Autoxidation of Poly(vinyl alcohol) in the Presence of *tert*-Butyl Hydroperoxide and Cobalt(II) and Cobalt(III) Acetylacetonate in Water and Dimethyl Sulfoxide

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ABSTRACT: The system cobalt(II) and/or -(III) acetylacetonate–*tert*-butyl hydroperoxide has been used to initiate autoxidation of poly(vinyl alcohol) in water and dimethyl sulfoxide solutions at 42 and 60°. Empirical kinetic equations are presented for *tert*-butyl hydroperoxide decomposition and oxygen absorption. Activation parameters from the kinetic data are presented. The autoxidation has been interpreted as two superimposed reactions, one involving peroxide decomposition through cobalt complexes with *tert*-butyl hydroperoxide or by a direct reaction between cobalt and *tert*-butyl hydroperoxide, and the other involving chain autoxidation of poly(vinyl alcohol). Effects of solvent and temperature on these processes are discussed.

Autoxidation and cleavage reactions of poly(vinyl alcohol) have been studied in several laboratories.[1-5] Dulog, Kern, and Kern[2] have investigated photochemically initiated poly(vinyl alcohol) autoxidation. Takayama[3] and Shiraishi and Matsumoto[4,5] have done work on poly(vinyl alcohol) degradation and oxidation in the presence of hydrogen peroxide.

This report concerns a kinetic investigation of poly(vinyl alcohol) autoxidation initiated by cobalt(II) and -(III) acetylacetonate and *tert*-butyl hydroperoxide in dimethyl sulfoxide and water solutions. Metal acetylacetonate–*tert*-butyl hydroperoxide initiated autoxidation of 1-octene in chlorooctane has been previously studied in this manner.[5,6]

Experimental Section

Chemicals. The chemicals for these experiments have been described previously.[1] Poly(vinyl alcohol) (K & K Laboratories) of viscosity averaged molecular weight 9.1 × 10^4 g/mol (measured in dimethyl sulfoxide) was used for this work.

Kinetics. The oxygen absorption apparatus has been described previously.[5] No oxygen was picked up over a period of 1.8 × 10^5 sec in the absence of cobalt(II) and -(III) acetylacetonate in dimethyl sulfoxide or water. In the absence of *tert*-butyl hydroperoxide, oxygen absorption was negligible. The autoxidation cell was cleaned between runs by soaking in hot aqueous solution several times, followed by methanol washings.

tert-Butyl hydroperoxide decomposition studies were carried out in the absence of oxygen in degassed new Carius tubes thermostated at 42.0 ± 0.1°. Peroxide was determined iodometrically.

Cobalt(II) and -(III) acetylacetonate concentrations were determined spectrophotometrically sampled from the peroxide decomposition tubes. A Cary 17 spectrophotometer was used for analysis. Cobalt(II) and -(III) acetylacetonate absorptions were recorded at 256 and 290 mμ. Since mixtures of these two compounds have overlapping peaks, concentrations were estimated from simultaneous equations of the form $a_\lambda = \epsilon_{\lambda_2} c_{\mathrm{II}} + \epsilon_{\lambda_3} c_{\mathrm{III}}$, where a_λ is the absorption at a given wavelength, ϵ_λ is the extinction coefficient of either cobalt(II) or -(III) acetylacetonate at a given wavelength λ, and c_{II} and c_{III} are the concentrations of cobalt(II) and -(III) acetylacetonate. Experimentally determined extinction coefficients derived from Beer's law plots for cobalt(II) and -(III) acetylacetonate in dimethyl sulfoxide and water are 1.63 × 10^4(H_2O) and 1.31 × 10^4(DMSO) at 290 mμ and 2.08 × 10^4(H_2O) and 3.8 × 10^4(DMSO) at 256 mμ. A *tert*-butyl hydroperoxide solution was prepared at the same concentration found in the reacted solution as determined by iodometric titration. This was used as a blank. Concentrations of *tert*-butyl hydroperoxide in the reaction mixtures were low (0.016 *M*) to avoid interference of *tert*-butyl hydroperoxide absorption.

The reproducibility of triplicate rate measurements was ca. ±5% for autoxidation measurements, ca. ±10% for *tert*-butyl hydroperoxide decomposition, and ca. ±5% for spectrophotometric ratios of cobalt(II) to cobalt(III) acetylacetonate.

Results and Discussion

The experimentally measured data points are of three kinds: *tert*-butyl hydroperoxide decomposition ($-\Delta[t\text{-BuOOH}]/\Delta t$), oxygen absorption ($-\Delta[O_2]/\Delta t$), and the ratio of cobalt(II) to cobalt(III) acetylacetonate concentration as assessed from uv absorption measurements. Table I contains data for the cobalt(II) and cobalt(III) concentrations determined spectrophotometrically in dimethyl sulfoxide and water. Table II contains rate data for *tert*-butyl hydroperoxide decomposition in water and dimethyl sulfoxide. Table III contains rate data for oxygen uptake in di-

Table I
Uv Spectral Changes[f]

$[\mathrm{Co} \times 10^5]_0$, *M*	$[\mathrm{PVA}]_0$, M^b	$B_1{}^c$	$B_2{}^d$	U^e
		Dimethyl Sulfoxide		
$Co(acac)_2$				
4.12	0.12	0.85	0.92	0.88
4.53	0.36	0.84	0.85	0.81
9.25	0.24	0.87	0.89	0.87
17.1	0.12	0.78	0.85	0.85
17.4	0.36	0.87	0.80	0.84
$Co(acac)_3$				
1.86	0.12	0.10	0.78	0.78
4.37	0.12	0.16	0.70	0.80
4.56	0.24	0.19	0.72	0.81
30.7	0.12	0.10	0.69	0.75
30.2	0.36	0.13	0.70	0.74
		Water		
$Co(acac)_2$				
17.5	0.12	0.57	0.22	0.81
17.5	0.24	0.57	0.19	0.80
17.5	0.36	0.57	0.25	0.77
39.1	0.24	0.48	0.32	0.81
$Co(acac)_3$				
10.1	0.12	0.29	0.16	0.81
10.3	0.24	0.23	0.14	0.80
10.5	0.36	0.23	0.16	0.83
35.1	0.24	0.25	0.20	0.75

[a] $[t\text{-BuOOH}]_0 = 0.016$ *M*. [b] Moles/liter of C_2H_4O units. [c] $B_1 = [\mathrm{Co(acac)_2}]/\{[\mathrm{Co(acac)_2}] + [\mathrm{Co(acac)_3}]\}$ measured at 1 × 10^4 sec. [d] $B_2 = [\mathrm{Co(acac)_2}]/\{[\mathrm{Co(acac)_2}] + [\mathrm{Co(acac)_3}]\}$ measured at 2 × 10^5 sec. [e] $U = \{[\mathrm{Co(acac)_2}] + [\mathrm{Co(acac)_3}]\}/[\mathrm{Co(acac)}_n]_0$ measured at 2 × 10^5 sec. [f] Cobalt(II) and -(III) acetylacetonate in the presence of poly(vinyl alcohol) and *tert*-butyl hydroperoxide[a] in dimethyl sulfoxide and water at 42°.

Table II
Rates of Peroxide Decomposition[a]

$[\text{Co} \times 10^5]_0$, M	$[t\text{-BuOOH}]_0$, M	$[\text{PVA}]_0$, M^b	$([t\text{-BuOOH}]/\Delta t)_0 \times 10^9$, M/sec
	Dimethyl Sulfoxide		
Co(acac)_2			
4.12	0.016	0.12	16.3
4.53	0.016	0.36	22.7
9.60	0.016	0.36	34.2
17.1	0.016	0.12	33.2
17.4	0.016	0.36	46.7
2.72	0.160	0.24	32.5
6.85	0.060	0.12	25.1
6.85	0.660	0.12	82.3
6.85	0.016	0.24	24.5
6.85	0.660	0.24	98.0
6.85	0.016	0.36	29.0
6.85	0.160	0.36	67.0
6.85	0.960	0.36	118.2
13.70	0.160	0.12	60.1
13.70	0.660	0.24	163.1
13.70	0.160	0.36	101.1
Co(acac)_3			
1.86	0.016	0.12	9.61
1.95	0.016	0.24	11.5
4.37	0.016	0.12	14.2
4.25	0.016	0.36	21.2
31.2	0.016	0.24	48.1
30.2	0.016	0.36	55.1
	Water		
Co(acac)_2			
17.5	0.016	0.12	5.50
2.0	0.016	0.24	2.45
39.1	0.016	0.24	10.90
17.5	0.160	0.24	28.3
17.5	0.68	0.24	91.2
Co(acac)_3			
10.1	0.016	0.12	3.45
10.5	0.016	0.36	5.51
35.1	0.016	0.24	8.45
10.6	0.160	0.24	19.5
10.6	0.660	0.24	65.6

[a] *tert*-Butyl hydroperoxide in the presence of cobalt(II) and -(III) acetylacetonate and poly(vinyl alcohol) in water and dimethyl sulfoxide at 42°. [b] Moles/liter of C_2H_4O units.

methyl sulfoxide and water. Table IV gives rate "constants" and concentration superscripts of the various rate equations obtained from log–log plots of initial rates vs. initial concentrations in dimethyl sulfoxide and water. These tables represent only a small portion of the experimental data collected.

Cobalt(II) and -(III) Acetylacetonate Spectral Changes. A steady state concentration was reached by cobalt(II) and -(III) acetylacetonate in dimethyl sulfoxide and aqueous solutions within 1 × 10^5 sec in the presence of *tert*-butyl hydroperoxide and poly(vinyl alcohol) (Table III). Presumably the steady state concentration is brought about by the following reactions.

$$\text{ROOH} + \text{Co(II)} \longrightarrow \text{RO}\cdot + \text{Co(III)} + \text{OH}^- \quad (1)$$

$$\text{ROOH} + \text{Co(III)} \longrightarrow \text{ROO}\cdot + \text{Co(II)} + \text{H}^+ \quad (2)$$

The columns labeled B_1 and B_2 in Table I are the fraction of Co(acac)_2 present in sealed reaction tubes (oxygen excluded) after 1 × 10^4 and 2 × 10^5 sec, respectively. It may be seen that regardless of the species initially present Co(acac)_2 predominates in dimethyl sulfoxide whereas Co(acac)_3 predominates in water under the concentration conditions studied. The column labelled U reflects the overall loss of Co(acac)_n (both Co(II) and Co(III)) measured at 2 × 10^5 sec. The combined absorption accounts for only 75–85% of the cobalt acetylacetonate initially present regardless of the medium and regardless of the initial cobalt oxidation state. Some of this depletion can be accounted for in the case of Co(acac)_2 by the unavailability of the acetylacetonate ligand in the conversion of Co(II) to Co(III) but in the reverse situation, when Co(acac)_3 is initially present, a surplus of the ligand is present.

Table III
Rates of Oxygen Uptake[a]

$[\text{Co} \times 10^5]_0$, M	$[t\text{-BuOOH}]_0$, M	$[\text{PVA}]_0$, M^b	$[\Delta O_2/\Delta t]_0 \times 10^7$, M/sec	
			II[c]	III[d]
		Dimethyl Sulfoxide		
6.85	0.16	0.12	1.64	1.08
13.7	0.16	0.12	2.16	1.60
13.7	0.96	0.12	3.10	3.50
27.4	0.16	0.12	3.31	2.72
27.4	0.96	0.12	4.00	4.20
6.85	0.16	0.24	2.24	1.52
13.7	0.96	0.24	4.00	3.56
27.4	0.16	0.24	4.48	3.56
6.85	0.66	0.36	5.36	3.12
13.7	0.16	0.36	4.92	2.88
27.4	0.16	0.36	6.80	4.48
27.4	0.96	0.36	8.40	6.68
202	0.66	0.24	8.50	7.50
1010	0.66	0.24	8.40	9.10
6.85	0.016	0.24	1.06	0.92
6.85	0.016	0.00	0.30	0.20
		Water		
6.85	0.16	0.12	3.00	*e*
13.7	0.16	0.12	4.20	*e*
27.4	0.66	0.12	12.0	*e*
6.85	0.66	0.24	6.44	6.72
13.7	0.66	0.24	9.21	9.60
27.4	0.66	0.24	12.9	13.5
6.85	0.96	0.36	4.48	*e*
6.85	0.96	0.36	6.24	*e*
13.7	0.66	0.36	12.3	*e*
27.4	0.16	0.36	8.81	*e*
27.4	0.66	0.36	17.5	*e*
6.85	0.016	0.00	0.25	*e*

[a] Poly(vinyl alcohol) in the presence of cobalt(II) and -(III) acetylacetonate and *tert*-butyl hydroperoxide in dimethyl sulfoxide and water at 42°. [b] Moles/liter of C_2H_4O units. [c] Co(acac)_2 initially present. [d] Co(acac)_3 initially present. [e] No data.

The most likely explanation for the decrease in overall absorption then is some form of ligand exchange with the solvent or the peroxide. Reaction mixtures containing cobalt(II) acetylacetonate produce precipitates when titrated with 0.01 N NaOH in either dimethyl sulfoxide or aqueous solution, although stock solutions of cobalt(II) acetylacetonate in dimethyl sulfoxide or water do not. A stock solution of cobalt(II) acetylacetonate (10^{-2} M) which was allowed to air oxidize to cobalt(III) acetylacetonate (pink color to green) also failed to give a precipitate with 0.01 N NaOH. This suggests that the acetylacetonate ligand has been exchanged in solution for another ligand in the course of per-

Table IV
Empirical Rate Equations

$[Co \times 10^5]_0$, M	$[t\text{-BuOOH}]_0$, M	$[PVA]_0, M$	a	b	c	$k \times 10^4$
tert-Butyl Hydroperoxide Decomposition at 42° $(\Delta[t\text{-BuOOH}]/\Delta t) = k[Co]^a[t\text{-BuOOH}]^b[PVA]^c$						
Dimethyl Sulfoxide						
$Co(acac)_2$						
4.12–17.5	0.016	0.12–0.36	0.55 ± 0.01			0.12 ± 0.02
2.7–13.7	0.160	0.12–0.36	0.55 ± 0.01			0.60 ± 0.03
6.85	0.016–0.06	0.12–0.36		0.14 ± 0.01		0.10 ± 0.02
6.85	0.06–0.96	0.12–0.36		0.47 ± 0.02		0.61 ± 0.03
4.12–17.5	0.016–0.66	0.12–0.36			0.35 ± 0.05	0.60 ± 0.05
$Co(acac)_3$						
1.86–30.7	0.016	0.12–0.36	0.52 ± 0.02			0.41 ± 0.03
1.86–4.50	0.016	0.12–0.36			0.30 ± 0.05	0.42 ± 0.04
30.5	0.016	0.12–0.36				0.41
2.0	0.016–0.66	0.24		0.48		0.40
Water						
$Co(acac)_2$						
2.00–39.1	0.016	0.24	0.50 ± 0.05			0.13
17.5	0.016–0.16	0.24		0.66 ± 0.04		0.12
17.5	0.16–0.66	0.24		0.81 ± 0.10		0.26
17.5	0.016	0.12–0.36			0.47 ± 0.03	0.13
$Co(acac)_3$						
2.00–35.1	0.016	0.24	0.49 ± 0.05			0.072
10.6	0.016–0.16	0.24		0.53 ± 0.06		0.073
10.6	0.16–0.66	0.24		0.78 ± 0.10		0.16
10.6	0.016	0.24			0.46 ± 0.03	0.071
Autoxidation of Poly(vinyl alcohol) at 42° $(\Delta[O_2]/\Delta t) = k[Co]^a[t\text{-BuOOH}]^b[PVA]^c$						
Dimethyl Sulfoxide						
$Co(acac)_2$						
6.85–27.4	0.16–0.96	0.12–0.36	0.47 ± 0.05	0.45 ± 0.20	0.55 ± 0.15	0.81 ± 0.30
$Co(acac)_3$						
6.85–27.4	0.16–0.96	0.12–0.36	0.55 ± 0.10	0.50 ± 0.20	0.40 ± 0.10	0.61 ± 0.40
Water						
$Co(acac)_2$						
6.85–27.4	0.16–0.96	0.12–0.36	0.50 ± 0.10	0.50 ± 0.05	0.40 ± 0.03	2.1 ± 0.30

oxide decomposition, which will exchange with OH^- to produce a precipitate. The decrease of the overall cobalt acetylacetonate concentration was more rapid at 60° than at 42°, implying that the rate of the exchange reaction increases with temperature and has an activation energy.

The Decomposition of *tert*-Butyl Hydroperoxide. Rates, empirical kinetic equations, and activation parameters for *tert*-butyl hydroperoxide decomposition in vacuo are listed in Tables I, IV, and V for both dimethyl sulfoxide and water.

Richardson[8] has devised a kinetic scheme for metal catalyzed peroxide decomposition which involves a metal–hydroperoxide complex. The reaction order with respect to *tert*-butyl hydroperoxide and metal is between 0.5 and 1.0 in this kinetic scheme. In order to secure additional evidence for the existence of metal–peroxide complexing, observations were made in the NMR on the effect of line broadening of the OOH proton by added cobalt species. It was found that marked broadening of this peak occurred in the presence of 10^{-3} M cobalt(II) acetylacetonate-*tert*-butyl hydroperoxide reaction mixtures in carbon tetrachloride.[9] After reacting for 6.5×10^5 sec solutions of cobalt(III) acetylacetonate and *tert*-butyl hydroperoxide do exhibit broadening, presumably because the cobalt(II) form is present as a result of reaction 2. The mechanism of Richardson can be contrasted to a more general reaction mechanism for *tert*-butyl hydroperoxide decomposition devised by Hiatt, et al.[10] Hiatt's mechanism involves a metal cycling reaction (reactions 1 and 2), with reaction 3 involving a radical induced decomposition of *tert*-butyl hydroperoxide and termination reactions 4 and 5. This is similar to the scheme employed by Richardson except that no metal complex reaction with *tert*-butyl hydroperoxide is invoked to explain the results.

$$RO\cdot + ROOH \longrightarrow ROH + ROO\cdot \qquad (3)$$

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2 \qquad (4)$$

$$2ROO\cdot \longrightarrow ROOR + O_2 \qquad (5)$$

Assuming steady state concentrations for ROO· and RO· and a rapid cycling reaction for the metal and substituting for total cobalt concentration ($Co_T = Co(II) + Co(III)$) eq 6

$$-d[t\text{-BuOOH}]/dt = [2k_4/k_5 + 3]\left[\frac{k_1k_2}{k_1 + k_2}\right][Co_T][t\text{-BuOOH}] \qquad (6)$$

Table V
Activation Parameters for the Autoxidation of Poly(vinyl alcohol)[a] and the Decomposition of *tert*-Butyl Hydroperoxide[b] in the Presence of Cobalt Acetylacetonates, 42–60°, in Dimethyl Sulfoxide and Water

$[Co \times 10^5]_0$, M		E_a, kcal/mol		$\Delta H^\dagger$, kcal/mol		$\Delta S^\dagger$, cal/(deg mol)	
II	III	DMSO	H_2O	DMSO	H_2O	DMSO	H_2O
		Autoxidation of Poly(vinyl alcohol)					
17.5		7.8	7.4	6.5	6.1	−43	−48
	10.6	10.1	8.7	8.8	7.4	−35	−36
		Decomposition of *tert*-Butyl Hydroperoxide					
17.5		27.1	28.2	25.8	26.9	+82.7	+93.7
	10.6	27.3	28.5	26.0	27.2	+82.4	+103

[a] $[t\text{-BuOOH}]_0 = 0.016$ M. [b] $[PVA]_0 = 0.24$ M in C_2H_4O units.

Table VI
Kinetic Chain Lengths for the Autoxidation of Poly(vinyl alcohol) in the Presence of Cobalt(II) Acetylacetonate and *tert*-Butyl Hydroperoxide in Dimethyl Sulfoxide and Water at 42°

$[Co \times 10^5]_0$, M	$[t\text{-BuOOH}]_0$, M	$[PVA]_0$, M[a]	Kinetic chain length[b] DMSO	Kinetic chain length[b] H_2O
6.85	0.16	0.12	4.0	24.0
13.7	0.66	0.12	4.0	14.9
27.4	0.96	0.12	4.0	*c*
13.7	0.66	0.24	3.1	11.4
6.85	0.66	0.36	4.1	12.4
27.4	0.66	0.36	3.4	12.3

[a] Moles/liter of C_2H_4O units. [b] $[\Delta O_2/\Delta t]_0/(\Delta[t\text{-BuOOH}]/\Delta t)_0$. [c] No data.

is obtained. The approach to first-order kinetics with respect to *tert*-butyl hydroperoxide in water may indicate that complexation is not an important reaction for *tert*-butyl hydroperoxide decomposition in aqueous solution, whereas in dimethyl sulfoxide this reaction may take on significance. The importance of a complexation reaction in dimethyl sulfoxide as contrasted with aqueous solution is supported by data on the relative ligand strengths of cobalt complexes in dimethyl sulfoxide and water and on the basis of previous work from this laboratory on poly(vinyl alcohol)–cobalt(II) complexation in dimethyl sulfoxide and water.[11]

The role of poly(vinyl alcohol) in *tert*-butyl hydroperoxide decomposition may be related to the ability of α hydroxy ketones to promote peroxide decomposition and metal reduction.[12] Reactions such as reactions 7 and 8 may be involved.

$$\text{Co(III)} + RCH_2OH \longrightarrow RCH_2O\cdot + H^+ + \text{Co(II)} \quad (7)$$

$$\text{Co(III)} + RCH_2O\cdot \longrightarrow RCHO + H^+ + \text{Co(II)} \quad (8)$$

tert-Butyl hydroperoxide concentration above 0.66 M does not seem to increase the rate of peroxide decomposition significantly. This may be related to viscosity effects on termination reactions 4 and 5,[13,14] saturation of metal sites by peroxide complexing, and increased deactivation of the catalyst as a result of the added *tert*-butyl hydroperoxide.[14]

Autoxidation. Initial oxygen absorption rates, empirical kinetic equations, and activation parameters for the autoxidation of poly(vinyl alcohol) with cobalt(II) and -(III) acetylacetonate and *tert*-butyl hydroperoxide are listed in Tables I, II, III, and IV. Table IV lists the ratios $(\Delta[O_2]/\Delta[t\text{-BuOOH}])_0$, which can be taken as a measure of the kinetic chain length for autoxidation, assuming the rate of initiation (R_i) is equal to the rate of peroxide decomposition (i.e., that chain lengths for *tert*-butyl hydroperoxide decomposition are equal to unity). Chain lengths for autoxidation appear to be greater in aqueous than in dimethyl sulfoxide solution from the data in Table VI. One possible explanation for this is that propagating poly(vinyl alcohol) radicals have a lower rate of termination in water than in dimethyl sulfoxide. The poly(vinyl alcohol) is more coiled in aqueous solution and as a result radicals on the chain are less likely to terminate. This possibility has been supported by polymerization studies.[16] Another possible explanation is that water might solvate terminating pairs of polymer radicals (reactions 12 and 13) more effectively than dimethyl sulfoxide, increasing the proportion of reaction 13 to 12. Niki and Kamiya[13] have data to support this contention in polypropylene autoxidation. Chain transfer to solvent appears to be minimal in either aqueous[16] or dimethyl sulfoxide solution,[17] although chain transfer constants are higher for dimethyl sulfoxide than water. The results are in reasonable agreement with autoxidation schemes devised by Tobolsky[18] or Mayo[19] for the autoxidation of bulk polypropylene. These schemes are based on the following autoxidation steps, where PH is the polymer and I is the initiator.

$$I \longrightarrow I\cdot\ (t\text{-BuOO}\cdot \text{ or } t\text{-BuO}\cdot) \quad (9)$$

$$t\text{-BuO}\cdot + PH \longrightarrow t\text{-BuOH} + P\cdot \quad (10)$$

$$P\cdot + O_2 \longrightarrow PO_2\cdot \quad (11)$$

$$PO_2\cdot \longrightarrow P_2O_2 + O_2 \quad (12)$$

$$2PO_2\cdot \longrightarrow 2PO\cdot + O_2 \quad (13)$$

Using steady state approximation for the polymer radical, Tobolsky derived the following equations from reactions 9–13.

$$\begin{aligned} d[O_2]/dt &= R_i + k_p k_t^{-1/2}[PH]R_i^{1/2} \\ \frac{(d[O_2]/dt)}{R_i} &= 1 + k_p k_t^{-1/2}[PH]R_i^{-1/2} \end{aligned} \quad (14)$$

A plot of chain length vs. $R_i^{-1/2}$ ought to yield intercept 1 and slope $\alpha k_p/k_t^{1/2}$. Figure 1 presents data which show reasonable agreement with this mechanism.

In aqueous solution $k_p/k_t^{1/2}$ obtained from the slope of the line passing through 1.0 is $\sim 1 \times 10^{-2}$ and $\sim 3 \times 10^{-3}$ in dimethyl sulfoxide (see Figure 1). The oxidizability of poly(vinyl alcohol) in aqueous solution is greater than in dimethyl sulfoxide, evidently because of the higher chain

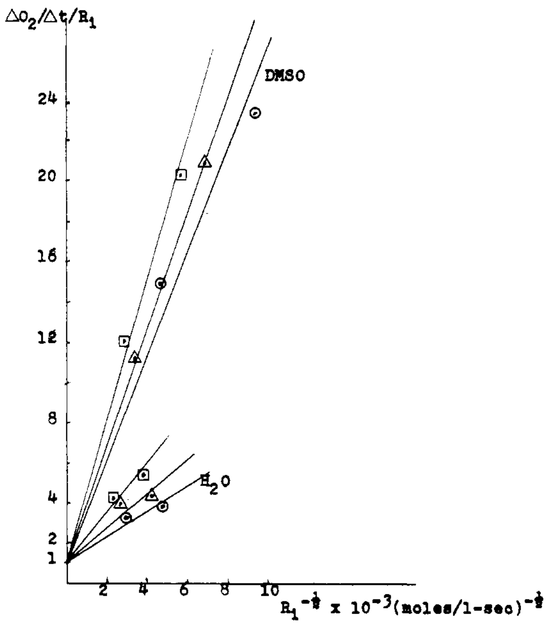

Figure 1. Kinetic chain length for the autoxidation of poly(vinyl alcohol) vs. $R_i^{-1/2}$ in the presence of 1.3×10^{-4} *M* cobalt(II) acetylacetonate, 0.16–0.66 *M* *t*-BuOOH, and (⊙) 0.53 g/dl, (△) 1.06 g/dl, and (⊡) 1.60 g/dl poly(vinyl alcohol) (0.12 *M*, 0.24 *M*, and 0.36 *M* in C_2H_4O units) in water and dimethyl sulfoxide at 42°.

lengths for autoxidation in aqueous solution.

In a similar manner Mayo derived eq 15 for the rate of autoxidation, in which the first term on the right-hand side

$$d[O_2]/dt = aR_i + \tfrac{1}{2}R_i^{1/2}k_pk_t^{-1}[PH] \qquad (15)$$

is for nonpropagating autoxidation reactions and the second for propagating autoxidation reactions. A plot similar to that employed for Tobolsky's equation should yield an intercept of *a*. The advantage of this approach is that the constant *a* is a complex function of solution viscosity and therefore allows for a more complete explanation for the results. Our data do not permit a distinction between eq 14 and 15. Reaction orders in Table IV are consistent with these equations. It should be noted that the reaction order of poly(vinyl alcohol) with respect to autoxidation decreases with an increasing concentration of *tert*-butyl hydroperoxide. This may result from an increase in the viscosity of the medium, increasing cage termination of polymer radicals with initiator fragments.[13,14] At high peroxide concentrations (>0.66 *M*) the rate of autoxidation decreases in both dimethyl sulfoxide and aqueous solution. This may be related to the decreased *tert*-butyl hydroperoxide decomposition rates mentioned above. It is also possible that the increased viscosity at higher *tert*-butyl hydroperoxide concentration affects initiator efficiency or polymer termination reactions.[13]

Additional work from this laboratory includes reports on the effects of different acetylacetonates on the cleavage and autoxidation of poly(vinyl alcohol),[20] the effects of biologically important metal complexes on the same reactions, and a study of the products of these reactions.

References and Notes

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