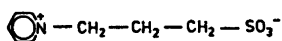


## Synthesis of Pyridinium-1-propane-3'-sulfonate (PPS). A Powerful Electron Scavenger and Positronium Inhibitor

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The study of the hydrated positron ( $e_{aq}^+$ ) and the physical and chemical reactions in which it participates is of increasing interest, as it complements studies of the hydrated electron important in radiation chemistry.<sup>1</sup> Furthermore, due to the short lifetime of positrons (300–500 ps), it is possible to study very fast kinetics by employing positron annihilation techniques,<sup>2</sup> thereby gaining access to information not easily obtainable by other means. However, when positrons are injected into, e.g., an aqueous medium, positronium (Ps), a bound state between a positron and an electron, is formed as well as  $e_{aq}^+$ . As Ps behaves quite differently from  $e_{aq}^+$ , it is most often advantageous to dispose of the disturbing Ps-parts of a measurement, and concentrate on  $e_{aq}^+$  itself. We give here the rationale which originally led to the proposal of using pyridinium-1-propane-3'-sulfonate (1, PPS) as an inhibitor of Ps formation in water, and we disclose the detailed synthetic route giving high purity PPS together with some important physical properties of PPS.



1

A few years ago a new model for Ps formation was proposed: the spur reaction model.<sup>3</sup> According to this, Ps is assumed to be formed by a reaction between a spur electron and a positron in the positron spur. The positron spur is the assembly of reactive intermediates (the positron, electrons, ions, etc.), which is created when the positron transfers the last amount of its kinetic energy to the stopping medium. Ps formation must compete with electron-ion recombinations, with electron and positron reactions with solvent and scavengers, and with electron and positron diffusion out of the spur. The removal of electrons from the spur is correspondingly assumed to restrain Ps formation, and as a result of this, electron acceptors are expected to inhibit Ps formation by scavenging the electrons from the spur. However, it is of paramount importance that the electron acceptor be able to trap and localize the electron for periods longer than approximately  $10^{-11}$  s, which is the

Ps formation time.<sup>4</sup> Likewise, acceptor reactions with the spur electrons taking place after a time typical for the Ps formation will have virtually no impact on the Ps formation.

It has been argued that large acceptor molecules, in which the excess energy obtained by attaching an electron can be rapidly distributed amongst several degrees of vibrational freedom, should act better as Ps inhibitors than smaller electron acceptors.<sup>5</sup> Likewise, experiments indicate that electron acceptors already engaged in weak charge transfer interactions can dispose of part of the excess energy by transferring it to their partners by disrupting the interaction. Small electron acceptors by themselves, on the other hand, do not have any easy way of accommodating the excess energy, and may expell the electron again within  $10^{-13}$  s.<sup>5</sup>

PPS is a zwitterion with a very high solubility in water. Solutions 3.5 M in PPS are easily made. The pyridinium part of the molecule should warrant good electron accepting properties, and it is a fairly large species. The ability to accept electrons was indeed verified by Hickel, who determined its rate constant with hydrated electrons to be  $(2.5 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>6</sup> Furthermore, PPS carries the possibility of weak intra-molecular charge transfer interactions, as the propane chain can allow the sulfonate group to approach the pyridinium system, thereby facilitating any such interactions. An indication in favour of this really happening is found in the ultraviolet spectrum of PPS in water, where an absorption is found at 210 nm. This absorption is neither present in pyridinium perchlorate nor in sodium methanesulfonate, and may hence be interpreted as a charge transfer absorption.

With these characteristics PPS ought to be a very efficient Ps inhibitor, and as is visualized in Fig. 1 this is indeed true.

*Experimental.* NMR spectra were recorded on a JEOL JNM-FX100 instrument operated at 99.60 MHz ( $^1\text{H}$ ) and at 25.05 MHz ( $^{13}\text{C}$ ) with a broad band noise  $^1\text{H}$  decoupling. UV spectra were obtained with a CARY 16 instrument, and IR spectra with a Perkin Elmer model 221 spectrophotometer. Melting points are uncorrected.

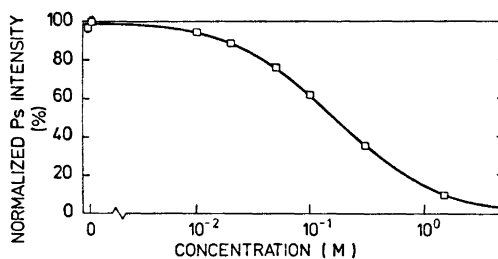


Fig. 1. Normalized positronium intensity versus concentration of PPS. The uninhibited positronium yield in water is 36 %.

**Pyridinium-1-propane-3'-sulfonate (PPS).** To a solution of 1,3-propanesultone (1.5 mol; Fluka-Buchs, Switzerland) in dioxane (1600 ml), pyridine (1.6 mol) was added in small portions during a period of 5 min. The solution was then heated to reflux for 2 h, after which the resulting thick crystal slurry was allowed to cool to ambient temperature. The solid was isolated by filtration on a coarse glass filter funnel, and was washed with dioxane (300 ml) followed by ether (500 ml). The yield was 85 % of white microcrystals melting at 274–276 °C. The crude product was purified by recrystallization from 90 % ethanol (18 ml/g) to give an 80 % recovery of well-formed colourless crystals melting at 277–278 °C. Anal.  $C_8H_{11}NO_3S$ : C, H, N, S.  $^1H$  NMR( $D_2O$ )  $\delta$  8.97 (2H, d,  $J$  5.4 Hz; C2 + C6), 8.65 (1H, t,  $J$  7.8 Hz; C4), 8.18 (2H, t,  $J$  6.5 Hz; C3 + C5), 4.86 (2H, t  $J$  7.3 Hz; C3'), 3.07 (2H, t,  $J$  7.5 Hz; C1'), 2.54 (2H, q,  $J$  7.2 Hz; C2').  $^{13}C$  NMR( $D_2O$ )  $\delta$  148.21(C4), 146.69(C2 + C6), 130.75(C3 + C5), 62.40(C3'), 49.66(C1'), 28.80 (C2'). UV[ $H_2O$ , ( $\epsilon$ )] 265 (sh), 257 ( $4.1 \times 10^3$ ), 254 (sh), 210 ( $4.8 \times 10^3$ ) nm. IR(KBr): 3020(m), 2990(s), 2980(m), 1620(m), 1490(s), 1475(s), 1460(s), 1230(s), 1210(s), 1190(vs), 1160(s), 1130(s), 1030(vs), 760(s), 680(s)  $cm^{-1}$ .

*Supplementary Data.* Elemental analysis of PPS:

	C	H	N	S
Calc.	47.75 %	5.51 %	6.96 %	15.93 %
Found	47.60 %	5.43 %	6.79 %	16.18 %

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## Non-aqueous Cyclic Voltammetry at Ten Kilovolts per Second

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The two factors which limit the use of cyclic voltammetry for the study of the kinetics of homogeneous reactions coupled to charge transfer are the voltage sweep rate and the precision to which peak current ratios can be measured. The first factor deals with the range of rate constants which can be studied and the second with the precision of the rate constant measurements. A voltage sweep rate of 100  $V s^{-1}$  allows one to examine reactions with rate constants up to about  $5 \times 10^3 s^{-1}$  while a sweep rate of 10  $kV s^{-1}$  would extend that range up to about  $5 \times 10^6 s^{-1}$ . The problem of measuring peak current ratios for ordinary cyclic voltammetry is so severe that rate constants obtained in this way are very approximate.

We have recently described the use of derivative cyclic voltammetry to give very precise peak potential measurements which in turn allowed the precise determination of rate constants for heterogeneous charge transfer.<sup>1</sup> Here we report a further application of the technique which has enabled us to make quantitative determination of the peak current ratio during the reduction of anthracene in *N,N*-dimethylformamide (DMF) at a voltage sweep rate of 10  $kV s^{-1}$ .

Cyclic voltammetric measurements were made on a solution of anthracene (3.0 mM) in DMF containing  $Bu_4NBF_4$  (0.1 M) using a specially constructed  $Ag/AgClO_4$  (0.1 M) in aqueous  $NaClO_4$  (1.0 M) reference electrode. The tip of the reference electrode was made of porous glass and ground flat so that it could be placed in very close proximity to the mercury-covered platinum electrode (0.8 mm diameter). Five determinations of the derivative peak current ratio during the quasi-reversible reduction process are summarized in Table 1. Each value given is the average of ten scans and the errors listed are the standard deviations. The average, 0.98, is very close to the expected value 1.0. The derivative response is demonstrated in Fig. 1. Fig. 1a represents the observed signal and 1b is that obtained after subtracting out the curve for an identical solution which did not contain anthracene. The difference in the two curves is primarily the large signals at the points where the scan is initiated, reversed and terminated. These signals, connected with the potentiostat response, do not interfere

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