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Notes

Influence of Acids on Reaction Rates of Free Radical Scavenging by TEMPO. Relevance to “Living” Free Radical Polymerizations

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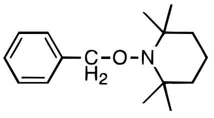
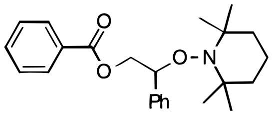
Recent reports on free radical polymerizations in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) show that this technique can lead to polymers with polydispersities below the theoretical limit of 1.5.[1−5] Reaction of the growing polymer chain with TEMPO reversibly terminates polymer growth by formation of a weak bond to the terminal TEMPO moiety. Work by Hawker[4] and by us[6] has shown that it is possible to prepare initiators by coupling TEMPO and a free radical, so as to already have the initiating radical and the TEMPO-cap in the correct 1:1 stoichiometry to initiate “living” free radical polymerizations. Structures **I** and **II** show representative initiators of this type.



I



II

It is generally believed that upon heating, the TEMPO group dissociates, thus providing an opportunity for additional molecules of monomers (most frequently styrene) to be added to the polymer chain; a detailed kinetic analysis of this mechanism has been recently reported.[7] This polymerization technique clearly has the potential for the synthesis of block[8] and star[9] polymers. An interesting observation reported by Georges and coworkers[2,3] is the enhancement of the polymerization rates by camphorsulfonic acid (CSA) in modest (≤0.04 M) concentrations. TEMPO is known to suppress the autopolymerization of styrene,[3] although the rate enhancement may be due to the consumption of TEMPO by reaction with CSA.[10] In this contribution we explore the idea that the rate enhancement induced by CSA and other acids operates on the recapping reaction between the growing polymer radical and TEMPO.

Beckwith, Bowry, and Ingold have reported a detailed study of the kinetics of the reactions between free radicals and TEMPO.[11,12] These reactions are solvent dependent; for example, for benzyl radicals reacting with TEMPO, the rate constants at room temperature are 4.8 × 10^8, 2.3 × 10^8, 1.8 × 10^8, and 1.3 × 10^8 M^{-1} s^{-1} in isooctane, tetrahydrofuran, benzene, and methanol, respectively.[12] We reasoned that a similar effect may be induced by addition of small concentrations of acids to nonpolar solvents. In order to explore this possibility, we have used laser flash photolysis techniques[13] to examine the effect of CSA and other acids on the kinetics of reaction 1.

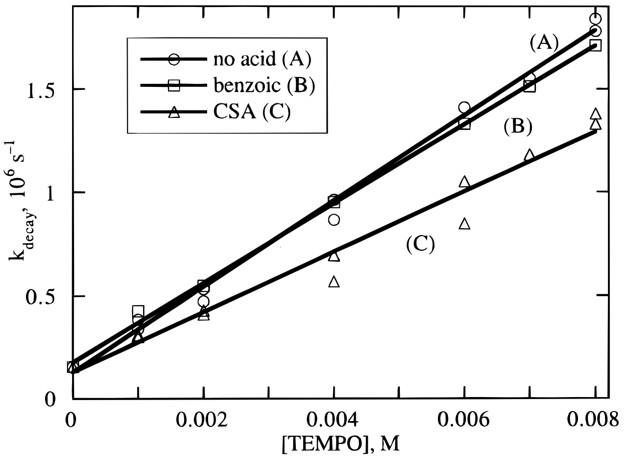
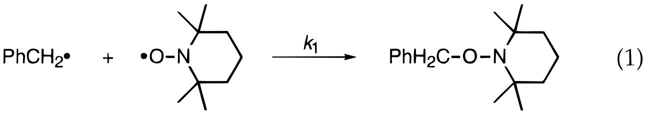
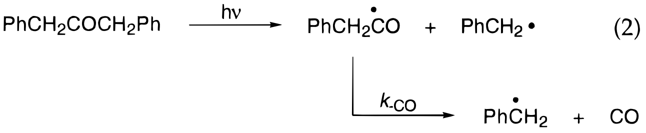


Figure 1. Representative TEMPO quenching plots for benzyl radicals generated from DBK in the absence and presence of 40 mM acid, in dry THF at room temperature.



I

The reaction can be readily examined by using dibenzyl ketone (DBK) as the precursor for benzyl radicals, reaction 2.



$$PhCH_2COCH_2Ph \xrightarrow{h\nu} PhCH_2\dot{C}O + PhCH_2{}^{\bullet} \qquad (2)$$
$$PhCH_2\dot{C}O \xrightarrow{k_{-CO}} Ph\dot{C}H_2 + CO$$

Reaction 2 can be initiated by photodecomposition at 308 nm, a wavelength where TEMPO and potential acid additives are sufficiently transparent. The phenylacetyl radical decarbonylates with rate constants (k_{-CO}) in the neighborhood of 10^7 s^{-1} in non-polar solvents.[14,15] Thus, the decay of $PhCH_2^{\bullet}$ can be easily monitored at 317 nm[16] in the presence of variable amounts of TEMPO and/or acid additives. The rate constant for reaction 1 can be determined from a plot of the pseudo-first-order rate constant for the decay of benzyl radicals as a function of TEMPO concentration. Representative plots in the absence of acids and for 40 mM acids in dry tetrahydrofuran are shown in Figure 1. The effect of acid addition on the dynamics of reaction 1 is clear; this is also illustrated in Figure 2, where two benzyl-radical decay traces are compared for the same TEMPO concentration, but with and without CSA. The data in the presence of CSA (Figure 1) show a linear behavior for TEMPO quenching with a rate constant of 1.4 × 10^8 M^{-1} s^{-1}, compared with 2.1 × 10^8 M^{-1} s^{-1} in the absence of CSA, in excellent agreement with the reported value in this solvent.[12] We note that rate measurements in

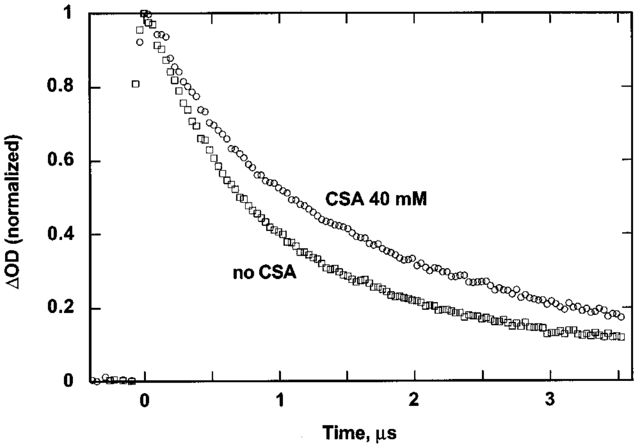


Figure 2. Benzyl radical decay traces monitored at 317 nm, for 4.5 mM TEMPO, in the absence and presence of 40 mM CSA. Conditions: solvent, tetrahydrofuran; laser excitation at 308 nm. The decays follow pseudo-first-order kinetics.

Table 1. Effect of Acid Addition on the Reaction of Benzyl Radicals with TEMPO in Dry Tetrahydrofuran at Room Temperature[a]

acid	conc (M)	$10^{-8}k_1$ (M^{-1} s^{-1})
none	0	2.1 ± 0.2
CSA	0.03−0.06	1.4 ± 0.2
benzoic acid	0.04	1.9 ± 0.2
diphenylacetic acid	0.04	1.6 ± 0.2
methanesulfonic acid	0.04	1.5 ± 0.3
p-toluenesulfonic acid	0.04	1.4 ± 0.3

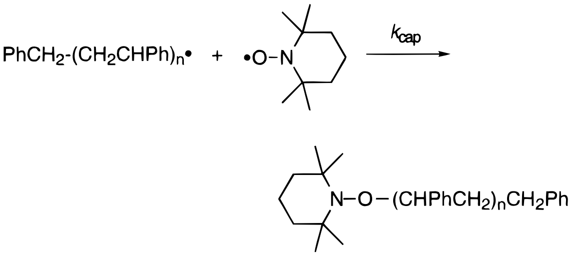
[a] All rate constant measurements were performed in the 0−8 mM TEMPO range.

the presence of acid were always performed within minutes (usually ≤15 min) of sample preparation, so as to avoid (particularly for CSA) any concern related to possible acid consumption by reaction with TEMPO.[10] Other concentrations of CSA, in the 30−60 mM range led to essentially the same effect as the 40 mM concentration of Figures 1 and 2. Significant effects were also observed with other sulfonic acids; see Table 1.[17] In the case of carboxylic acids, the effect was significant for diphenylacetic, but essentially no effect was observed for benzoic (see Table 1). Interestingly, the latter has been reported to have no dramatic effect on TEMPO-mediated polymerizations.[10]

Laser excitation (266 nm) of **I** (examined in *n*-pentane) leads to readily detectable benzyl radicals which decay by second-order kinetics.[6] The two radicals of reaction 1 are formed in identical concentrations; we were initially surprised by the observation that addition of 40 mM CSA led to virtually no change in the second-order rate constant for radical decay.[18] In fact, the observation results from the fact that benzyl−benzyl radical recombination (reaction 3) is over 1 order of magnitude faster than reaction 1.[19] Thus, since photolysis of **I** produces TEMPO and benzyl radicals in equimolar concentrations, the overall rate for reaction 3 will be about 1 order of magnitude faster than for reaction 1, and any reduction in this rate plays a relatively minor role on the overall radical decay process.

$$PhCH_2\bullet + PhCH_2\bullet \longrightarrow PhCH_2CH_2Ph \qquad (3)$$

The implication of the observation above is that even stoichiometric initiators (such as **I** and **II**) will not lead to equal steady state concentrations of TEMPO and the carbon-centered radical. In fact, one would expect the termination of initiator radicals or growing polymer chains to dominate until sufficient TEMPO builds up for the capping reaction (e.g. reaction 4 in the case of **I** and styrene) to take over. The situation is very similar to that described by Fischer, where suppression of fast reaction modes is caused by the initial buildup of a persistent intermediate.[20,21]



(4)

When one takes into account that reaction 4 must occur successfully many times during polymer growth in a *living* polymerization, while one carbon−carbon termination would be sufficient to irreversibly terminate polymer growth, one can anticipate that TEMPO concentrations under steady state conditions will have to exceed the concentration of active growing polymer chains by ≥1000.[20] If this criterion were not met, it would be impossible to grow long chains, particularly given that reaction 1 (and presumably 4) is moderately slow, compared with the benzyl−benzyl combination reaction. A detailed analysis of the kinetic expressions for TEMPO-mediated polymerizations has recently been reported.[7]

In conclusion, addition of acids causes a reduction in the rate of reaction 1 between benzyl radicals and TEMPO, in a way reminiscent of the solvent effects that are established in these reactions.[12] A similar effect on the polymerization of TEMPO-capped polymers is likely to be a contributor (but not necessarily the only or main one) to the increase in polymerization rates observed in those systems. It is clear that acid and polar effects on polymerization are significantly larger than those observed in Table 1;[2,10,22] it is possible that the slow down of reaction 1 is accompanied by an acceleration of the thermal dissociation (i.e., the reverse of reaction 1) in which case both effects would influence the observable rate of polymerization. Current studies try to address this question.

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(13) The laser system uses Lumonics EX-510 and EX-530 for excitation wavelengths of 248 and 308 nm, Surelite lasers from Continuum for the Nd-YAG wavelengths of 266, 355, and 532 nm and a Molectron UV-24 nitrogen laser for 337 nm. All pulse durations are <10 ns, and typical pulse energies, between 5 and 50 mJ. The signals from the monochromator/photomultiplier system were initially captured by a Tektronix 2440 digitizer and transferred to a PowerMacintosh computer that controlled the experiment with software developed in the LabVIEW 3.1.1 environment from National Instruments. Other aspects of the system are similar to those described earlier: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

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(17) It will eventually be desirable to obtain kinetic data at typical polymerization temperatures (90−130 °C), for example in toluene, a solvent frequently chosen for nitroxide-mediated polymerizations.

(18) CSA causes a decrease in the quantum yield of photodecomposition of **I**; the observation was not pursued further, since in practice cleavage of the C−TEMPO bond is done thermally.

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