suggests that the order obtained is correct. Further confirmation is provided by the agreement between the results obtained from metastable ions and from collisionally activated ions.

### Comparison with proton and sodium ion affinities

In Table 3 are shown the order of proton, lithium ion and sodium ion affinities of the 20 common α-amino acids. The order of $Cu^+$ affinity has also been established by the kinetic method.[13] An order of proton affinities was first determined

**Table 3** Comparison of proton, lithium ion and sodium ion affinities of the 20 common α-amino acids

| Order | Proton affinity[a] | | Lithium ion affinity[b] | | Sodium ion affinity[c] | |
|---|---|---|---|---|---|---|
| 1 | Arg | 242.8 | Arg | | Arg | |
| 2 | His | 230.5 | His | | His | |
| 3 | Lys | 228.7 | Gln | | Gln | |
| 4 | Gln | 226.9 | Asn | | Asn | |
| 5 | Trp | 223.5 | Lys | | Trp | |
| 6 | Pro | 222.4 | Trp | | Glu/Lys | |
| 7 | Glu | 222.3 | Glu | | | |
| 8 | Asn | 222.1 | Asp | | Tyr | |
| 9 | Met | 221.0 | Tyr | | Asp | |
| 10 | Tyr | 220.7 | Met | | Phe/Pro | |
| 11 | Phe | 219.9 | Phe | | | |
| 12 | Thr | 219.2 | Thr | | Thr | |
| 13 | Ile | 219.2 | Pro | | Met | |
| 14 | Leu | 218.7 | Ser | | Ser | |
| 15 | Asp | 218.1 | Ile/Leu | | Ile/Leu | |
| 16 | Val | 218.1 | | | | |
| 17 | Ser | 217.2 | Val | 54.8 | Val | 41.0 |
| 18 | Cys | | Cys | | Cys | |
| 19 | Ala | | Ala | 52.6 | Ala | 39.4 |
| 20 | Gly | | Gly | 51.0 | Gly | 37.9 |

[a] From refs. 1(*a*) and 1(*d*). [b] From this work and ref. 1(*c*). [c] From ref. 1(*c*).

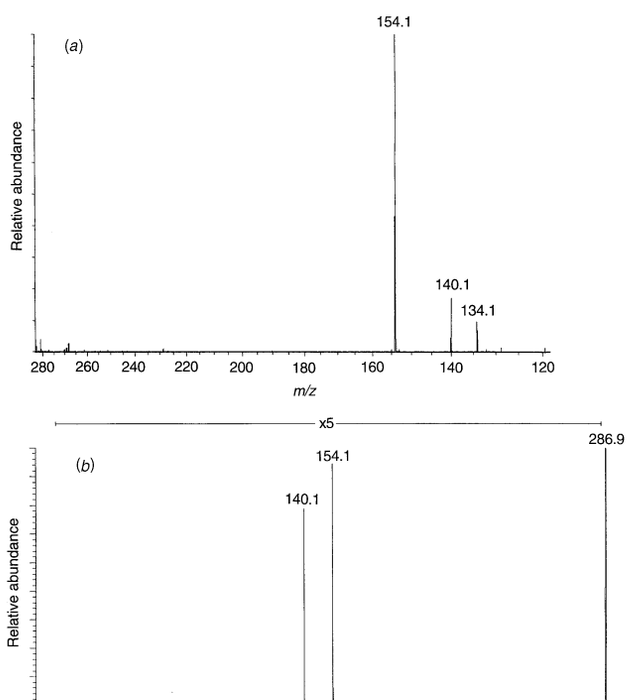


**Fig. 2** Spectra of fragment ions formed from the lithium ion-bound dimer Glu-Li$^+$-Asp. (*a*) Linked scan (B/E). The peaks are AspH$^+$ (*m/z* 134.1), AspLi$^+$ (*m/z* 140.1), GluLi$^+$. (*b*) MS–MS spectrum from four-sector instrument with CID of the parent ion Glu-Li$^+$-Asp (*m/z* 286.9). Notice that the *m/z* scales in (*a*) and (*b*) increase in opposite directions.

in this laboratory, and other laboratories have obtained very similar results with the kinetic method.[1a,d,14] Bracketing measurements on an FT-ICR instrument have given slightly different results.[15] Combined with the measurements of the gas-phase acidities, the reaction enthalpies for proton transfer reactions of α-amino acids in the gas phase are now available.[16]

The differences in the orders shown in Table 3 reflect the different ways protons on the one side and lithium and sodium ions on the other bind to organic molecules. Protons are bound by covalent bonds whereas purely electrostatic interactions are more important for the binding of lithium and sodium ions to organic molecules. This results in a change of the functional groups that are involved in the binding of the ion. The results of *ab initio* calculations indicate that whereas protons bind to the amine functionalities, binding of the alkali ions involves the carboxylic acid functionalities.[17] The experimental results show that the largest differences in the order are observed for the amino acids proline and aspartic acid. Owing to the lack of flexibility in the proline molecule, Li$^+$- and Na$^+$-bound proline will probably have structures which are similar to the Li$^+$- and Na$^+$-bound glycine structures. The high proton affinity of proline arises from binding of the proton to the secondary amine functionality. This is likely to be less important for binding of Li$^+$ and Na$^+$ for which interactions with the carboxylic acid group are more important. Furthermore, it has been shown that the lithium ion affinity of amines does not increase regularly with an increasing number of methyl substituents as does the proton affinity,[18] and that for a wide range of different organic compounds there is generally a poor correlation between the proton affinity and the lithium ion affinity.[19]

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