Pyridinium-1-propane-3'-sulfonate (PPS). To a solution of 1.5-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. C12H11NO8S: C, H, N, S. 

1H NMR (D2O) δ 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').

13C NMR (D2O) δ 148.21 (C4), 146.69 (C3 + C6), 130.75 (C3 + C5), 62.40 (C3'), 49.66 (C1'), 28.80 (C2'). UV[H2O, (s)] 265 (sh), 257 (4.1 × 10³), 254 (sh), 210 (4.8 × 10⁴) 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:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc</td>
<td>47.75%</td>
<td>5.51%</td>
<td>6.96%</td>
<td>15.93%</td>
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<tr>
<td>Found</td>
<td>47.60%</td>
<td>5.43%</td>
<td>6.79%</td>
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</table>


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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 × 10⁸ s⁻¹ while a sweep rate of 10 kV s⁻¹ would extend that range up to about 5 × 10¹⁰ 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. 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 Bu₄NBF₄ (0.1 M) using a specially constructed Ag/AgClO₄ (0.1 M) in aqueous NaClO₄ (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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when the starting and switching potentials are properly selected. The exact current ratio during a kinetic process is dependent upon the switching potential relative to the reversible potential. Thus, even though we can make the peak current ratio measurement to a very high degree of precision some error can be expected in rate constants. Nevertheless, our results indicate the possibility for using cyclic voltammetry to measure rate constants approaching $10^6$ s$^{-1}$ and small errors can be tolerated.

We are aware of only one other attempt to use cyclic voltammetry in a quantitative manner at very high sweep rates. Savéant and Tessier analyzed voltammograms measured at sweep rates up to 2300 V s$^{-1}$ and concluded that measurements in the kilovolt region are possible. The latter authors used an analysis which requires very precise current-potential data. This brings in the possibility of large errors due to uncompensated resistance and to potentiostat response. The peak current ratio measurements that we describe are much less sensitive to the latter two factors and are thus much easier to apply.

Acknowledgement. We gratefully acknowledge the Norwegian Research Council for Science and the Humanities for support for E. A.


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**Table 1.** Derivative peak current ratios during the reduction of anthracene in DMF.*

<table>
<thead>
<tr>
<th>Measurement</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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</thead>
<tbody>
<tr>
<td>$I_a'/I_c'$</td>
<td>0.976</td>
<td>0.974</td>
<td>0.975</td>
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<td>0.975</td>
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<tr>
<td>Error $^c$</td>
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<td>0.0044</td>
<td>0.0039</td>
<td>0.0062</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

* Voltage sweep rate equal to 10 kV s$^{-1}$. Measurements made with a PAR 173D potentiostat.

$^b$ Ratio of anodic to cathodic first derivative peak currents.

$^c$ Standard deviation in ten measurements.