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Quantitative Rate Constants for Radical Reactions in the Nanopores of Cotton

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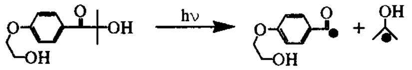
Received February 4, 2002

Porous materials are crystalline or amorphous solids that allow the reversible passage of molecules through their structure.[1] Well-known examples are zeolites with their regular networks of nanochannels and cages, carbon nanotubes, and fibers such as cotton.[2] In cotton, the porosity arises from the amorphous regions which are well-defined slit pores of 1−3 nm situated between crystallites of polysaccharide.[3] For the technical use of all porous materials, it is very useful to understand what controls chemical reactions within the pores. Radical reactions are important in this context, being widely used in synthesis[4] and involved in the degradation of many porous materials.[5] In solution, radical chemistry is well understood using a large set of quantitative rate constants[6] as a backbone. Unfortunately, in porous materials little data exist,[7] presumably because of measurement difficulties caused by the nature of the materials. Here a simple method is introduced to obtain reliable rate constants of some radical reactions in porous materials, using cotton as a model substrate.

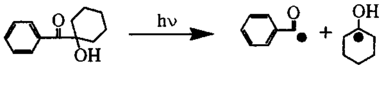
The best method to measure a rate constant is to measure and fit the kinetic behavior of one of the products/reactants.[6] In liquids, one of the easiest radical reactions to observe kinetically is the bleaching of a dye,[8] as the large color change provides a big signal for transient optical absorbency measurements. This should also be true in cotton; however, because of the opaque nature of the substrate, signals must be observed via diffuse reflectance spectroscopy.[9] As a test case, the reactions of two α-hydroxy radicals (2-hydroxy-2-propyl and 1-hydroxy-1-cyclohexyl) with azo dyes in solution and in wet and dry nonmercerized cotton were investigated.

The radicals were created by 355 or 260 nm laser flash photolysis of the corresponding α-hydroxy ketones:

(1)



(2)



On excitation, both ketones intersystem cross from the initial excited singlet state into a triplet state and then undergo α cleavage yielding α-hydroxy and carbonyl radicals, within a few nanoseconds.[10] In cotton, the ketones were deposited into the amorphous zone by soaking woven cotton fabric in a methanol solution of the ketones for 30 s, removing, and then drying in air.[11] This delivers a known weight to the cotton.

In the presence of dyes, α-hydroxy radicals undergo a 1 electron reduction with the dye,[6] thereby giving the dye anion and bleaching, that is

(3)

The carbonyl radicals do not react with the dye on the current time scale,[8] and in the absence of ketone the dyes are photostable. Figure 1 shows the change in optical absorption of a solution of the dye reactive red 3 and the change in reflectance of wet and dry cotton, dyed with reactive red 3, following creation of 2-hydroxy-2-propyl radicals by laser flash photolysis, reaction 1. In all three cases, a microsecond concentration-dependent bleaching of the dye is observed.

In the solution experiment, an upper estimate of the initial radical concentration may be calculated from the irradiated volume (0.7 mL), light absorbed by the ketone (<40%), quantum yield of reaction 1 (0.3),[10] and laser power (18 mJ/pulse) as $<1.8 \times 10^{-5}$ mol L^{-1}, which is smaller than the dye concentration of $5-30 \times 10^{-5}$ mol L^{-1}. For α-hydroxy radicals, the rate constants for reaction 3, k_{dye}, and the competing second order reactions of radical self- and cross-termination are similar,[6] and therefore reaction 3 will dominate because of the high dye concentration.[12] A simple kinetic analysis then shows:

$$[\mathrm{dye}] = [\mathrm{dye}]_{t=0} - [(\mathrm{CH_3})_2\mathrm{COH}]_{t=0} \exp(-k_{\mathrm{dye}}[\mathrm{dye}]t) \quad (4)$$

Hence, an exponential fit of the decay curve and then a plot of the fitted rate constant k_{obs} versus [dye] should give a straight line of gradient k_{dye}, as is observed, Figure 1.

If the radical reaction in cotton follows liquid-phase kinetics, this approach should also yield k_{dye} in cotton. Here the change in reflectance rather than the absorbance is proportional to the change in dye concentration.[9] Both reflectance and absorbance measurements were made using a shuttered 300 W xenon arc lamp and a fast photomultiplier attached to a digitizing oscilloscope.[9] The effective dye concentration in cotton is the dye concentration in the amorphous regions, which is the pore space available to external molecules.[13] It is calculated from the dye loading in mol kg^{-1}, the density (1.5 g/mL), and the accessible amorphous volume fraction (42%).[3] Using this method, we obtained good fits to the data, Figure 1, supporting the liquid-phase assumption.

The measured rate constants are presented in Table 1. In methanol, both radicals react with approximately the same k_{dye} with reactive red 3, and the value for reactive orange 4/1-hydroxy-1-cyclohexyl is one-half of this. Neta and Levanon[14] measured a lower value of 3×10^7 mol^{-1} L s^{-1} for 2-hydroxy-2-propyl radicals bleaching azobenzene in propan-2-ol. However, the dyes used here have electron-withdrawing subsistent sulfonate, hydroxy, and amine groups which will aid reduction.[15]

The values in dry cotton are smaller than those in wet cotton which are smaller than those in solution. This follows the respective viscosities of the three environments of 30, ∼10, and 1 cP[11,13] and

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10.1021/ja0201808 CCC: $22.00

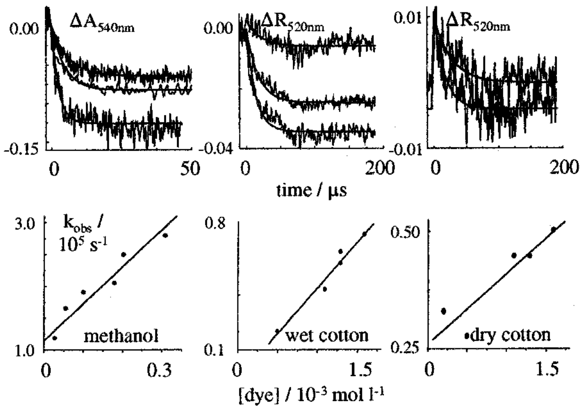
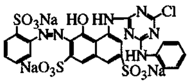
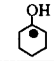
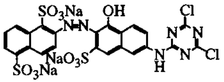
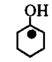


Figure 1. Dye bleaching kinetics of reactive red 3 following laser flash creation of 2-hydroxy-2-propyl radicals. The dye concentrations were methanol 0.12, 0.15, and 0.22 $\times$ 10^{-3} mol L^{-1}; wet cotton 0.5, 1.3, and 1.6 $\times$ 10^{-3} mol L^{-1}; dry cotton 0.2 and 1.6 $\times$ 10^{-3} mol L^{-1} (cotton values are for the amorphous region). The decay kinetics were fitted with single exponentials, and the dependence of the observed rate constants on dye concentration is also shown.

Table 1. Measured Rate Constants for Radical Dye Bleaching in Methanol and Wet and Dry Cotton

		k_{dye} / 10^7 mol^{-1} l s^{-1}		
dye	Radical	Meth-anol	wet cotton	dry cotton
Reactive red 3 		77	4.9	1.5
Reactive red 3		67	2.0	0.9
Reactive orange 4 		29	5.4	1.7

the calculated diffusion-limited rate constant ($k_d = 8RT/3\eta$) of 0.22, 0.66, and 6.6 $\times$ 10^9 mol^{-1} L s^{-1}. For wet and dry cotton, k_d is lower than k_{dye} measured in methanol, and therefore in cotton reaction should be diffusion-controlled.[16] The dyes are reactively bound to the pore walls in cotton[17] and cannot diffuse, reducing the diffusion-limited rate constant for reaction 3 by a factor of 2. A further statistical drop of 2 should be included as only one side of the dye is available for reaction. Hence, rough estimates[18] for k_{dye} in wet and dry cotton are 1.6 $\times$ 10^8 and 5.5 $\times$ 10^7 mol^{-1} L s^{-1}, respectively, and should be independent of the dye and the radical. In agreement, the experimental k_{dye} is smaller in dry than wet cotton by a factor of 3, and within error the values are identical for both dyes unlike in methanol. A tolerable match is also seen with the absolute values, Table 1. Thus, reaction 3 follows simple liquid-phase kinetics in the nanopores of cotton. Previous spin probe work showed that Heisenberg spin exchange of nitroxide radicals[13] and the development of electron spin polarization (ESP) in reactive radical pairs[11] also follow liquid-phase kinetics in cotton. Additionally, work on the quenching of the excited triplet state of a dye by oxygen gave a rate constant of 1 $\times$ 10^7 mol^{-1} L s^{-1} in wet cotton[19] which agrees with the current values.

The pore size in cotton is 1−3 nm, and it is surprising that even for such narrow pores, surface effects play little or no role in the chemical kinetics. However, a large cage effect can be inferred in cotton, because twice as much dye is bleached in wet cotton than in dry, Figure 1. The difference is too large to ascribe to the change in viscosity, and control experiments showed it was not because of changes in the amount of absorbed light. ESP experiments with the ketone in reaction 1 showed that approximately 50% of the radical pairs in dry cotton were caged[11] and that the cages were destroyed when the cotton was wet. Again, this shows a good match between the two techniques.

The simple method described here could be easily transferred to other opaque porous media and could be extended to other reactions using the dye bleaching as a competitive probe.

References

(1) Lamgley, P. J.; Hulliger, J. *Chem. Soc. Rev.* **1999**, *28*, 279.
(2) Hearle, J. W. S.; Peters, R. H. *Fiber Structure*; Butterworth: Woburn, MA, 1963.
(3) (a) Krässig, H. A. *Cellulose*; Gordon Breach Science Publishers: Langhorne, PA, 1993. (b) Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W. *Comprehensive Cellulose Chemistry*; Wiley-VCH: Weinheim, 1998; Vol. 1.
(4) Perkins, M. J. *Radical Chemistry*; Ellis Horwood: London, 1994.
(5) Pospīšil, J.; Klemchuk, P. P. *Oxidation Inhibition in Organic Materials*; CRC Press: Boca Raton, FL, 1990; Vols. 1 and 2.
(6) (a) Fischer, H., Hellwege, K.-H., Eds. *Landolt-Bornstein: Radical Reactions in Liquids*; Springer-Verlag: Berlin, 1963−1997. (b) Neta, P.; Grodkowski, J. *J. Phys. Chem. Ref. Data* **1996**, *25*, 709.
(7) (a) Turro, N. J. *J. Photochem. Photobiol., A* **1996**, *100*, 53. (b) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267.
(8) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1999**, *121*, 3921.
(9) Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2073.
(10) (a) Fouassier, J. P.; Ruhlmann, D.; Graff, B.; Morlet-Savary, F.; Wieder, F. *Prog. Org. Coat.* **1995**, *25*, 235. (b) Jockusch, S.; Landis, M. S.; Freiermuth, B.; Turro, N. J. *Macromolecules* **2001**, *34*, 1619.
(11) (a) Batchelor, S. N.; Shushin, A. I. *J. Phys. Chem. B* **2001**, *105*, 3405. (b) Batchelor, S. N.; Shushin, A. I. *Appl. Magn. Reson.* **2002**, *22*, 47.
(12) Radical addition to oxygen provides another major reaction path. In solution, it was removed by bubbling with nitrogen; however, for technical reasons this was not possible in cotton. This additional first order reaction affects the intercept but not the gradient of the plot.
(13) (a) Batchelor, S. N. *J. Phys. Chem. B* **1999**, *103*, 6700. (b) Scheuermann, R.; Roduner, E.; Batchelor, S. N. *J. Phys. Chem. B* **2001**, *105*, 11474.
(14) Neta, P.; Levanon, H. *J. Phys. Chem.* **1977**, *81*, 2288.
(15) (a) Zbaida, S.; Brewer, F.; Levinem, W. G. *Drug Metab. Dispos.* **1986**, *14*, 19. (b) Zbaida, S.; Levine, W. G. *Chem. Res. Toxicol.* **1991**, *4*, 82.
(16) (a) Von Smoluchowski, M. *Z. Phys. Chem.* **1917**, *92*, 129. (b) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129.
(17) The dye is attached to a polysaccharide chain via the triazinyl group, see: *Colourants and Auxiliaries*; Shore, J., Ed.; Soc. of Dyers and Colourists: Manchester, 1990; Vol. 1.
(18) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200.
(19) Jansen, L. M. G.; Wilkes, I. P.; Greenhill, D. C.; Wilkinson, F. *J. Soc. Dyers Colour.* **1998**, *114*, 327.

JA0201808