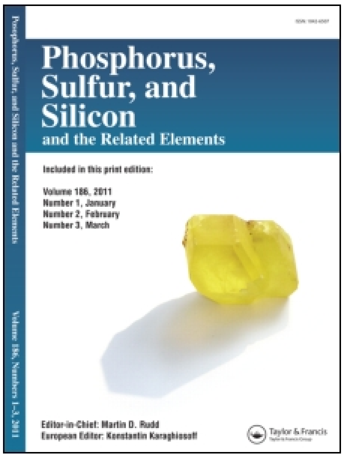

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Phosphonic and Phosphinic Acids: Monitoring Protolytic and Complex Formation Equilibria by Titration Dependend Stopped-Flow-NMR-Techniques

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

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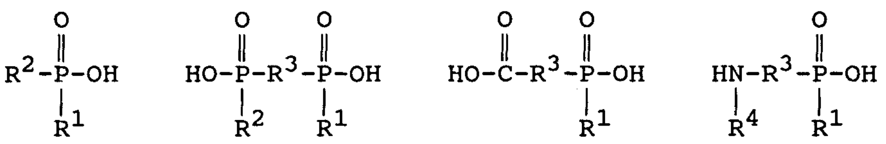
Abstract: Protolytic and complex formation equilibria are investigated by fully automated titration dependend NMR.

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):

$$(1) \quad <\delta> = \Sigma_i\, x(H_iL)*\delta(H_iL) \qquad i=0\text{-}n$$

$$(2) \quad x(H_iL) = 10\exp(\lg\beta_i - i*pH)/(\Sigma_j\, 10\exp(\lg\beta_j - j*pH) \qquad j=0\text{-}n$$

$$(3) \quad \lg\beta_i = \Sigma_k\, pK_{n-k+1} \qquad k=0\text{-}i$$

b[$x(H_iL)$: molar fraction of H_iL; $\delta(H_iL)$: "ion-specific" chem. shift of H_iL; $\lg\beta_i = +{}^{10}\log\beta_i$; β_i: stab. const. for $iH+L$ <==> H_iL; $\beta_0=1$; $pK_k=-{}^{10}\log K_k$; 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. $FCH_2CH_2PO_3H_2$).

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}-$pK_1 > 3$) as shown in several examples. De- and 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 $(H_2O_3PCH_2)_2NCH_2CH_2(CH_2PO_3H_2)_2$ and phosphono-carboxylic acids are studied. Particular interests are paid towards biorelevant phospha-analoques of natural amino acids. Examples: NMR controlled titrations of phospha-alanin NH_2-$CH(CH_3)$-PO_3H_2 are shown in *figs. 2* and *3*. Results are discussed and supported by molecular modelling studies.

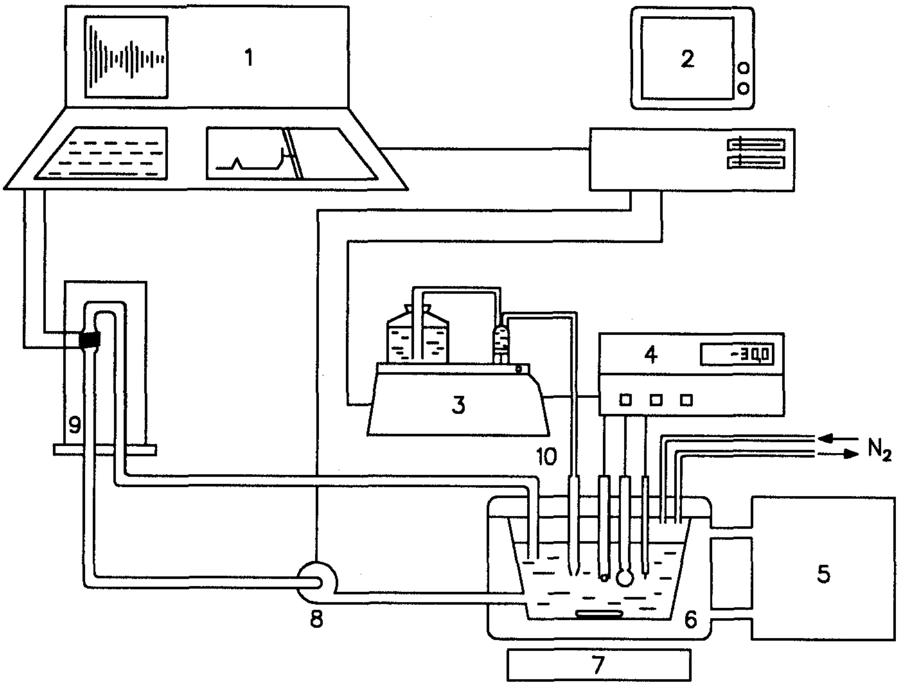


Figure 1: Hard ware set up for Stopped-Flow-NMR:

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-$^{31}P\{^1H\}$-NMR. Techique used: δ-τ contour spectra.

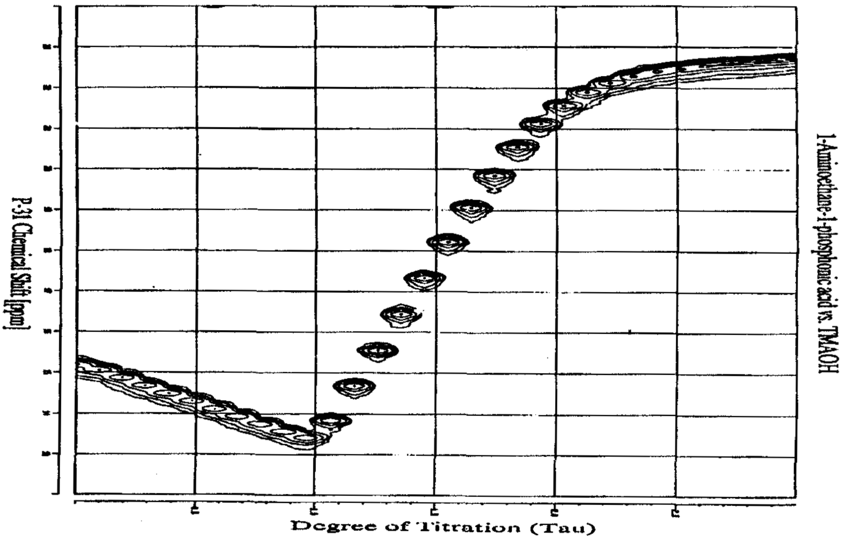

Figure 2: Titration of Phospha-Alanin vs. TMAOH. y-axis: $\delta_{min}=12$ ppm, $\delta_{max}=24$ ppm; x-axis: $\tau_{min}=0$, $\tau_{max}=3$.

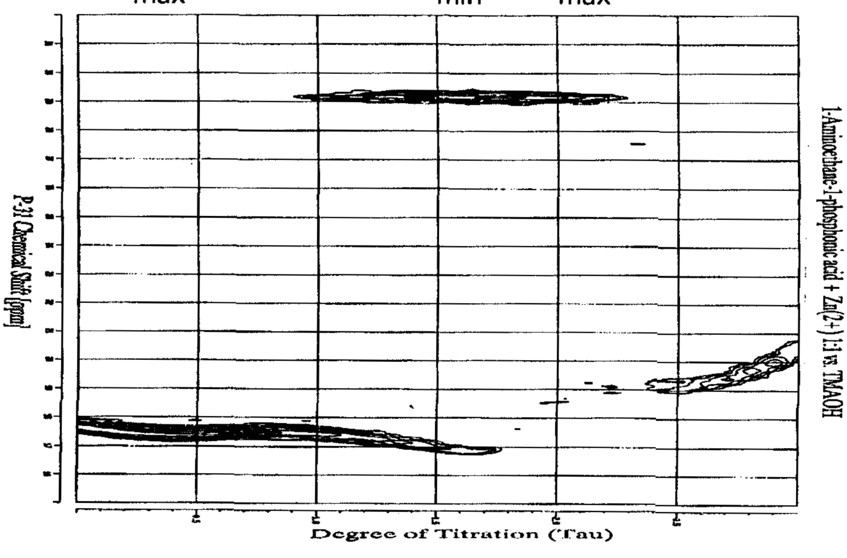

Figure 3: Titration of Phospha-Alanin + Zink (1:1) vs. TMAOH. y-axis: $\delta_{min}=15$ ppm, $\delta_{max}=32$ ppm; x-axis: $\tau_{min}=0$, $\tau_{max}=3$.