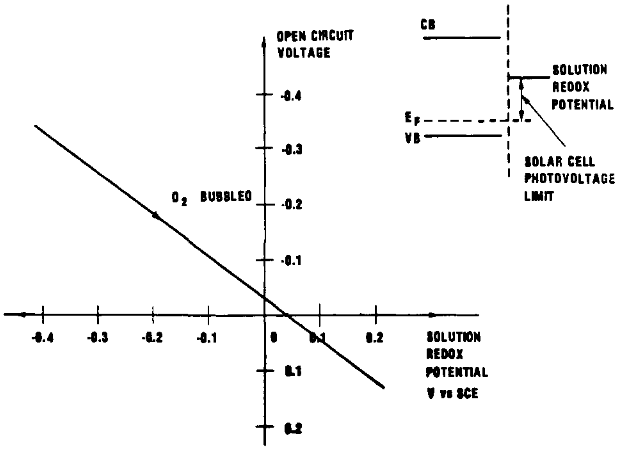

Figure 1. p-Si/VCl_3-VCl_2-HCl/C cell open-circuit voltage under tungsten–halogen illumination recorded against the solution redox potential. Insert on top right shows theoretical expectation for ordinate with no pinning by surface states and sufficient light intensity to flatten the bands. The silicon Fermi level intercept shown on the abscissa is negative of the true flat-band condition to the extent that the ordinate values are below the light intensity saturation limit.

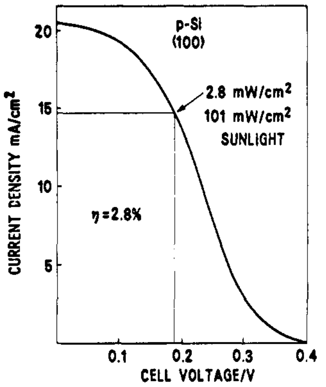

Figure 2. Current-voltage characteristics of the cell ⟨100⟩ p-Si/0.35 M total V(II) + V(III), 4 M HCl (E_{soln} = –0.47 V vs. SCE)/C, under 101 mW cm^{-2} sunlight.

passage of 20 000 C cm^{-2} under tungsten–halogen illumination over a 120-h period. The cell was placed under a 10-Ω load, wherein the p-Si potential was ~+80 mV from its short-circuit value throughout. Dissolution by 2 e/mol in that time would correspond to a loss of 2800 mg cm^{-2} and by 4 e/mol to 1400 mg cm^{-2}. In this experiment the initial current was 66.7 mA cm^{-2}, which declined after 120 h to 37.5 mA cm^{-2} (56% of initial). These approximate 2 and 3 times, respectively, the levels observed at short circuit under AM1 solar illumination. In a 116-h run with total vanadium and HCl increased to 1.8 and 6 M, respectively, and more focused white light, an initial 71.7 mA cm^{-2} reading declined to 51.7 (72% of initial) after passage of 23 700 C cm^{-2}.

Figure 2 shows the current–voltage curve of the cell, p-Si/0.35 M total V(II)–V(III), 4 M HCl (E_{soln} = –0.47 V vs. SCE)/C, at 101 mW cm^{-2} irradiance of natural sunlight. The maximum power output is 2.8 mW cm^{-2} for a solar-to-electrical power conversion efficiency of 2.8%. The short-circuit current of 20.4 mA cm^{-2} may be compared to the theoretical limit of ~43 mA cm^{-2} for the 1.1-eV band gap of Si.[6]

The initial condition of the Si surface is critical to cell performance. The highest current is observed after a 10–30-s CP-4 etch. The current drops, however, over a short time (~1 min) to a relatively stable level. During this period some H_2 evolution is detected when the electrode is held within +100 mV of the short-circuit potential. After a 30% HF etch the current is at the level to which the CP-4-etched electrode drops after the first minute. No H_2 evolution, even at short circuit, is observed after this etch.

The respectable stability and quantum efficiency obtainable with silicon in these strongly acidic environments, a shift of photovoltage as expected by Schottky models without pinning, and the variations in behavior observed with the two etchants and with cell cycling can be reconciled with the properties of the Si interface. Since SiO_2 is an excellent insulator whose presence is responsible for failure of n-Si photoanodes in aqueous environments, the thickness of any SiO_2 film must be limited to tunneling dimensions, permitting significant currents to be drawn, as is the present case for p-Si.

Ellipsometry shows that the surface of silicon exposed to air can be schematically represented as Si/SiO_x/SiO_2.[7] The composition denoted by SiO_x is apparently not removed by HF, but is removed by CP-4, and is reformed rapidly in the acidic solution, even in the presence of a strong reducing agent. A thicker (SiO_2) film forms on standing near open circuit, as is evident from hysteresis in the I–V curves, if the voltage is allowed to approach open circuit. However, even on long operation at high light near short circuit, or even near the maximum power point, the thickening of the SiO_2 layer is extremely slow and approaches a steady-state value. Exhaustive stability runs would be required to establish the limit of the maintenance of output current. Weight loss measurements establish that surface attack is restricted to minimal dimensions in the sense of removal of electrode material.

The shifts in cell voltage with solution redox potential indicate that, in spite of the involvement of electrode films shown by the cyclic cell and etching results, the interface is responsive to solution Nernst potentials. This observation is consistent with recently reported results for p-InP[8] and in contrast to recent publications asserting wide applicability of pinning of surface Fermi levels for p-Si and other covalent semiconductors.[1-4] While the p-Si/VCl_2–VCl_3–HCl/C cell is not as stable or as efficient as that with a p-InP photocathode, the stability and efficiency are the best for any Si-based photoelectrochemical cell so far.

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Absence of Internal Return in the Reaction of (4-Nitrophenyl)nitromethane with Amine Bases in Toluene Solution. Implication on Unusually Large Isotope Effects Reported for This Reaction

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Very large isotope effects have been reported for the acid ionization of (4-nitrophenyl)nitromethane in nonpolar solvents in the presence of strongly basic amine proton acceptors (eq 1).[1]

$$ArCH_2NO_2 + B \rightleftharpoons ArCHNO_2^-HB^+ \qquad (1)$$

Some of these rate ratios are as great as k_H/k_D = 50 at 25 °C, which exceeds by a considerable margin the maximum value attributable to complete loss of all of the zero-point energy of a C–H bond. These isotope effects were therefore interpreted in terms of quantum-mechanical tunneling through the reaction barrier, and they soon came to be regarded as among the best evidence for the tunnel effect in proton-transfer reactions.[2]

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(1) (a) Caldin, E. F.; Mateo, S. *J. Chem. Soc., Chem. Commun.* **1973**, 854–855. (b) *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1876–1904. (c) *Ibid.* **1976**, *72*, 112–121.

Table I. Rates of Exchange and Isotope Effects in the Reaction of 4-(Nitrophenyl)nitromethane with Bases in Toluene Solution at 25 °C

base	k_T, M^{-1} s^{-1}		k_H/k_T	$(k_H/k_T)^{1/1.442}$	k_H/k_D
	observed	estimated[a]			
tetramethylguanidine	25.0 ± 0.6	4.75 ± 0.34	45.8 ± 1.1	14.2 ± 0.2	45 ± 2[b]
quinuclidine	63.8 ± 1.5	21.8 ± 0.9	17.2 ± 0.4	7.20 ± 0.12	15.6 ± 0.6[c]
triethylamine	2.71 ± 0.04	2.08 ± 0.13	24.3 ± 0.5	9.14 ± 0.13	11.0 ± 0.7[c]
tri-*n*-butylamine	0.675 ± 0.008	0.480 ± 0.032	31.7 ± 0.5	11.0 ± 0.1	14 ± 1[c]
diethyl-*n*-butylamidine	12.6 ± 0.2	9.93 ± 0.81	27.1 ± 1.4	9.84 ± 0.36	11.7 ± 1.0[d]
diethyl-*n*-nonylamidine	34.9 ± 0.1	19.6 ± 1.2	11.4 ± 0.6	5.39 ± 0.19	8.0 ± 0.3[d]
pentamethylguanidine	499 ± 5	518 ± 13	44.1 ± 1.1	13.8 ± 0.2	13.7 ± 0.4[e]

[a] Estimated by using $k_T = k_H/2(k_H/k_D)^{1.442}$ and published[1,10] values of k_H and k_H/k_D. [b] Reference 1b. [c] Reference 1c. [d] Reference 10a. [e] Reference 10b.

It was recently pointed out, however, that these large isotope effects could be experimental artifacts if isotopic exchange, and consequent loss of deuterium from the deuterated substrate, occurred under the ionization-reaction conditions.[3] Detailed kinetic analysis showed that values of k_D would then be erroneously low, and treatment of some data under this assumption reduced very large isotope effects to values of the order of k_H/k_D = 10–15.[4]

This criticism was countered by the argument that the rate of hydrogen exchange in this substrate was not known and that internal return[5] could easily make exchange much slower than ionization;[6] in that eventuality, deuterium would not be lost during the course of kinetic measurements, and the original claim of very large isotope effects would stand. We wish to report that we have now measured rates of hydrogen exchange in this system and find internal return to be absent.

We performed our work using (4-nitrophenyl)nitromethane-*1-t*.[7] This material, in the presence of amine bases in toluene solution, loses essentially all of its tritium smoothly under conditions where at equilibrium only a few percent of the substrate is converted to ion pair; this indicates that the process being followed is in fact isotope exchange and not just ionization.[8] Rates of loss of tritium are accurately first order over their entire course, and first-order rate constants are proportional to amine base concentration.[9] Second-order specific rates of exchange, obtained by least-squares analysis of the relationship between first-order rate constants and base concentration, are listed in column 2 of Table I.

Comparison of these data with specific rates of ionization of the C–T bond (Table I, column 3), estimated by using published values of k_H and k_H/k_D[1,10] and the Swain–Schaad relationship[11] to convert k_H/k_D into k_H/k_T, shows that in no case is exchange slower than ionization; internal return must therefore be absent. In fact, in all cases but one, the measured rate of exchange exceeds the estimated rate of ionization by a substantial amount. This is an implausible situation, but that can be remedied if smaller values of k_H/k_D are used in the ionization rate constant estimates; smaller values are of course also required by the fact that the isotopic integrity of the deuterated substrate is not being maintained by internal return.

When internal return is absent, rates of isotope exchange are equal to rates of ionization. The detritiation rate constants measured here may therefore be combined with published values of k_H to give tritium isotope effects on ionization. These, together with corresponding values of k_H/k_D $(=(k_H/k_T)^{1/1.442})$, are listed in columns 4 and 5 of Table I. It may be seen that these isotope effects are generally lower than the previously published values (column 6); in particular, the very large isotope effect reported for tetramethylguanidine as the proton acceptor, k_H/k_D = 45, is now reduced to k_H/k_D = 14. This is still a rather large isotopic rate ratio, and it could signify some proton tunneling. Support for this idea comes from the fact that rates of detritiation in the presence of this base measured over the temperature interval 5–45 °C gives a difference in activation energies of $E_a^T - E_a^H = 3.2 \pm 0.2$ kcal mol^{-1} and a ratio of preexponential factors of $A_T/A_H = 6 \pm 2$. These are just outside the limits generally considered to signify no tunneling; they contrast with the values found for detritiation by quinuclidine, $E_a^T - E_a^H = 1.5 \pm 0.1$ kcal mol^{-1} and $A_T/A_H = 0.7 \pm 0.1$, and triethylamine, $E_a^T - E_a^H = 1.4 \pm 0.6$ kcal mol^{-1} and $A_T/A_H = 0.5 \pm 0.5$.

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(7) This substance was prepared by an adaptation of the method used for making the deuterated substrate.[1]

(8) The isotopic label accumulates in the amine, present in large excess, if the latter has an exchangeable N–H bond, and in adventitious water, which cannot be removed from the system completely. We found that deliberately added water, in concentrations up to its saturation solubility (0.02 M), has no effect on detritiation rates.

(9) This is strictly true only at base concentrations sufficiently low to give little ion-pair formation; at higher concentrations the order in base falls off according to expectation for an accompanying "dead end" reaction giving an ion pair with the isotopic label in a nonexchangeable position: $ArCHTNO_2 + B \rightleftharpoons ArCTNO_2^-HB^+$.

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Kinetics of the Reaction of (4-Nitrophenyl)nitromethane with Tetramethylguanidine in Toluene

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The proton-transfer reaction of the carbon acid (4-nitrophenyl)nitromethane (4-NPNM; $NO_2C_6H_4CH_2NO_2$; AH_2) with tetramethylguanidine (TMG; $HN{=}C(NMe_2)_2$; BH) and the corresponding deuteron-transfer reaction (eq 1), in various aprotic

$$AH_2 + BH \underset{k_b^H}{\overset{k_f^H}{\rightleftharpoons}} AH^-HBH^+ \text{ and } AD_2 + BH \underset{k_b^D}{\overset{k_f^D}{\rightleftharpoons}} AD^-DBH^+ \qquad (1)$$

solvents, were studied by Caldin and Mateo.[1] With base in excess (concentration *b*), the kinetics were pseudo first order, and the

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