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Kinetics and Thermochemistry of the Ethyl Radical. The Induction Period in the Pyrolysis of Ethane

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Ethane has been pyrolyzed at 902 K and 1.8×10^{-4}–4.5×10^{-3} mol L^{-1} in a flow system. An induction period was interpreted as evidence of the initial increase in the ethyl radical concentration. Rate constants for the following reactions have been determined: $2C_2H_5 \rightarrow C_4H_{10}$, $k_{5a} = (9 \pm 2) \times 10^9$ L mol^{-1} s^{-1}; $2C_2H_5 \rightarrow C_2H_6 + C_2H_4$, $k_{5b} = (4 \pm 1) \times 10^9$ L mol^{-1} s^{-1}. Quoted uncertainties are standard deviations. The pressure dependences of the rate constants determined for reactions $C_2H_6 \rightarrow 2CH_3$ and $C_2H_5 \rightarrow C_2H_4 + H$ were interpreted by unimolecular reaction rate theory. When the limiting high-pressure value of k_1 was combined with literature data on the reverse rate constant and with the calculated entropy change for this reaction, the heat of formation of the methyl radical, $\Delta_f H^\circ_{298}(CH_3)$, was confirmed to be 147 ± 2 kJ mol^{-1}. Similarly, $\Delta_f H^\circ_{298}(C_2H_5)$ was found to be 119 ± 2 kJ mol^{-1}.

Introduction

Heats of formation of radicals are of fundamental importance to our understanding of bonding and of many reactions. Nevertheless, the values of some of the simplest of these quantities are still controversial. In particular, values between 108 and 121 kJ mol^{-1} have recently been quoted[1-5] for the heat of formation of the ethyl radical, $\Delta_f H^\circ(C_2H_5)$.

The present article is the first full report[6,7] of a new approach to this matter. The pyrolysis of ethane has been investigated in a flow system. Conventionally, this process had been interpreted by making the steady-state approximation for the free radical intermediates.[8] In this way it was only possible to determine the rate constant for the initiation reaction and certain quotients of other rate constants. In the present work, product yields have been measured at very short reaction times when the ethyl radicals had not reached their steady-state concentration. The results enable calculation of the concentrations of ethyl radicals and of independent rate constants for three reactions of ethyl radicals. From two of these rate constants and from data in the literature, it has been possible to calculate $\Delta_f H^\circ(C_2H_5)$. The experimental results also permit the determination of $\Delta_f H^\circ(CH_3)$.

Experimental Section

The basic apparatus and the experimental techniques were the same as used in ref 6 and 8. Ethane (Matheson research purity, 99.96%) was purified by pumping off lower boiling fractions at 77 and 113 K. The remaining impurities observed by gas chromatography were ethylene and methane, with mole fractions of 3×10^{-5} and $(1-3) \times 10^{-6}$, respectively.

Reactors were constructed of cylindrical quartz tubing, with internal diameters and surface to volume ratios (S/V) of 0.2 cm (23 cm^{-1}), 0.3 cm (14 cm^{-1}), 0.4 cm (8.8 cm^{-1}), 0.8 cm (9.9 cm^{-1}), and 1.7 cm (3 cm^{-1}). The latter two reactors had 0.4-cm-o.d. axial thermocouple wells; the others had external thermocouple wells. The reactors were cleaned with concentrated HNO_3 and rinsed with distilled H_2O. During an experiment, a 45-cm-long section was heated by a resistive furnace. The reactor temperature was measured with a platinum/platinum–13%-rhodium thermocouple, calibrated against the melting point of gold. The average residence time, t, of molecules in the reactor was calculated from the measured pressure, temperature, and dimensions of the reactor and from the ethane flow rate.[8]

Samples of reactor effluent were analyzed by gas chromatography on a 4.75-m long, 10% squalane on Chromosorb P (NAW100/120 mesh) column in an ice bath. The column, flame ionization detector, and electronics were calibrated each day by injecting known pressures of a mixture of 5.0×10^{-4} mole fraction ethylene and 7.7×10^{-6} mole fraction methane in nitrogen.

Results

Ethane at concentrations from 1.8×10^{-4} to 1.8×10^{-3} mol L^{-1} was pyrolyzed at reactor temperatures of 902 ± 1 K. Residence times, t, of molecules in the reactor were between 0.01 and 2.0 s, resulting in reactant conversions of 0.2% or less.[9] Chromatographically measured product concentrations were divided by the corresponding values of t to determine chordal rates, $[X]/t$. The rate of formation of methane was found to be independent of t; at each reactant concentration, values of $[CH_4]/t$ were averaged to find $\overline{[CH_4]/t}$. The rate of formation of ethylene, as shown in Figure 1, increased with increasing t for $t \lesssim \tau_i$, an induction period, and then approached a constant plateau rate, $R^{ss}_{C_2H_4}$, for $t > \tau_i$. (A plot of $[C_2H_4]$ against t would approach a straight line of slope $R^{ss}_{C_2H_4}$ with an intercept, τ_i, on the time axis.)

A possible contributor to the induction period is the delay in transferring heat to the flowing gas. The thermal conductivity of ethane may be calculated by the methods of ref 10 or extrapolated from experimental data at lower temperatures.[11] The induction periods, τ_h, for heat transfer were calculated[9,12,13] and found to be only 3% as long as observed induction periods, τ_i, on the average.

The induction period was interpreted as being caused mainly by the growth in the concentration of C_2H_5 toward its steady-state value.[6,7] The generation and consumption of radicals were accounted for by the following equations.[6-8,14-17]

$$C_2H_6 \rightarrow 2CH_3 \tag{1}$$

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$$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5 \quad (2)$$

$$C_2H_5 \rightarrow C_2H_4 + H \quad (3)$$

$$H + C_2H_6 \rightarrow H_2 + C_2H_5 \quad (4)$$

$$2C_2H_5 \rightarrow C_4H_{10} \quad (5a)$$

$$2C_2H_5 \rightarrow C_2H_6 + C_2H_4 \quad (5b)$$

Making the steady-state approximation[6,7] for H and CH_3 but not for C_2H_5 and neglecting the rate of formation of C_2H_4 by reaction 5b in comparison with the chain propagation reaction (3), one may obtain eq 6–9.[6,9,18] Here $k_5 = k_{5a} + k_{5b}$ and the chemical

$$\frac{[C_2H_4]}{t} = \frac{R^{ss}_{C_2H_4}(\tau_c + \tau_h)}{t \ln 2} \ln \cosh\left((t \ln 2)/(\tau_c + \tau_h)\right) \quad (6)$$

$$k_1 = \overline{[CH_4]/t}/(2[C_2H_6]) \quad (7)$$

$$k_5 = (\ln 2)^2/(4k_1[C_2H_6]\tau_c^2) \quad (8)$$

$$k_3 = R^{ss}_{C_2H_4}(k_5/k_1[C_2H_6])^{1/2} \quad (9)$$

induction period $\tau_c = \tau_i - \tau_h$. For each initial reactant concentration, rates of ethylene formation at differing residence times were fitted by nonlinear least squares to eq 6, as in Figure 1, to determine the parameters $R^{ss}_{C_2H_4}$ and τ_c. The rate coefficients, $\underline{k_1, k_5, \text{and } k_3}$, at each reactant concentration, were then calculated from $\overline{[CH_4]/t}$, τ_c, $R^{ss}_{C_2H_4}$, and eq 7–9.

The rate coefficients, k_1, k_3, and k_5, were adjusted, as described in an appendix[9], to take into account three minor reactions, eq 10–12.[8,19,20] These adjustments changed the values of k_1, k_3, and

$$C_2H_5 \xrightarrow{W} \text{products} \quad (10)$$

$$H + C_2H_5 \rightarrow 2CH_3 \quad (11)$$

$$CH_3 + C_2H_5 \rightarrow C_3H_8 \quad (12)$$

k_5 by −2%, +3%, and −2%, respectively, on the average.

Resulting values[9] of k_3 and k_1 are shown in Figures 2 and 3, respectively. Also shown are values of k_3 determined in this laboratory by the method of ref 14 from ethylene and *n*-butane yields[9] at higher pressures. Values[9] of k_5 under 12 reaction conditions were found to have an order of 0.02 ± 0.07, indicating that this combination of rate constants is independent of pressure. The average value of k_5 was found to be $(1.30 \pm 0.24) \times 10^{10}$ L mol^{-1} s^{-1}.

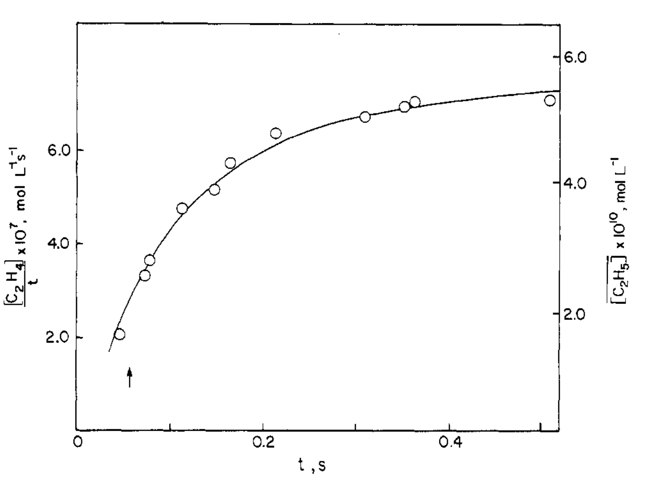

Figure 1. Chordal rates of formation of C_2H_4 from pyrolysis of 5.3×10^{-4} mol L^{-1} of C_2H_6 at 902 K, as a function of reactor residence time. The circles are experimental, and the smooth curve is a least-squares fit to eq 6. The vertical arrow shows the corresponding value of the induction period, τ_i. Calculated average C_2H_5 concentrations in the reactor are shown at the right ($\overline{[C_2H_5]} = [C_2H_4]/(k_3t)$).

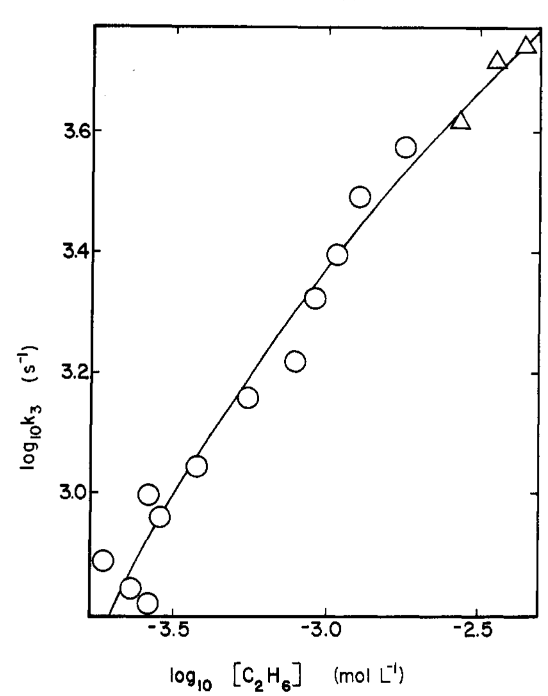

Figure 2. Logarithmic concentration dependence of k_3: (○), from eq 9; (△) from experimental ethylene and butane yields[9] and from the present value of k_{5a} by the method of ref 14; (—), least-squares fit to eq 13 with $F^{SC}_C = 0.52$ and $\beta_C = 1.0$.

TABLE I: Comparison of Termination Rate Constants

ref	T, K	$10^{-9}k_{5a}$, L mol^{-1} s^{-1}	$10^{-9}k_{5b}$, L mol^{-1} s^{-1}
this work	902	9.0 ± 1.7	4.0 ± 1.0
21	860	5–20	ca. 7
22	300	8 ± 2	1.0 ± 0.3
23	298	12.4 ± 2.3	1.7 ± 0.4

Discussion

Termination Reactions. Combining the average value of k_5 with the value of $k_{5b}/k_{5a} = 0.44 \pm 0.07$, determined in this laboratory,[19] one obtains k_{5a} and k_{5b}, as shown in Table I. Comparison with results in the recent literature[21-23] indicates that k_{5a} is approximately independent of temperature and that k_{5b} increases at high temperatures.[19,24]

Ethyl Radical Decomposition. According to Figure 2, k_3 is strongly pressure dependent; its average order is 0.70 ± 0.03. It has been observed that the shapes (as opposed to the absolute positions) of plots like Figure 2 for unimolecular reactions are

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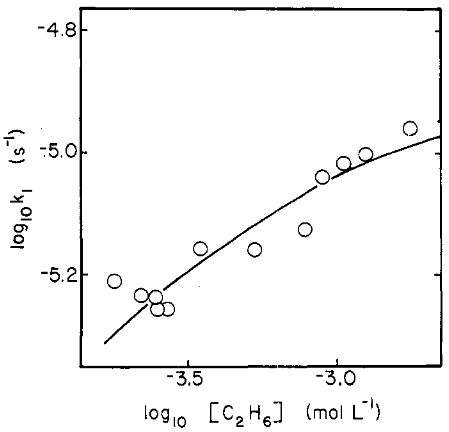

Figure 3. Dependence of k_1 on the concentration. Points are experimental (from eq 7). The curve is a least-squares fit to eq 13 with F_C^{SC} = 0.30 and β_C = 1.0.

relatively insensitive to the details of the energy transfer and reactive processes occurring.[25,26] Troe[25] has proposed an analytic expression (eq 13) for this pressure dependence. Here k_0 and k_∞

$$\ln k = \ln (k_0[M]F^{SC}(k_0[M]/k_\infty,F_C^{SC}) \times F^{WC}(k_0[M]/k_\infty,\beta_c,S_K)/(1 + k_0[M]/k_\infty)) \quad (13)$$

are the limiting low- and high-pressure rate coefficients. F^{SC} and F^{WC} are strong and weak collision broadening factors, whose forms are given in ref 25. The significance and input values of the other parameters are as follows: F_C^{SC}, strong collision broadening factor[27] when $k_0[M] = k_\infty$, 0.52 ± 0.05; β_c, collisional deenergization efficiency, 0.1–1.0; S_K, effective number of vibrational modes,[27] 6.0 ± 0.5. Equation 13 was fitted by nonlinear least squares to the data in Figure 2. The rate coefficients $k_{3,0}$ and $k_{3,\infty}$ were found to be (5 ± 2) × 10^6 L mol^{-1} s^{-1} and (2.7 ± 0.9) × 10^4 s^{-1}. Here the uncertainties incorporate experimental scatter and the uncertainties in the input parameters, F_C^{SC}, β_C, and S_K.

There are no earlier independent measurements of $k_{3,\infty}$ or $k_{3,0}$. The value of $k_{3,\infty}/k_{5a}^{1/2}$, 0.28 $L^{-1/2}$ $mol^{1/2}$ $s^{-1/2}$, from the present work, may be compared to values of 0.16 and 0.21 $L^{-1/2}$ $mol^{1/2}$ $s^{-1/2}$ calculated from Arrhenius parameters in the literature.[14,28] The value of $k_{3,0}/k_{5a}^{1/2}$ = 50 $L^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$ is less than literature values[14,28] of 80 and 200 $L^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$.

Initiation Reaction. The data in Figure 3 were also fitted to eq 13, with F_C^{SC} = 0.35 ± 0.05, β_c = 0.1–1.0, and S_K = 6.0 ± 0.5.[27] The high-pressure limiting rate constant, $k_{1,\infty}$, was found to be (1.7 ± 0.3) × 10^{-5} s^{-1}, in agreement with values of 1.5 × 10^{-5}, 1.4 × 10^{-5}, 1.4 × 10^{-5}, 1.7 × 10^{-5}, and 1.5 × 10^{-5} s^{-1} calculated from Arrhenius parameters in the literature.[8,14-17] We found the value of $k_{1,0}$ to be 0.4 ± 0.2 L mol^{-1} s^{-1}, an order of magnitude less than the value found in ref 14 using a different method of extrapolation.

In the non-steady-state pyrolysis of ethane at 803 K, the value of k_1 reported[7] was larger than predicted from the literature.[8,14-17] The induction period itself[17] was in agreement with values calculated from literature values of k_1 and the present value of k_5.

Radical Concentrations. When experimental values of [C_2H_4]/t are divided by k_3, one obtains the average ethyl radical concentrations in the reactor. These are calculated to be between 1.0 × 10^{-10} and 11 × 10^{-10} mol L^{-1}. Examples may be seen by referring to the right-hand axis in Figure 1. The minimum radical concentraiton which can be determined by the present technique may be shown to be roughly equal to the sensitivity of the gas chromatograph to the products. The minimum concentration above is less than concentrations of 3 × 10^{-10} and 17 × 10^{-10} mol L^{-1} in very low pressure pyrolysis[21] and molecular modulation spectroscopy experiments,[22] respectively.

Thermochemistry. The molar enthalpy change for reaction 5a may be calculated from the forward and reverse rate constants and from the statistical-mechanical entropy change as follows:

$$\Delta_{5a}H°_T = T\Delta_{5a}S°_T + RT \ln (k_{-5a}AT/k_{5a}) \quad (14)$$

Here A is 0.082 L K^{-1} mol^{-1} and the standard state is an ideal gas at 1 atm. In applying this equation, we calculated the entropy of C_2H_5 from recent spectroscopic measurements.[9,29,30] The entropy of butane was taken from ref 31, k_{5a} from the present work, and k_{-5a} from ref 2, 32, 33, and 34. Reaction enthalpies have been adjusted to 298 K by using Kirchoff's equation. From the literature value of $\Delta_fH°_{298}(n\text{-}C_4H_{10})$,[31] values of $\Delta_fH°_{298}(C_2H_5)$ were found to be 120 ± 4,[2] 119.6 ± 2.6,[32] 118.8 ± 1.5,[33] and 118.8 ± 1.6[34] kJ mol^{-1}. Similarly, a value of 123 ± 5 kJ mol^{-1} has been calculated from the present value of $k_{3,\infty}$, Arrhenius parameters for $k_{-3,\infty}$,[35,36] and thermodynamic properties for C_2H_4.[37] Uncertainties in the temperatures and the kinetic and thermodynamic parameters have been combined.

The above results agree well with recent values of 117–121[2] and 117 ± 4[4] kJ mol^{-1} which are also based on statistical-mechanical entropy changes and equilibrium constants or ratios of forward and reverse rate constants. Other workers have indicated that forward and reverse rates for reactions 3, 4, and 12 are consistent with these results.[29,38,39]

However, McMillen and Golden[5] have argued in a recent review that $\Delta_fH°(C_2H_5)$ should be only 108 ± 4 kJ mol^{-1}, based on studies of the reactions of iodine atoms with C_2H_6 and C_2H_5I. The enthalpy changes for these reactions were calculated as the differences in the activation energies for the forward and reverse processes, without using entropies.

$$\Delta H°_T = E_{Af} - E_{Ar} + \Delta nRT \quad (15)$$

Here Δn is the difference in the molecularity of the reverse and forward reactions. Applying eq 15 to activation energies in the literature for other reactions, we obtain the following values of $\Delta_fH°(C_2H_5)$: reaction 3,[14,35] 123 ± 9 kJ mol^{-1}; reaction 3,[28,35] 110 kJ mol^{-1}; reaction 4,[40] 121 ± 6 kJ mol^{-1}; reaction 5a[33] (Table I), 107 ± 9 kJ mol^{-1}. These numbers are less consistent than those obtained from eq 14. The reason is the different propagation of errors in rate constants. In the iodination work,[5] an error of 20% at one end of the temperature range would lead to an error in $\Delta_fH°(C_2H_5)$ of 9 kJ mol^{-1}. In the present work, using eq 14, an error of 20% in k_{5a} would lead to an error in $\Delta_fH°(C_2H_5)$ of only 0.7 kJ mol^{-1}. For this reason, we recommend the use of absolute rate constants and entropies, in eq 14, instead of activation energies and eq 15.

McMillen and Golden[5] indicated that two weaknesses in the "high" values of radical enthalpies were the uncertainties in $\Delta S°$ and the fact that some values were obtained in solution. $\Delta S°$ values are now better known because of recent spectroscopic work.[30] The present results have the further advantages that k_{5a} is not subject to unimolecular pressure dependence, the temperature ranges of the forward and reverse kinetics overlap, the thermodynamic properties of C_4H_{10} are well-known, and the participation of two ethyl radicals in the reaction reduces the

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uncertainty in $\Delta_f H^\circ(C_2H_5)$. The mechanisms of pyrolysis are complex, but they have been repeatedly studied.

Taking $k_{1,\infty}$ from this work, $k_{-1,\infty}$ from ref 41 or 42, and other thermodynamic properties of CH_3 and C_2H_6 from ref 12, one may calculate that $\Delta_f H^\circ_{298}(CH_3)$ equals 146.9 ± 1.6[41] or 146.5 ± 1.8[42] kJ mol^{-1}. Here the rate coefficients are pressure dependent and the temperatures do not overlap. Nevertheless, the results agree well with most of the recent values: 145.7 ± 0.8,[43] 146.0 ± 0.5,[44] 146.9 ± 0.6,[45] and 144 ± 3[46] kJ mol^{-1}.

The change in $\Delta_f H^\circ(C_2H_5)$ is sufficient to change the predicted thermochemistry for some reactions from endothermic to exothermic. For transfer of the radicals X

$$CH_3X + C_2H_5 \rightarrow CH_3 + C_2H_5X \tag{16}$$

the following enthalpies of reaction (in kJ mol^{-1}) have been calculated:[43–45,47] H, 17.9 ± 1.7; CH_3, 6.8 ± 1.7; I, 4.2 ± 0.5;[4] Br, 2.3 ± 2.2; NH_2, 2.9 ± 1.8; Cl, −2.7 ± 1.8; OCH_3, −5.0 ± 1.8; OH, −5.8 ± 1.7. According to the final number, the C–O bond in ethanol is about 6 kJ mol^{-1} stronger than that in methanol.[48] The negative numbers would have been positive with the thermochemistry of ref 5.

Conclusion

Study of the establishment of the steady state in the pyrolysis of ethane has been shown to provide consistent values of the rate constants for chain initiation and for three reactions of ethyl radicals. Minor reactions and heat transfer have been taken into account but were found to have little effect. The rate constant for initiation, combined with a literature value for the reverse process, provides confirmation for the established thermochemistry of the methyl radical. The rate constant for the termination reaction, combined with literature data on the reverse process, indicates that the heat of formation of the ethyl radical is larger than the value most frequently quoted.[5] This method provides a new approach to the study of radical kinetics and thermochemistry, with a precision and sensitivity competitive with the best alternative techniques.

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Registry No. C_2H_6, 74-84-0; C_2H_5, 2025-56-1; CH_3, 2229-07-4.

Supplementary Material Available: Appendices describing the derivation of the rate expressions and presenting tables of data (13 pages). Ordering information is given on any current masthead page.

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Charge-Transfer Complexation between Methylviologen and Sacrificial Electron Donors EDTA, Triethanolamine, and Cysteine[1]

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Methylviologen dication (MV^{2+}) forms charge-transfer (CT) complexes with EDTA, triethanolamine (TEOA), and cysteine (Cys) in aqueous solution. The complexes of EDTA and TEOA show enhanced tail absorption from 320 nm well into the visible region; the Cys complex shows a discrete absorption band in the 350–380-nm region. By use of the Benesi–Hildebrand and other treatments for the variations of the absorbances of the complexes with the concentrations of the components, values of K_{eq} and ϵ_λ for the complexes are obtained as functions of pH. Values of K_{eq} range from 0.29 M^{-1} for the Cys complex at pH 3.5 to 18 M^{-1} for the EDTA complex at pH 11.2; K_{eq} values are significantly higher in alkaline solution where the deprotonated donors are better reducing agents. The emission at 525 nm observed in these and other MV^{2+} systems is believed to arise from a highly luminescent impurity, not a CT complex. The ramifications of CT complex formation on the photochemistry of systems containing MV^{2+} and sacrificial electron donors are discussed.

Introduction

By far, the most widely studied system for the photoreduction of water and the generation of H_2 has been the one involving methylviologen (1,1′-dimethyl-4,4′-bipyridinium dication; MV^{2+}).[2,3] Its photosensitized reduction to $MV^{+\cdot}$, mediated by the excited states of $Ru(bpy)_3^{2+}$ and other sensitizers, leads to the generation of H_2 in the presence of colloidal metals[4] or hydrogenase.[5] For this procedure to succeed, a sacrificial electron-transfer agent must be present at sufficiently high concentration in order to reduce competitively the oxidized sensitizer ($Ru(bpy)_3^{3+}$, for example) before it can react with $MV^{+\cdot}$ and annihilate the energy carrier. The most popular sacrificial reductant has been EDTA;[3,4,6] others used include triethanolamine,[7] mercaptoethanol,[8] and cysteine.[9] EDTA is also effective in

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