Notes

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

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As part of an investigation[2] of the reactions of metal acetylacetonates and *tert*-butyl hydroperoxide systems, the cleavage of poly(vinyl alcohol) by cobalt(II) and cobalt(III) acetylacetonates in the presence of *tert*-butyl hydroperoxide has been studied. The reaction has been observed in both water (at 42 and 100°) and dimethyl sulfoxide (at 42°) solutions at various acetylacetonate concentrations.

As well as acetylacetonates, a variety of cobalt salts were investigated at comparable concentrations. Peroxide analyses were performed to establish whether peroxide decomposition accounts for the difference in the two different cleavage rates observed in dimethyl sulfoxide and water. The effect of small amounts of water on the rate of cleavage by cobalt acetylacetonate and *tert*-butyl hydroperoxide in dimethyl sulfoxide was observed.

The use of contact shifts[3] on the nmr spectra was investigated as a method for determining the presence of cobalt–poly(vinyl alcohol) complexes and their sensitivity to water.

Experimental Section

Materials. Poly(vinyl alcohol) (K & K Laboratories), viscosity av mol wt 9.1 × 10^4 g/mol, was used throughout. Molecular weight was estimated from the eq 1 and 2[4] using an Ubbelohde

$$[\eta](\mathrm{H_2O}) = 4.53 \times 10^{-4}\,\bar{M}_{\mathrm{v}}^{\,0.64} \qquad (1)$$

$$[\eta](\mathrm{Me_2SO}) = 1.58 \times 10^{-4}\,\bar{M}_{\mathrm{v}}^{\,0.84} \qquad (2)$$

viscometer at 42.00 ± 0.02°. Polymer was dried in a vacuum oven (45°, 1 mm) 4 days and stored in a vacuum desiccator. Stock solutions were prepared by stirring solutions 2 days and filtering. Periodate-cleaved poly(vinyl alcohol) was prepared[5] by dissolving potassium metaperiodate in poly(vinyl alcohol) solution, warming, and reprecipitating with acetone. The cleaved polymer had a molecular weight of 5.5 × 10^3 g/mol. Following the method of Flory and Leutner[6] the mol % of 1,2-glycol structure ($\Delta \times 100$) is equal to 1.53.

tert-Butyl hydroperoxide (Wallace & Tiernan) was used as supplied. Iodometric analysis[7] indicated >90% purity.

Acetylacetonates (The MacKenzie Chemical Works, Inc.) were recrystallized from acetone and benzene. All salts were dried in a vacuum oven at 60°, 1 mm. Stock solutions were used immediately.

Dimethyl sulfoxide (Fischer Chemical Co.) was vacuum distilled and stored over Fischer Type 4A molecular sieve.

Viscometry. All viscometry was performed at 42.00 ± 0.02° in modified Ubbelohde viscometers. Flow times were all long enough to neglect kinetic energy corrections. Molecular weights were estimated from eq 1 and 2.

Table I
Decomposition Rates[a] of *tert*-Butyl Hydroperoxide[b] in the Presence of Cobalt(II) and Cobalt(III) Acetylacetonate in Water and Dimethyl Sulfoxide (42°)

$[\mathrm{Co(acac)_2}]_0$, × 10^5 *M*	$[\mathrm{Co(acac)_3}]_0$, × 10^5 *M*	$[-\Delta(t\text{-BuOOH})/\Delta t] \times 10^7$ *M*/sec $\mathrm{H_2O}$	$\mathrm{Me_2SO}$
0.00	1.79	0.497	0.486
2.12	0.00	2.32	2.28

[a]Total reaction time = 171 hr. [b]0.72 *M*.

The relative viscosities of our reactant solutions were corrected for the increase in viscosity due to the presence of *tert*-butyl hydroperoxide. Intrinsic viscosities were measured by extrapolation to infinite dilution.[8] Rates of polymer degradation are reported as initial rates. The usual total reaction time studied was about 300 hr. The periodate-cleaved polymer showed essentially no viscometric changes in water or dimethyl sulfoxide in the presence of acetylacetonates and *tert*-butyl hydroperoxide over 190 hr at 42°. Experiments under nitrogen were performed directly in the viscometers. Reaction mixtures were kept under a slight positive pressure except for the times during which viscometric determinations were made. Reactions at 100° were performed in refluxing water. Aliquots were taken after 48 hr and introduced into the viscometers thermostated at 42.00 ± 0.02°. Replicate runs produced an uncertainty of ±5% in the rates.

Peroxide Analysis. Analysis of *tert*-butyl hydroperoxide has been described previously.[7] Table I presents iodometrically determined decomposition rates of *tert*-butyl hydroperoxide in water and $\mathrm{Me_2SO}$.

Nmr Spectroscopy. The Varian HA-100 was used with tetramethylsilane reference. Polymer was predried in a vacuum oven at 1 mm of Hg at 60° and was dissolved in dimethyl-d_6 sulfoxide (Stohler Isotopes), dried over molecular sieve (Fischer Type 4A), and poured through a molecular sieve column attached *via* a septum to an nmr tube. Cobalt(II) chloride was dried in a vacuum oven and then dissolved in dimethyl-d_6 sulfoxide and stored over molecular sieve. The solution was added with a microliter syringe through the septum.

Results and Discussion

Table II sets forth results obtained viscometrically for molecular weight changes of poly(vinyl alcohol) in water and dimethyl sulfoxide with added cobalt acetylacetonates and *tert*-butyl hydroperoxides. A salient feature of the results is the enhanced rate in dimethyl sulfoxide as compared to water at 42° (see Figure 1). In the absence of either metal or peroxide the reaction proceeds to a negligible extent or only after a prolonged induction period. The presence of either cobalt(II) or cobalt(III) acetylacetonate enhances the rate of reaction although addition of cobalt(II) generally increases the rate more than cobalt(III) in both water and dimethyl sulfoxide.

An important aspect of the mechanism is the apparent specificity of the cleavage reaction. Periodate cleaved poly(vinyl alcohol) did not undergo further cleavage in the presence of cobalt acetylacetonates and *tert*-butyl hydroperoxide. Mino *et al.*[9] have described a similar reaction with

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[2] N. Indictor, T. Jochsberger, and D. Kurnit, *J. Org. Chem.*, **34**, 2855 (1969), and references therein.

[3] W. A. Szarek and M. C. Baird, *Tetrahedron Lett.*, **No. 24**, 2097 (1970).

[4] J. G. Pritchard, "Poly(Vinyl Alcohol)," Gordon and Breach Science Publishers, Inc., New York, N. Y., 1970, pp 12, 16.

[5] D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., New York, N. Y., 1967, pp 278 ff.

[6] P. J. Flory and F. S. Leutner, *J. Polym. Sci., Part A*, **3**, 880 (1948).

[7] N. Indictor and T. Jochsberger, *J. Org. Chem.*, **31**, 4271 (1966).

[8] Appropriate corrections for concentration effects due to reaction were made.

[9] G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polym. Sci., Part A*, **39**, 523 (1959).

Table II
Initial Cleavage Rates of Poly (vinyl alcohol)^a in the Presence of Cobalt(II) and Cobalt(III) Acetylacetonates and *tert*-Butyl Hydroperoxide^b in Water and Dimethyl Sulfoxide

$[Co(acac)_2]_0$, × 10^5 *M*	$[Co(acac)_3]_0$, × 10^5 *M*	$-\Delta\bar{M}_v/\Delta t]_0 \times 10^2$ g/(mol sec) H_2O	Me_2SO
	42°		
0.00	0.00	0.00	1.90
0.00	0.402	n^c	2.53
0.00	1.48	0.656, $0.943^{d,e}$	*n*
0.00	1.71	*n*	$7.22,^e$ 4.84
0.00	1.79	*n*	$1.56^{d,f}$
0.00	13.6	*n*	7.50
0.00	14.2	1.39^e	*n*
0.622	0.0	*n*	2.53
1.97	0.0	1.33^e	*n*
2.06	0.0	0.578	*n*
2.12	0.0	*n*	8.67, $0.348^{d,f}$
2.12	1.79	*n*	19.4
2.49	0.0	*n*	8.67
9.96	0.0	*n*	18.5
30.3	0.0	$0.522,^{e,f}$ 0.00^f	*n*
30.3	0.0	1.75	*n*
30.3	1.58	$1.24,^{e,f}$ 0.00^f	*n*
30.3	1.58	1.31, 2.39^e	*n*
135	0.0	$0.0,^f$ $1.39^{e,f}$	*n*
135	0.0	3.98^e	*n*
	100°		
0.00	0.00	$2.88,^f$ 43.6	*n*
0.00	1.58	47.0	*n*
30.3	0.0	47.2	*n*
30.3	1.58	$0.00,^f$ 50.0	*n*

^{a}1.06 g/dl. ^{b}0.72 *M*. ^{c}*n* = no data. ^{d}After induction period. ^{e}Under N_2 atmosphere. ^{f}[*t*-BuOOH] = 0.00.

cerium salts in which reaction at the 1,2-diol site proved to be much more rapid than at the 1,3 site. In all reactions in our study, molecular weight changes corresponded to fewer cleavages than the total number of 1,2-diol linkages present in the poly(vinyl alcohol).

In view of the possibility of a rate determining complex in this reaction, nmr studies were conducted with cobalt(II) chloride solutions (concentration range 1.7×10^{-6} to 1.7×10^{-5} *M*) and poly(vinyl alcohol) in dried dimethyl-d_6 sulfoxide. A shift of the methinyl proton of 8–14 Hz upfield was observed. This is consistent with the results of Szarek and Baird[3] on *cis*- and *trans*-1,2-cyclohexanediols. These authors showed that a contact shift takes place as a result of a paramagnetic complex between cobalt(II) acetylacetonate and diols. A plot of the chemical shifts observed *vs.* cobalt(II) chloride concentration (Figure 2) shows increasing values up to about 3.5×10^{-6} *M* followed by a leveling off. The concentration at which leveling off occurs corresponds to the concentration of 1,2-diol linkages. This shifting with poly(vinyl alcohol) is not observed when trace amounts of water are present in solution. The cobalt ion is probably preferentially complexed with the water in this case.

Small amounts of water (0.04–0.2 *M*) were added to dimethyl sulfoxide reaction mixtures and the observed rates of cleavage decreased.

In order to test the hypothesis that the cleavage reaction involves rate determining competition for complex sites at cobalt, a series of other cobalt salts (CoF_2, CoF_3, $CoCl_2$, $CoBr_2$, CoI_2, $Co(NO_3)_2$) was used as catalysts for the cleavage reaction ([Co salt] ~ 2×10^{-5} *M*; [PVA] = 1.06 g/dl; [*t*-BuOOH] = 0.72 *M*; *T* = 42°). Although a 25-fold range was observed in the cleavage rates in dimethyl sulfoxide among the salts studied (indicating the generality of the reaction), no obvious correlation (with, *e.g.*, ligand exchange ability, electron transfer, size, or the spectrochemical series)[10] was noted. Presumably, the observed effect represents a combination of several factors.

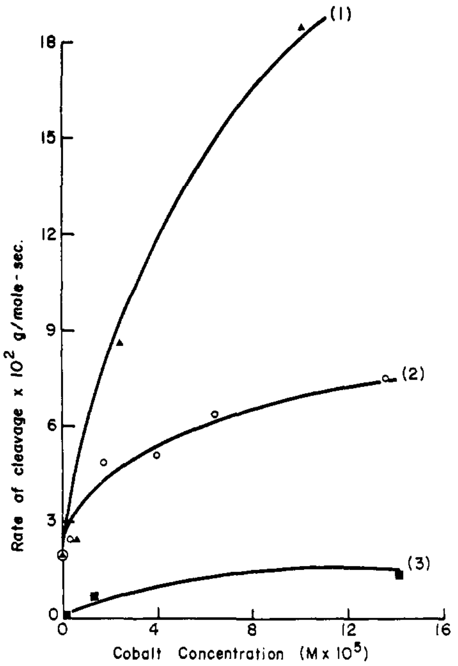

Figure 1. The effect of cobalt concentration on the rate of cleavage under different conditions: (1) $Co(acac)_2$ in Me_2SO; (2) $Co(acac)_3$ in Me_2SO; (3) $Co(acac)_2$ in water.

Work[11] in this laboratory indicates that the UV spectra of the cobalt acetylacetonates undergo changes under the above reaction conditions. It has also been observed that the rate of cobalt acetylacetonate induced decomposition of *tert*-butyl hydroperoxide proceeds at essentially the same rate in dimethyl sulfoxide as in water (Table I), implying that the cleavage rate is not a function of peroxide decom-

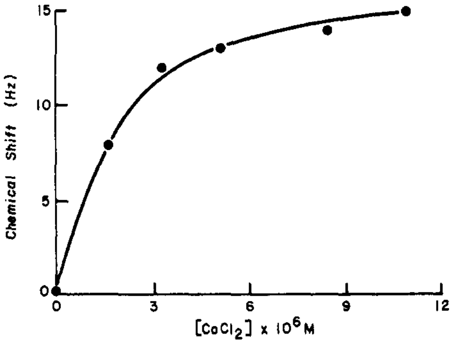

Figure 2. The effect of cobalt concentration on the chemical shift of the methinyl proton of poly(vinyl alcohol).

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(10) (a) H. Taube, *Can. J. Chem.*, **37**, 129 (1959). (b) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Publishing Co., Inc., New York, N. Y., 1968, pp 324 ff.

(11) A. Auerbach and A. Kruger, unpublished results.

position. The effect of molecular oxygen is also being studied. These reaction solutions absorb oxygen readily at 42°. A full report of these results and their implications for the mechanism of the cleavage of poly(vinyl alcohol) will be presented shortly.

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Domain Size in Ionomers

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Metal salts of carboxylic acid substituted hydrocarbon polymers (called ionomers) show considerably higher stiffness and tensile strength values than their free acid counterparts. This fact is attributed to aggregation of the ionizable groups into clusters, similar to the formation of micelles of metal salts of low molecular weight carboxylic and sulfonic acids in hydrocarbon solution.[1-3]

The size of the clusters in still in dispute, however. Some authors suggest the presence of a separate polar phase dispersed as domains of over 10 nm in size[4,5] with the clusters located in the domains; others state that the aggregation is nothing but dimerization of carboxylic groups.[6]

We take the view that the ionomers contain polar domains of a limited size, being identical with the clusters mentioned. This view is based on the following facts. (1) X-Ray diffractograms of metal salts of ethylene-methacrylic acids show a specific, rather broad peak[4,5] at about 4°, 2 ϑ, besides the ordinary ones due to crystalline polyethylene. Melting (of the crystalline polyethylene) does not cause this peak to disappear but soaking the material in water does. (2) Since alkali and alkaline-earth metal ions require a 6 coordination of oxygen (or other negatively charged atoms) electric neutrality requires most oxygens to be attached to more than one metal ion. This should lead to polar clusters of appreciable size. On the other hand, space requirements of the pendant polymer chains as well as the entropy of dilution associated with the breaking up of the clusters tend to reduce the size of the latter.

The 4° peak can be attributed to the clusters being areas of higher electron density than their surroundings. Uptake of water reduces the electron density of the clusters, causing disappearance of the peak.

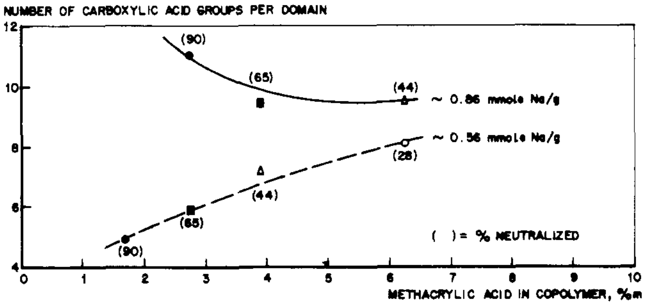

Figure 1. Size of polar domains in ethylene-methacrylic acid copolymers partially neutralized with sodium hydroxide.[4]

The idea of polar clusters being located in domains of at least 10 nm in size[4,5] is based on the general knowledge that in small crystals a repetition of at least five lattice planes is required for a well observable X-ray diffraction, the 4°, 2 ϑ, being related to a repeat distance of about 2.1 nm. However, the 4° peak might as well be due to a most frequently occurring distance between nearest-neighbor clusters, similar to the diffuse diffraction peaks observed with liquids. In accordance with this we may assume the domains to be located in the centers of spheres that are loosely and randomly packed, the packing density being roughly 55%. In this model, each cluster is, on an average, associated with a volume of d^3, d being the distance between nearest neighbors as determined from the peak at about 4°.

We can now calculate the number of carboxylic groups per cluster. If m is the equivalent weight per carboxylic group, the number of carboxylic groups per cluster is Nd^3/m, on the assumption that the density of the ionomer is 1 kg/l., while N is Avogadro's number.

Using the data of Wilson, Longworth, and Vaughan,[4] we have calculated the number of carboxylic groups per cluster for a series of ethylene-methacrylic acid copolymers and plotted these numbers *vs.* acid content in Figure 1.

In a theoretical treatment of the subject, Eisenberg[3] demonstrated that the number of carboxylic groups per cluster cannot be much higher than we have found here. Since the volumes associated with the clusters of the size calculated fill space completely, we can assume the clusters to be identical with the polar domains of the material. If, on the other hand, the clusters had been located in much larger domains, the former would have had to be of a much larger size, which is to be discarded according to Eisenberg.

The figure shows that at a high degree of neutralization the domain size strongly increases with acid content, but less so at a lower degree of neutralization. The change in domain size with acid content is small at constant content of ions.

This indicates that the functionality of the ionic cross-link depends both on carboxyl content and on degree of neutralization.

Since the position of the 4°, 2 ϑ peak is hardly dependent on temperature, the domain size is not either.

(1) C. Singleterry, *J. Amer. Oil Chem. Soc.*, **32**, 446 (1955).
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