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Phosphonic and Phosphinic Acids: Monitoring Protolytic and Complex Formation Equilibria by Titration Dependend Stopped-Flow-NMR-Techniques

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PHOSPHONIC AND PHOSPHINIC ACIDS: MONITORING PROTO-LYTIC AND COMPLEX FORMATION EQUILIBRIA BY TITRATION DEPENDEND STOPPED-FLOW-NMR-TECHNIQUES.

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Abstract: Protolytic and complex formation equilibria are investigated by fully automated titration dependend NMR.

Substituted phosphonic and phosphinic acids e.g.

 $(R^1-R^2=OH, H, Alkyl, Aryl; R^3=-(CH_2)_{n^-}, -CH(CH_3)-; R^4=H, Alkyl,$ Aryl) and related structures give rise to protolytic and complex formation equilibria relevant to chemistry, biology, medicine, agriculture and technical chemistry. Handling these model systems as n-basic acids of general type H_nL the dynamic chemical shift $<\delta>$ in protolytic equilibria may be described as the weighted mean according to eqs (1)-(3):

(1)
$$\langle \delta \rangle = \Sigma_i \times (H_i L) * \delta(H_i L)$$
 $i = 0-n$

(2)
$$x(H_iL) = 10exp(lg\beta_i-i*pH)/(\Sigma_i 10exp(lg\beta_i-j*pH))$$
 $j = 0-n$

(3)
$$\lg \beta_i = \Sigma_k p K_{n-k+1}$$
 $k = 0-i$

 $b[x(H_iL): molar fraction of H_iL; \delta(H_iL): "ion-specific" chem. shift of H_iL;$
$$\label{eq:const.} \begin{split} \lg \S_i = + \, ^{10} log \S_i; \;\; \S_i: \;\; \text{stab. const. for } \; iH + L < \Longrightarrow H_iL; \;\; \S_0 = 1; \;\; pK_k = -1; \;\;$$
 $^{10}logK_k$; K_k : diss. const. for $H_{n-k+1}L < => H + H_{n-k}L$; $K_{n+1} = 1$].

Analogous expressions are derived involving stability constants in complex formation processes.

New tools were developed in our laboratories combining automated high-precision titration and NMR-methods in "Stopped-Flow" techniques of nuclei ^{31}P (and ^{19}F in case of fluorinated phosphonic acids, e. g. FCH₂CH₂PO₃H₂).

A solution of H_nL (in absence or presence of metal ions) is titrated vs. NaOH or TMAOH. One-dimensonal FIDs are taken for each step of titration, stored and Fourier transformed. The set of one-dimensonal NMR spectra is plotted in two-dimensional techniques (stacked plot, contour plot) correlating the observable chemical shift δ vs. pH or τ , the degree of titration. Two-dimensional spectra result resembling the more familiar COSY-type. A special program package SPECTROTIT was designed to organize fully automated Stopped-Flow-NMR. The hardware set up used is shown in fig. 1.

Protonation constants may be assigned conveniently from δ -pH-spectra for first order cases (pK_{i+1}-pK₁>3) as shown in several examples. Deand re-protonation schemes, hydrogen-bridges, conformational changes during protolysis are discussed. In addition Stopped-Flow-NMR is a powerful tool to analyze reaction mixtures and to differentiate diastereomers. Polyfunctional structures of technical importance like (H₂O₃PCH₂)₂NCH₂CH₂(CH₂PO₃H₂)₂ and phosphono-carboxylic acids are studied. Particular interests are paid towards biorelevant phosphanaloques of natural amino acids. Examples: NMR controlled titrations of phospha-alanin NH₂-CH(CH₃)-PO₃H₂ are shown in *figs. 2* and *3*. Results are discussed and supported by molecular modelling studies.

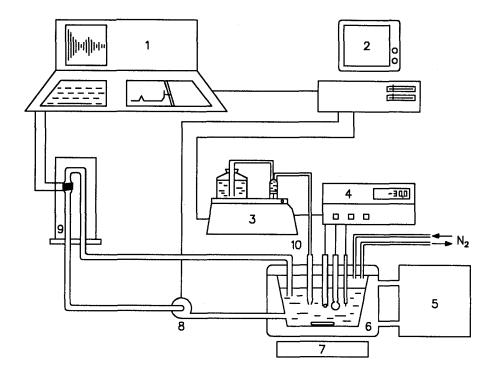


Figure 1: Hard ware set up for Stopped-Flow-NMR:

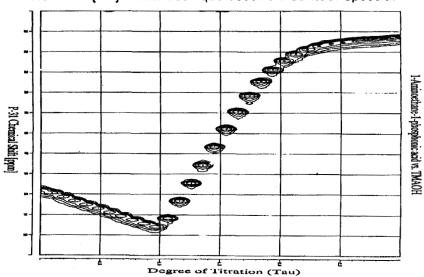
1: AM 200 SY NMR spectrometer [1]; 2: IBM compatible PC; 3: Motor burette T 200 [2]; 4: pH-Meter CG 841 [2]; 5: Thermostat, optional; 6: Titration vessel, home made; 7: magnetic stirrer; 8: magnetically driven pump [3]; 9: special probe head for Stopped-Flow-NMR [1] or home made version; 10: titration equipment (electrode N62, Pt1000 W2130) [2];

- [1] BRUKER Analytische Meßtechnik; [2] SCHOTT Geräte GmbH;
- [3] Reichelt-Chemie-Technik.

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Monitoring Protolytic and Complex Formation Equilibria by Stopped-Flow- 31 P{ 1 H}-NMR. Techique used: δ - τ contour spectra.



<u>Figure 2</u>: Titration of Phospha-Alanin vs. TMAOH. y-axis: $\delta_{min} = 12$ ppm, $\delta_{max} = 24$ ppm; x-axis: $r_{min} = 0$, $r_{max} = 3$.

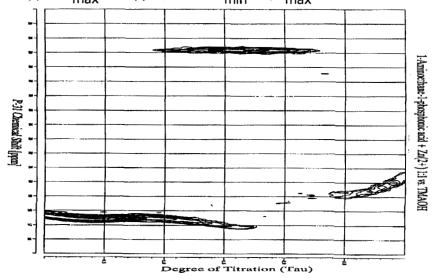


Figure 3: Titration of Phospha-Alanin + Zink (1:1) vs. TMAOH. yaxis: $\delta_{min} = 15$ ppm, $\delta_{max} = 32$ ppm; x-axis: $\tau_{min} = 0$, $\tau_{max} = 3$.