Investigations into the Chemistry of Thermodynamically Unstable Species. The Direct Polymerization of Vinyl Alcohol, the Enolic Tautomer of Acetaldehyde

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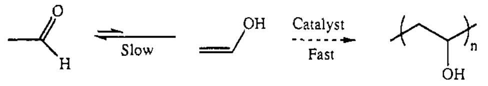
Although thermodynamics provide an important driving force in determining the direction of chemical reactions, it is often possible to circumvent this dictate by taking advantage of kinetics. In fact, considerable leverage can be realized by exploiting favorable relative rates even under conditions in which there is an opposing and significant energetic bias such as in the case of enol-keto tautomerizations. Kinetic supremacy will be illustrated in this report by the near quantitative polymerization of vinyl alcohol generated *in situ* through the decomposition of a precursor and siphoned off at a rate faster than it can tautomerize to acetaldehyde.

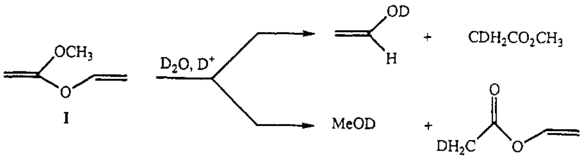
Poly(vinyl alcohol), PVA, is normally synthesized through a two-step process involving the polymerization of vinyl acetate followed by its controlled hydrolysis.[1,2] This circuitous route is necessitated by the unfavorable equilibrium that lies between vinyl alcohol and acetaldehyde (K = [enol]/[keto] $\approx 3 \times 10^{-7}$ at 25 °C).[3] An attractive, but hitherto unobtainable goal would be the direct polymerization of vinyl alcohol. Unfortunately, no catalyst or initiator has ever been able to selectively scavenge the equilibrium amount of vinyl alcohol present in solution (Scheme 1). We postulated that if we could start at the vinyl alcohol side of the equilibrium and if the rate of tautomerization was slow relative to the rate of reaction, successful polymerization could be obtained.

The slow tautomerization of vinyl alcohol to acetaldehyde has been reported previously by Capon *et al.*, who investigated the acid-catalyzed hydrolysis of vinyl orthoesters at low temperature.[3-7] Although the rate of tautomerization is highly pH dependent, it was found that at the minimum of the pH rate profile only 20% of the tautomerization could be accounted for by specific acid- or base-catalyzed reactions; it was suggested that the remainder of ketonization occurs via a water-mediated pathway.[3] We report that, through preparation of O-D vinyl alcohol using only slightly more than a stoichiometric amount of water, we have been able to extend the half-life of this species from 10 min[4] to many hours at room temperature. The stability of the enol tautomer appears to stem from the reduced water concentration in the system, as well as from a favorable deuterium kinetic isotope effect ($k_{H^+}/k_{D^+} = 4.75$, $k_{H_2O}/k_{D_2O} = 12$).[3] Having a significant lifetime at room temperature under these conditions, vinyl alcohol can now be thought of as a synthetically useful substrate.

Scheme 1



Vinyl alcohol was generated through the hydrolysis of ketene methyl vinyl acetal **I** (eq 1).[8] In general, we have observed that



(1)

room temperature addition of 0.9 mol equiv of **I** to a 1% (v/v) D_2O solution in acetone-d_6, made such that the concentration of the overall solution is 10^{-4} M in DCl, yields 90% O-D vinyl alcohol which tautomerizes to acetaldehyde only very slowly at ambient temperature[9] ($k_t \approx 10^{-6}$ M/s, *vide infra*). The remaining 10% of **I** is converted into vinyl acetate, a side product in the hydrolysis, as well as to a small amount of acetaldehyde from tautomerization. Spectroscopic data for the vinyl alcohol were identical to previously reported data.[4] Our observations suggest that the key to generating persistent vinyl alcohol solutions is to drive the system toward an anhydrous state through use of nearly stoichiometric amounts of water in the rapid hydrolysis step. To our knowledge, this is the first report of hydrolysis conditions that yield metastable vinyl alcohol solutions at room temperature.[7]

NMR kinetic studies of the room temperature tautomerization in acetone solution were performed. Preliminary results show a correlation between water concentration and the mechanism of tautomerization. When <1 equiv of D_2O is in solution along with the O-D vinyl alcohol, the kinetics of tautomerization have a zero-order dependence upon the concentration of vinyl alcohol ($k_{obs} = 3.5 \times 10^{-6}$ M/s).[10] The observed catalyst saturation behavior could be explained by the slow autoionization of water becoming rate determining at low water concentrations. Further studies to elucidate the zero-order ketonization mechanism are in progress. As an excess of D_2O is added to the sample, a transition to first-order dependence of the rate of ketonization upon O-D vinyl alcohol occurs ($k_{obs} = 2.73 \times 10^{-4}$ s^{-1}).[11] This result is in agreement with previous work which showed the ketonization in completely aqueous solution to be first order in vinyl alcohol.[3,12] Although the room temperature rate of vinyl alcohol tautomerization under first-order conditions is still sufficiently slow ($t_{1/2}$ = 42 min)[11] to allow for polymerization of the enol, the ultraslow zero-order tautomerization rate substantially increases the longevity of vinyl alcohol.

With a metastable enol tautomer in hand, the reactivity of this species was probed. Polymerization by cationic initiation (normally ideally suited for vinyl ether polymerizations)[13,14] was

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(2) Marten, F. L.; Zvanut, C. W. In *Poly(vinyl alcohol) Developments*; Finch, C. A., Ed.; John Wiley and Sons: New York, 1992.

(3) Capon, B.; Zucco, C. *J. Am. Chem. Soc.* **1982**, *104*, 7567-7572.

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(6) Capon, B.; Guo, B.; Kwok, F. C.; Siddhanta, A. K.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135-140.

(7) A particular elegant catalytic route into the higher enolate homologues has recently been reported. See: Bergens, S. H.; Bosnich, B. *J. Am. Chem. Soc.* **1991**, *113*, 958.

(8) Compound **I** has been previously synthesized by Capon *et al.* (see ref 3). We modified the synthesis by use of KH and preformed *t*-BuOK in tetraethylene glycol dimethyl ether in the elimination step. The elimination was carried out at 0 °C over a 20-min period to provide **I** in 80% yield. Spectroscopic data for our sample was identical to that previously reported for **I**.

(9) Previous preparation of O-H vinyl alcohol from this precursor was carried out at -30 °C in acetone-d_6 (99% (v/v)) and H_2O (1% (v/v)) containing 10^{-4} M HCl (see ref 3). We were not successful in reproducing these results but did find that the hydrolysis reaction is extremely sensitive to trace impurities.

(10) [D_2O] = 0.16 M, [D^+] = 1.3×10^{-5}, [vinyl alcohol]$_0$ = 0.26 M, T = 22 °C.

(11) [D_2O] = 6.8 M, [D^+] = 1.3×10^{-5}, [vinyl alcohol]$_0$ = 0.18 M, T = 22 °C.

(12) Chiang, Y.; Hojatti, M.; Keeffe, J. R.; Kresge, A. J.; Schepp, N. P.; Wirz, J. *J. Am. Chem. Soc.* **1987**, *109*, 4000-4009.

(13) Higashimura, T.; Sawamoto, M. In *Comprehensive Polymer Science: The Synthesis, Characterization, Reactions, and Applications of Polymers*; Eastmond, G., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: New York, 1989; Vol. 3, pp 673-696.

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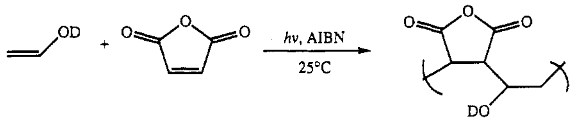
deemed unsuitable due to detrimental proton-transfer reactions; instead, free radical methods were pursued. Initial attempts at radical homopolymerization (AIBN, *hν*, −10 to 25 °C) of vinyl alcohol yielded unsatisfactory results.[15] However, by taking advantage of stabilizing electron donor–acceptor interactions,[16] the free radical copolymerization of O–D vinyl alcohol and maleic anhydride proved successful (eq 2). The hydrolysis mixture containing vinyl alcohol (0.25 M) was combined with freshly recrystallized maleic anhydride and reagent grade AIBN (1 mol %). Photolysis of the deoxygenated mixture at 350 nm and 25 °C for 1 h gave polymer in 90–100% yield by NMR. The polymer was isolated by precipitation into benzene and spectroscopic data established its identity.[17]



(2)

Polymerization kinetics were studied at −10 °C by measuring the concentration of vinyl alcohol and acetaldehyde versus a *m*-xylene standard.[18] The polymerization was determined to be first order in both maleic anhydride and vinyl alcohol. As expected for free radical polymerizations at low monomer concentrations, the rate of polymerization has no dependence on initiator concentration.[19] The k_{obs} for polymerization was found to be 4.41×10^{-4} s^{-1} at −10 °C. Integration also indicated that equimolar amounts of maleic anhydride and vinyl alcohol were consumed in the formation of polymer, suggesting that an alternating one to one coplymerization occurs analogously to known vinyl ether maleic anhydride copolymerizations.[20] Since the rate of polymerization is far greater than that of tautomerization under these conditions (*ca.* 30 times faster at −10 °C), there is no significant increase in acetaldehyde concentration during polymerization (Figure 1). Thus, this favorable balance of reaction kinetics allows for the first direct use of vinyl alcohol as a monomer for polymerization.

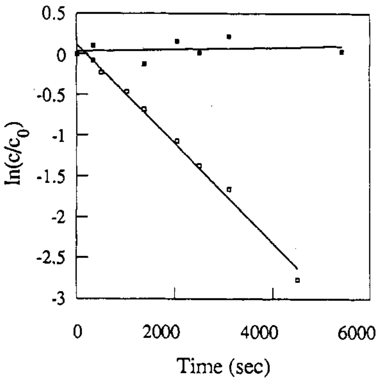


Figure 1. Polymerization kinetics showing the disappearance of vinyl alcohol (open squares) without a concomitant increase in acetaldehyde concentration (filled squares).

In conclusion, we have demonstrated that, by selectively regulating the kinetic rates, vinyl alcohol can be generated and polymerized faster than the competing tautomerization process. We are currently investigating alternative catalyst systems that may allow us to carry out the homopolymerization of this and other thermodynamically unstable enols.

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(15) This is consistent with the negative results obtained during the attempted homopolymerization of vinyl ether substrates at these temperatures. See: (a) Matsumoto, A.; Nakana, T.; Oiwa, M. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 277. (b) Kamachi, M.; Tanaka, K.; Kuwae, Y. *J. Polym. Sci., Part A* **1986**, *24*, 925.

(16) Munk, P. *Introduction to Macromolecular Science*; John Wiley and Sons: New York, 1989, p 142.

(17) Representative physical data for maleic anhydride–vinyl alcohol copolymer: ^{1}H NMR (DMSO) 400 MHz δ (ppm) 4.37, 2.84, 2.69, 1.92, 1.58 (all broad peaks); ^{13}C NMR (DMSO) δ (ppm) 176.1, 172.4, 76.8, 50.1, 38, 30; IR (KBr) 1171.0 (s), 1780–1700 (m), 2601.9 (b), 2920–3495 (b).

(18) Aliquots of the reaction mixture were sealed in individual ampules, photolyzed for an appropriate period, and quenched by cooling to liquid nitrogen temperature. The samples were further diluted with acetone-d_6 and immediately analyzed for the concentration of vinyl alcohol using NMR spectroscopy.

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