JOC Article

Kinetics and Mechanism of *p*-Isopropenylphenol Synthesis via Hydrothermal Cleavage of Bisphenol A

Shawn E. Hunter and Phillip E. Savage*

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

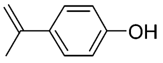
psavage@umich.edu

Received November 18, 2003

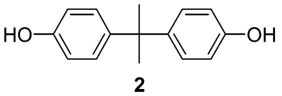
Although bishydroxyarylalkanes are known to be reactive in high-temperature (T > 200 °C) liquid water (HTW), no mechanistic insight has been given to explain the reactivity of methylene bridge-containing diaryls under hydrothermal conditions. We examined the kinetics and mechanism of *p*-isopropenylphenol (IPP) synthesis via bisphenol A (BPA) cleavage in HTW. The cleavage reaction is first order in BPA. Cleavage of BPA in HTW occurs by specific acid catalysis, by specific base catalysis, and by general water catalysis. Under neutral conditions, the dominant mechanism is general base catalysis with water serving as the proton acceptor. We generated a detailed chemical kinetics model for the decomposition reaction based on a base-catalyzed mechanism in the literature. This three-parameter model fit the experimental data for BPA disappearance and formation of IPP and phenol and accurately predicted the yield of the IPP hydrolysis product acetone. Using acid- and base-catalyzed mechanisms, we explain the reactivity in HTW reported for other diaryl groups linked by methylene bridges and propose criteria for assessing the reactivity of methylene bridges under hydrothermal conditions.

Introduction

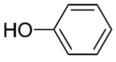
p-Isopropenylphenols are used as reactants in the preparation of indanols[1] and unsymmetrically alkylated 4,4′-isopropylidenebisphenols[2] and also serve as intermediates for stabilizer and dyestuff production.[3] The parent compound, *p*-isopropenylphenol (IPP) (**1**), is most easily synthesized via bisphenol A (BPA) (**2**) cleavage.[4] This reaction occurs at low pressures ($P = 0.02$ atm) and elevated temperature (T > 150 °C) in the presence of an alkaline catalyst.[5] However, high IPP yields can be difficult to obtain due to oligomerization of the product IPP.[6,7] High-boiling alcohols[6] and supercritical gases[7] have been used as solvents to obtain IPP in high yield from BPA, although basic catalysts are still required.



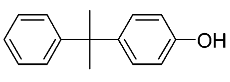
1



2



3



4

Recently, we demonstrated that IPP is synthesized from BPA cleavage in high-temperature (T > 200 °C) liquid water (HTW) without oligomer formation and without any added catalyst.[8] Phenol (**3**) forms as a coproduct, and acetone is produced from IPP hydrolysis. High-temperature water is a unique solvent that has gained much attention as a medium for conducting synthetic organic chemistry.[9] At elevated temperatures, liquid water exhibits physicochemical properties that are dramatically different from those properties of water at 20 °C. For instance, the relative permittivity[10] and degree of hydrogen bonding[11] both decrease with temperature. Hence, small organic molecules achieve greater solubility in HTW than in water at room temperature. Additionally, the ion product K_w of HTW is up to 3 orders of magnitude greater than that of 20 °C water.[12] This simultaneous decrease in pH and pOH, coupled with elevated temperature, enables many acid- and base-catalyzed reactions to proceed in HTW without the strong acid or base catalysts that are typically required.[13]

In HTW, chemical reactions can proceed by acid-catalyzed, base-catalyzed, and free-radical mechanisms.[13] The cleavage of BPA can also proceed by these three chemical mechanisms.[5] Thus, it is not clear a priori which of these mechanisms are significant for BPA cleavage in

---

[1] Voges, H. W. *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 25, p 636.

[2] Kahovec, J.; Pivcová, H.; Pospíčil, J. *Collect. Czech. Chem. Commun.* **1971**, *36*, 1986.

[3] Krimm, H.; Schnell, H. Br. Patent 905,994, 1962.

[4] Buysch, H. J. *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 25, pp 644−646.

[5] Schnell, H.; Krimm, H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 373.

[6] Mimaki, K.; Takase, T.; Iwasa, M.; Yamamori, T. U. S. Patent 4,054,611, 1977.

[7] Inoue, K. U. S. Patent 4,594,459, 1986.

[8] Hunter, S. E.; Felczak, C. A.; Savage, P. E. *Green Chem.* **2004**, *6*, 222.

[9] Savage, P. E. *Chem. Rev.* **1999**, *99*, 603.

[10] Harvey, A. H.; Peskin, A. P.; Klein, S. A. *NIST Standard Reference Database 10*, version 2.2; National Institute of Standards and Technology: Boulder, CO, 1996.

[11] Gorbaty, Y. E.; Gupta, R. B. *Ind. Eng. Chem. Res.* **1998**, *37*, 3026.

[12] Marshall, W. L.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1981**, *10*, 295.

[13] Akiya, N.; Savage, P. E. *Chem. Rev.* **2002**, *102*, 2725.

10.1021/jo0356964 CCC: $27.50

HTW, or if any one mechanism dominates the reaction. To address this ambiguity, we conducted a detailed kinetic and mechanistic study of the synthesis of IPP from BPA under hydrothermal conditions.

The study of BPA reactivity in HTW also permits examination of the reactivity of methylene-bridged diaryl cross-links under hydrothermal conditions. Herein, we designate both $-CH_2-$ and $-CR_2-$ bridges by the term "methylene" bridge, although other authors have referred to the latter as a "carbene" bridge. The methylene bridge is resistant to thermal cleavage,[14,15] and there have been varying reports concerning the reactivity of these linkages in HTW. Siskin and Katritzky[16] state that methylene bridges are stable in HTW at 350 °C but that cleavage can be achieved through the addition of strong acid. Additionally, Townsend et al.[17] reported diphenylmethane to be stable in HTW at 405 °C for 1 h, and Katritzky et al.[18] confirmed the diaryl to be unreactive after 1 h at 460 °C. Di-*p*-tolylmethane was also stable at 430 °C for 1 h, and cleavage was not induced by the addition of phenol to the reaction mixture.[19] The stability of these methylene bridge-containing diaryl compounds contrasts with the reactivity of bishydroxyarylalkanes in HTW. For example, BPA cleavage is possible at temperatures as low as 200 °C.[8] Further, 4,4′-dihydroxydiphenylmethane and 2,2′-dihydroxydiphenylmethane both cleave in HTW at 300 °C.[19] Although the reactivity of bishydroxyarylalkanes has been confirmed in HTW, a detailed kinetic study has not been carried out, and no mechanism has been proposed to explain the reactivity or stability of different methylene bridge-containing compounds in HTW. Thus, our investigation was further motivated by the desire to shed light on the mechanism of methylene bridge cleavage under hydrothermal conditions.

Here, we present new experimental results to obtain kinetic and mechanistic information about the cleavage of BPA to yield IPP in HTW. We then discuss structural features required for methylene bridge cleavage in a hydrothermal environment.

Results

Kinetics. To determine the global reaction order for BPA disappearance, we conducted seven experiments at 250 °C and 20 min wherein the initial concentration of BPA was varied by over an order of magnitude. The results of these experiments are displayed in Table 1. The uncertainty reported in Table 1 and elsewhere in this article represents the 95% confidence interval, unless otherwise stated. Table 1 shows that the conversion was not significantly affected by varying the initial BPA loading.

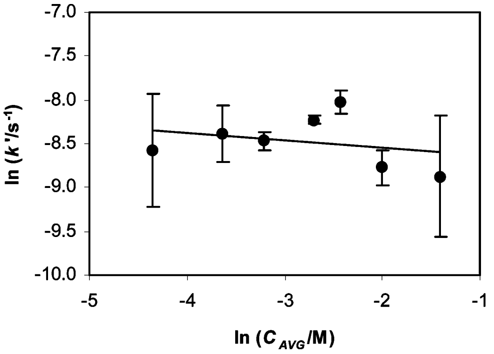


FIGURE 1. Effect of BPA concentration on pseudo-first-order rate constant.

TABLE 1. Effect of Initial BPA Concentration C_0 on Conversion at 250 °C and 20 Min of Reaction Time

C_0 (M)	X
0.01	0.21 ± 0.11
0.03	0.24 ± 0.07
0.05	0.22 ± 0.02
0.08	0.27 ± 0.01
0.11	0.32 ± 0.04
0.15	0.24 ± 0.04
0.27	0.16 ± 0.10

A log−log plot of the pseudo-first-order rate constant obtained at each initial concentration against the mean concentration during the experiment provides a means to estimate the global reaction order. This method is most precise when the conversion is not high and the reaction order is not far from unity.[20] Also, requiring the conversion to be low minimizes any effects of a possible reverse reaction on reaction order determination. Equation 1 provides the pseudo-first-order rate constant k' as

$$k' = \frac{-\ln(1 - X)}{t} \tag{1}$$

where X is the conversion and t is the reaction time. The average concentration C_{AVG} was calculated as the arithmetic mean of the initial and final BPA concentrations. Qualitatively, Figure 1 shows that the initial concentration had very little influence on the pseudo-first-order rate constant. Quantitatively, the reaction order can be determined from the slope m of the log−log plot as $1 + m$.[20] Linear regression of the data in Figure 1 leads to a slope of -0.09 ± 0.33, so the apparent reaction order is 0.91 ± 0.33. Thus, the decomposition reaction is essentially first order in BPA.

Mechanism. Having determined the reaction order, we next sought a mechanism for BPA decomposition consistent with first-order kinetics. Cleavage of BPA occurs by thermal, acid-catalyzed, and base-catalyzed mechanisms.[5] We performed experiments to deduce which of these mechanisms is favored in HTW. To test for the thermal mechanism, we conducted an experiment at 300 °C in benzene, a nonpolar aprotic solvent that is stable at 300 °C and not expected to react with BPA. Thus, the only cleavage mechanism available to BPA in benzene is pyrolysis. The critical temperature of benzene is 289 °C, and hence benzene is supercritical at 300 °C. This fact implies that the solvent will occupy the entire

---

[14] McMillen, D. F.; Ogier, W. C.; Ross, D. S. *J. Org. Chem.* **1981**, *46*, 3322.

[15] Allen, D. T.; Gavalas, G. R. *Fuel* **1984**, *63*, 586.

[16] Siskin, M.; Katritzky, A. R. *Chem. Rev.* **2001**, *101*, 825.

[17] Townsend, S. H.; Abraham, M. A.; Huppert, G. L.; Klein, M. T.; Paspek, S. C. *Ind. Eng. Chem. Res.* **1988**, *27*, 143.

[18] Katritzky, A. R.; Barcock, R. A.; Balasubramanian, M.; Greenhill, J. V.; Siskin, M.; Olmstead, W. N. *Energy Fuels* **1994**, *8*, 487.

[19] Tagaya, H.; Suzuki, Y.; Kadokawa, J.; Karasu, M.; Chiba, K. *Chem. Lett.* **1997**, 47.

[20] Savage, P. E.; Smith, M. A. *Environ. Sci. Technol.* **1995**, *29*, 216.

TABLE 2. Summary of p[H$^+$] Experiments for BPA Cleavage in HTW at 250 °C and 30 Min of Reaction Time

additive	p[H$^+$] at 250°C	X	log(k') [a]
H_2SO_4	2.0	0.87 ± 0.03	−2.94 ± 0.04
HCl	2.4	0.62 ± 0.08	−3.27 ± 0.05
HCl	4.0	0.32 ± 0.09	−3.68 ± 0.16
None	5.7	0.36 ± 0.01	−3.61 ± 0.02
NaOH	7.4	0.25 ± 0.02	−3.80 ± 0.04
NaOH	8.4	0.53 ± 0.03	−3.38 ± 0.04
NaOH	9.0	0.82 ± 0.03	−3.02 ± 0.05

[a] Units for k' are s^{-1}.

reactor volume. Roughly 14 mg of BPA was loaded into the reactors, along with 240 μL of benzene. After 60 min of reaction in supercritical benzene, 100 ± 5% of BPA was recovered unreacted. In HTW at 300 °C, in contrast, BPA at nearly the same initial concentration was completely converted after 60 min of reaction.[8] These results indicate that the thermal cleavage of BPA is not significant in the hydrothermal experiments.

To test for the existence of acid- and base-catalyzed mechanisms for BPA decomposition in HTW, we investigated the dependence of the reaction on the system p[H$^+$].[21] By adding HCl, H_2SO_4, and NaOH to the reactors, we examined the conversion of BPA at 250 °C and 30 min over a p[H$^+$] range of 2.0−9.0. At 250 °C, HCl[22] and H_2SO_4[23] are strong acids, whereas NaOH[24] is a strong base. The p[H$^+$] experiments are summarized in Table 2. At low p[H$^+$], the conversion increases rapidly with added acid. Similarly, the conversion increases rapidly with added base at high p[H$^+$]. At neutral p[H$^+$] (p[H$^+$] = 5.7), however, there is little discernible effect on the conversion with either added acid or added base. These data suggest that the reaction occurs by an acid-catalyzed mechanism under acidic conditions and also by a base-catalyzed mechanism under basic conditions. The conversion data, however, do not clarify if the reaction is dominated by either acid or base catalysis under neutral conditions, nor if there are other possible mechanisms occurring under neutral conditions.

To gain mechanistic insight concerning BPA cleavage under neutral conditions, we calculated pseudo-first-order rate constants from the conversion data in Table 2. For acid−base reactions in aqueous media, the pseudo-first-order rate constant can be described[25] as

$$k' = k_A[H^+] + k_B[OH^-] + k_W \qquad (2)$$

where k_A and k_B are the rate constants for specific acid and base catalysis by H$^+$ and OH$^-$ ions, respectively, k_W is the rate constant for general acid/base catalysis by water, and the brackets represent molar concentration. Additional terms may be necessary if general acid/base catalysis by species other than water is significant. To determine whether specific acid catalysis, specific base catalysis, and general acid/base catalysis by water occur for BPA cleavage in HTW, we fit the pseudo-first-order rate constant data to eq 2. We used the modeling software Scientist[26] to estimate k_A, k_B, and k_W. We assumed that all concentrations of charged intermediate species were small compared to the H$^+$ and OH$^-$ concentrations, such that [OH$^-$] could be estimated by K_w/[H$^+$].

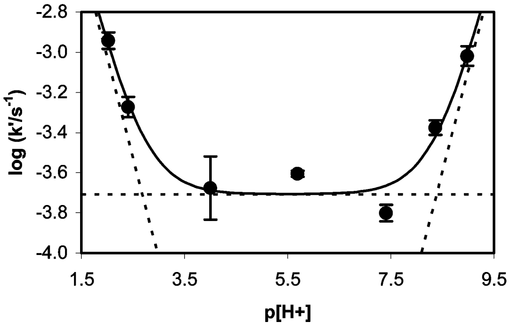


FIGURE 2. Effect of H$^+$ concentration on pseudo-first-order rate constant for BPA cleavage in HTW at 250 °C. The solid line represents the fit of eq 2 to the log k' data. Vertical dashed lines represent contributions to k' from specific acid catalysis at low p[H$^+$] and from specific base catalysis at high p[H$^+$], while the horizontal dashed line represents the contribution to k' from water catalysis.

Figure 2 shows that eq 2 is able to capture the trends in the k' data. The estimates for k_A, k_B, and k_W are 0.094 ± 0.053 L mol^{-1} s^{-1}, 0.19 ± 0.12 L mol^{-1} s^{-1}, and 2.0 × 10^{-4} ± 6.8 × 10^{-5} s^{-1}, respectively. Equation 2 assumes essentially first-order dependence of k' on [H$^+$] and [OH$^-$] at low and high p[H$^+$], respectively. The good agreement with the experimental data at these p[H$^+$] extremes indicates that specific acid catalysis and specific base catalysis occur for BPA cleavage in HTW. Further, the lack of p[H$^+$] dependence of k' at intermediate p[H$^+$] suggests that general catalysis by water is not only significant for the reaction but also the dominant mechanism under neutral conditions.

For acid−base reactions, water may act as both a general acid catalyst, as well as a general base catalyst. As BPA cleavage occurs by both acid- and base-catalyzed mechanisms, it is likely that water may act as both a general acid and a general base for BPA cleavage in HTW. Equation 2 does not provide insight as to the relative contribution of each of these mechanisms. However, Schnell and Krimm provide evidence to suggest that general base catalysis by water may be the more favored mechanism in HTW. They state that cleavage of 4,4′-dihydroxydiarylmethane derivatives occurs more readily under basic than under acidic conditions.[5] This statement implies that water should be more effective as a proton acceptor than as a proton donor for BPA cleavage. This speculation is supported by the estimated values of k_A and k_B. The specific base-catalyzed rate constant is greater than the specific acid-catalyzed rate constant by a factor of about two. Hence, for BPA cleavage in HTW, specific base catalysis is more easily achieved than

---

(21) Activity of the hydrogen ion is typically represented in terms of the molal concentration scale, so that pH is equal to −log((H$^+$)/m). Here, we chose the molar concentration scale, such that p[H$^+$] is equal to −log([H$^+$]/M), to give consistency between the hydrogen ion concentration used in eq 2 (molar units) and that used as the abscissa in Figure 2. At 250 °C, the density of saturated liquid water is 0.8 g cm^{-3},[12] so that pH = p[H$^+$] − 0.1.

(22) Frantz, J. D.; Marshall, W. L. *Am. J. Sci.* **1984**, *284*, 651.

(23) Oscarson, J. L.; Izatt, R. M.; Brown, P. R.; Pawlak, Z.; Gillespie, S. E.; Christensen, J. J. *J. Solution Chem.* **1988**, *17*, 841.

(24) Chen, X.; Gillespie, S. E.; Oscarson, J. L.; Izatt, R. M. *J. Solution Chem.* **1992**, *21*, 803.

(25) Gates, B. C. *Catalytic Chemistry*; John Wiley & Sons: New York, 1992; pp 26−27.

(26) *Scientist*, version 2.01; MicroMath, Inc.: Salt Lake City, UT, 1995.

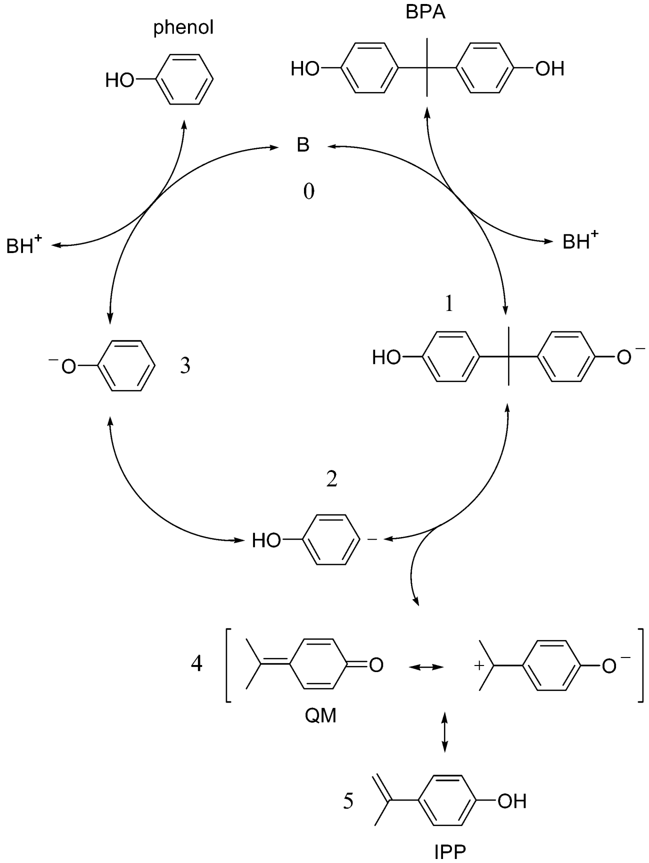
specific acid catalysis. If the acid- and base-catalyzed mechanisms for general catalysis are the same as those for specific catalysis, then general base catalysis by water should also be more easily achieved than general acid catalysis by water. Thus, we expect that general base catalysis by water should contribute more than general acid catalysis by water to the conversion of BPA in HTW and that general base catalysis is the dominant mechanism for BPA cleavage at neutral conditions.

To test the hypothesis that general base catalysis is more significant than general acid catalysis for BPA cleavage in neutral HTW, we performed an experiment with *p*-cumylphenol (**4**), a compound that is structurally similar to BPA. *p*-Cumylphenol reacts in the presence of acid to give α-methylstyrene, the analogue of *p*-isopropenylphenol, as well as phenol.[5] In the presence of base, however, *p*-cumylphenol is stable up to 300 °C.[5] Thus, examining the reactivity of *p*-cumylphenol in neutral HTW at temperatures below 300 °C provides a means of testing for the significance of an acid-catalyzed pathway for BPA decomposition in neutral HTW. Batch reactors were loaded with 15 mg of *p*-cumylphenol and 450 μL of water and placed in the sand bath at 250 °C. After 1 h of reaction, *p*-cumylphenol was recovered essentially unreacted, with a yield of 97 ± 7%. Only traces of α-methylstyrene and phenol were observed. The yield of BPA under the same experimental conditions was 42 ± 8%.[8] If an acid-catalyzed pathway were dominant for BPA decomposition, the reactivity of BPA should be similar to that of *p*-cumylphenol, under the same conditions. Here, BPA is clearly reactive, whereas *p*-cumylphenol is stable. Thus, an acid-catalyzed pathway cannot be solely responsible for the conversion of BPA. Hence, this analysis supports the notion that BPA cleavage in HTW occurs primarily via general base catalysis with water acting as the catalyst. Given the present evidence, we conclude that the most significant mechanism for BPA cleavage in neutral HTW is general base catalysis by water.

Schnell and Krimm[5] have proposed a specific base-catalyzed mechanism for the cleavage of BPA, which we modified for general catalysis as Scheme 1. Cleavage is initiated through proton abstraction from a hydroxyl group. Electron displacement throughout the resulting anion enables cleavage of the methylene bridge, yielding a resonance-stabilized quinone methide (QM) and an isomeric phenoxide anion as intermediates. The former rearranges to give IPP, while the latter reacts with the protonated base to yield phenol.

Mechanism-Based Model. To assess the consistency between the general base-catalyzed mechanism and the previous experimental results,[8] we developed a detailed chemical kinetics model based on the elementary steps shown in Scheme 1. Assuming general catalysis by water, [B] = [H_2O] and [BH^+] = [H_3O^+]. Helfferich[27] provides a general method for developing the rate equation of multistep networks, subject to the following constraints: (1) All intermediate species are present in trace concentration levels when compared to catalysts, reactants, and products. (2) No step involves the consumption or generation of more than one molecule of intermediate species. The first constraint is satisfied provided that the concentrations of intermediate species are much smaller than the BPA, IPP, phenol, and H_3O^+ concentrations. As a first approximation, we assume that [H_3O^+] is constant during the reaction and equal to $K_w^{1/2}$. The validity of the second assumption will be addressed subsequently. Using the Helfferich method, we obtained the following rate equation for BPA disappearance:

SCHEME 1. General Base-Catalyzed Mechanism for BPA Cleavage in HTW[5] [a]



[a] Numerical designation of the reacting species within the catalytic cycle is for the purpose of identifying rate constants in eqs 4−7.

$$-r_{BPA} = \frac{k_A[\mathrm{BPA}] - k_B[\mathrm{PhOH}][\mathrm{QM}]}{1 + k_C[\mathrm{QM}]} \quad (3)$$

where

$$k_A = \frac{k_{01}k_{12}[\mathrm{H_2O}]}{k_{12} + k_{10}K_w^{1/2}} \quad (4)$$

$$k_B = \frac{k_{03}k_{32}k_{21}k_{10}[\mathrm{H_2O}]}{k_{12}k_{23}k_{30} + k_{10}k_{23}k_{30}K_w^{1/2}} \quad (5)$$

$$k_C = \frac{k_{10}k_{21}k_{32} + k_{10}k_{21}k_{30}K_w^{1/2}}{k_{12}k_{23}k_{30} + k_{10}k_{23}k_{30}K_w^{1/2}} \quad (6)$$

and where [BPA], [PhOH], [QM], and [H_2O] are the concentrations of BPA, phenol, the quinone methide intermediate, and water, respectively, and k_{ij} is the rate constant for the reaction in which species i reacts to form

---

[27] Helfferich, F. G. *J. Phys. Chem.* **1989**, *93*, 6676.

TABLE 3. Parameter Estimates for the Model in Eqs 12−14[a]

	$\log(k_1)$	$\log(k_2)$	$\log(k_4)$
200 °C	-4.7 ± 0.1	-3.4 ± 0.4	-4.7 ± 0.6
250 °C	-3.6 ± 0.1	-3.9 ± 0.3	-4.4 ± 0.1
300 °C	-2.8 ± 0.4	-3.5 ± 0.5	-3.91 ± 0.04
350 °C	-2.6 ± 0.3		-3.40 ± 0.06
$\log A$ (s^{-1})	4 ± 1		0.6 ± 0.6
E_a (kcal mol^{-1})	19 ± 2		12 ± 2

[a] Rate constant uncertainties are the 95% confidence interval, whereas standard error is given for the Arrhenius parameter uncertainties. Units for rate constants are s^{-1}.

species *j*, with the species numbers shown in Scheme 1. Equation 3 is consistent with first-order kinetics for BPA, as determined experimentally.

Strict interpretation of the second step of the mechanism would result in a violation of the second Helfferich premise, as the bisphenol A anion decomposes into two intermediates. However, this requirement can be satisfied if the quinone methide intermediate quickly equilibrates with IPP ($k_{45} \gg k_{12}$). If cleavage of the bisphenol A anion results essentially in IPP and the isomeric phenoxide anion, then the step produces but one reactive intermediate. The quinone methide concentration can then be written in terms of IPP concentration as

$$[\mathrm{QM}] = \frac{k_{54}}{k_{45}}[\mathrm{IPP}] \tag{7}$$

To model completely the yields of phenol and IPP, one must account for the reactivity of IPP. In HTW, IPP reacts to yield phenol and acetone.[8] Previous experiments in HTW in which phenol and acetone were used as reactants produced no quantifiable products.[8] This result implies that the decomposition of IPP to yield phenol and acetone is irreversible. Assuming first-order kinetics for IPP disappearance leads to the following equation for the rate of formation of phenol and acetone from IPP:

$$r_{\mathrm{acetone}} = k_4[\mathrm{IPP}] \tag{8}$$

The differential equations governing BPA hydrothermolysis in a constant-volume batch reactor are

$$\frac{\mathrm{d}[\mathrm{BPA}]}{\mathrm{d}t} = r_{\mathrm{BPA}} \tag{9}$$

$$\frac{\mathrm{d}[\mathrm{PhOH}]}{\mathrm{d}t} = -r_{\mathrm{BPA}} + r_{\mathrm{acetone}} \tag{10}$$

$$\frac{\mathrm{d}[\mathrm{IPP}]}{\mathrm{d}t} = -r_{\mathrm{BPA}} - r_{\mathrm{acetone}} \tag{11}$$

Combining eqs 3, 7, and 8 with eqs 9−11, and converting the dependent variables from concentration to molar yield (moles of product formed per mole of BPA initially present) results in the final set of equations used to model the BPA decomposition network:

$$\frac{\mathrm{d}Y_{\mathrm{BPA}}}{\mathrm{d}t} = \frac{-k_1 Y_{\mathrm{BPA}} + k_2 Y_{\mathrm{PhOH}} Y_{\mathrm{IPP}}}{1 + k_3 Y_{\mathrm{IPP}}} \tag{12}$$

$$\frac{\mathrm{d}Y_{\mathrm{PhOH}}}{\mathrm{d}t} = \frac{k_1 Y_{\mathrm{BPA}} - k_2 Y_{\mathrm{PhOH}} Y_{\mathrm{IPP}}}{1 + k_3 Y_{\mathrm{IPP}}} + k_4 Y_{\mathrm{IPP}} \tag{13}$$

$$\frac{\mathrm{d}Y_{\mathrm{IPP}}}{\mathrm{d}t} = \frac{k_1 Y_{\mathrm{BPA}} - k_2 Y_{\mathrm{PhOH}} Y_{\mathrm{IPP}}}{1 + k_3 Y_{\mathrm{IPP}}} - k_4 Y_{\mathrm{IPP}} \tag{14}$$

where

$$k_1 = k_{\mathrm{A}} \tag{15}$$

$$k_2 = k_B \frac{k_{54}}{k_{45}} C_0 \tag{16}$$

$$k_3 = k_{\mathrm{C}} \frac{k_{54}}{k_{45}} C_0 \tag{17}$$

We used Scientist to perform parameter estimation for k_1, k_2, k_3, and k_4, while solving eqs 12−14 simultaneously. We used a weighted least-squares technique, with the reciprocal of the variance of each data point serving as the statistical weight. The weighted sum of squared deviations (WSSD), calculated by Scientist, was the objective function. The parameter values that minimized the WSSD were retained as those that best fit the data. The data at different temperatures were fit separately. At all four temperatures, the value of the WSSD was not significantly affected by varying the value of k_3 over several orders of magnitude. Eliminating this parameter from the model produced a lower value of the objective function at every temperature. Additionally, the WSSD at 350 °C was not sensitive to the value of k_2. Thus, we report optimized values for only those parameters that affected the ability of the model to fit the data. Table 3 provides the estimates for k_1, k_2, and k_4.

Both k_1 and k_4 display Arrhenius behavior. The relatively large uncertainty associated with k_2 made interpretation of the temperature dependence of k_2 difficult. Hence, in Table 3 we report the activation energies and preexponential factors, obtained through unweighted linear regression, for only k_1 and k_4. We also estimated the heat of reaction for BPA cleavage in high-temperature water using the estimates for k_1 and k_2 in Table 3. By assuming the heat of reaction to be independent of temperature, the van't Hoff equation can be used to find the heat of reaction by plotting ln K vs $1/T$, where K is the equilibrium constant for the reaction. By performing linear regression of $\ln(k_1/k_2)$ vs $1/T$ at 200−300 °C, we estimated the heat of reaction to be 25 kcal/mol with a standard error of 6 kcal/mol. The heat of reaction for bisphenol A cleavage has not been reported previously. However, the NIST Structures and Properties database[28] provides estimates of gas phase heats of formation and heat capacities by applying Benson's group additivity method.[29−31] Using this program, we estimated the gas

---

(28) Stein, S. E. *NIST Standard Reference Database 25*, version 2.0; National Institute of Standards and Technology: Gaithersburg, MD, 1994.

(29) Benson S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley & Sons: New York, 1976.

(30) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: Boston, 1987.

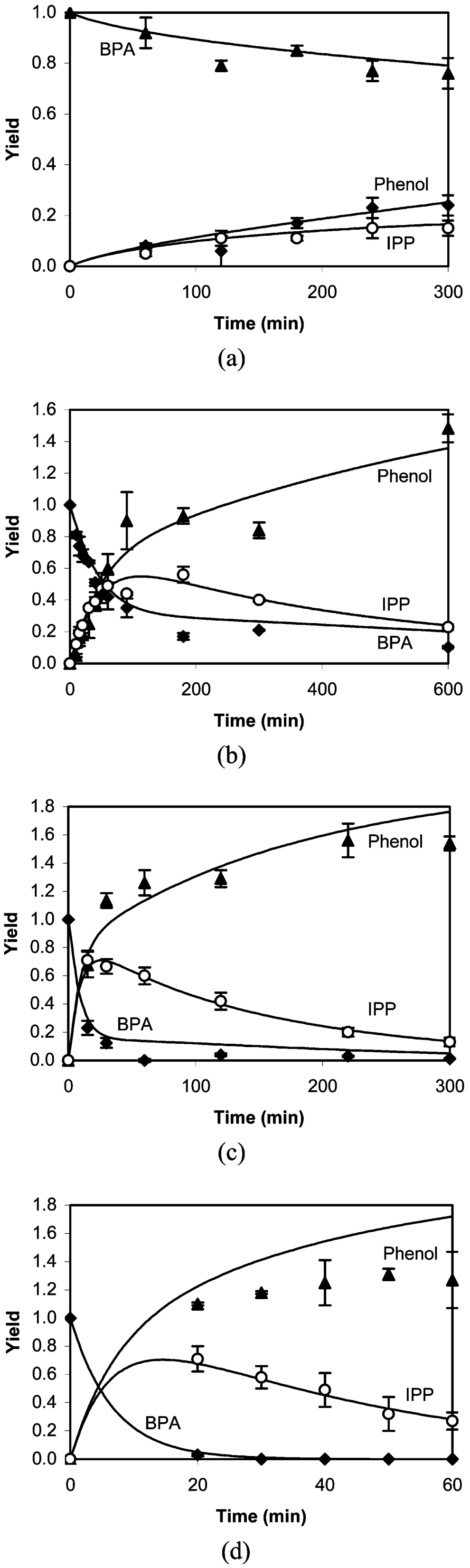


FIGURE 3. Comparison of experimental and calculated molar yields. (a) 200 °C. (b) 250 °C. (c) 300 °C. (d) 350 °C.

phase heat of reaction for BPA cleavage at 250 °C to be 22 kcal/mol, which shows good agreement with the experimentally determined value.

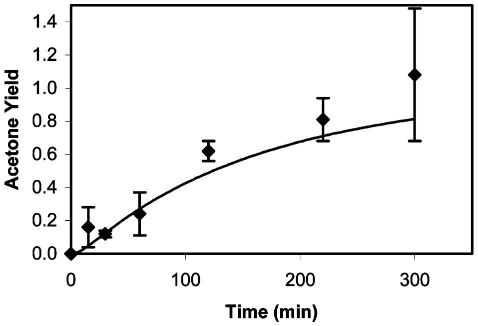


FIGURE 4. Comparison of experimental and predicted acetone yields at 300 °C.

Figure 3 shows the good agreement between the experimental[8] yields of BPA, phenol, and IPP and those calculated from the model with the parameters in Table 3. The model was not used to fit experimental acetone data. Hence, these yields can be used to test the model's predictive ability. Using the rate constants in Table 3, we predicted the acetone yields at all four temperatures. In each case, the predicted yield profile fell within the experimental error for most of the acetone data points. For example, Figure 4 demonstrates good agreement between the predicted and experimental[8] acetone yield at 300 °C. Thus, on the basis of the ability of the model to fit the data and to predict acetone yields accurately, we conclude that the general base-catalyzed mechanism is consistent with the data for BPA decomposition in high-temperature liquid water.

Discussion

Reactivity of Methylene Bridges in HTW. The methylene bridge of BPA can be cleaved under hydrothermal conditions via both acid- and base-catalyzed mechanisms. Schnell and Krimm[5] provide a mechanism for the acid-catalyzed reaction, shown in Scheme 2 as general acid catalysis. In this acid-catalyzed mechanism, protonation of the hydroxyl group enables cleavage of the bond between the protonated phenol group and the bridging carbon atom. Cleavage of this bond results in a tertiary isopropylphenol cation and a phenol isomer. The former surrenders a hydrogen β to the bridging carbon to regenerate the catalyst and form IPP, while the latter rearranges through charge stabilization to give phenol.

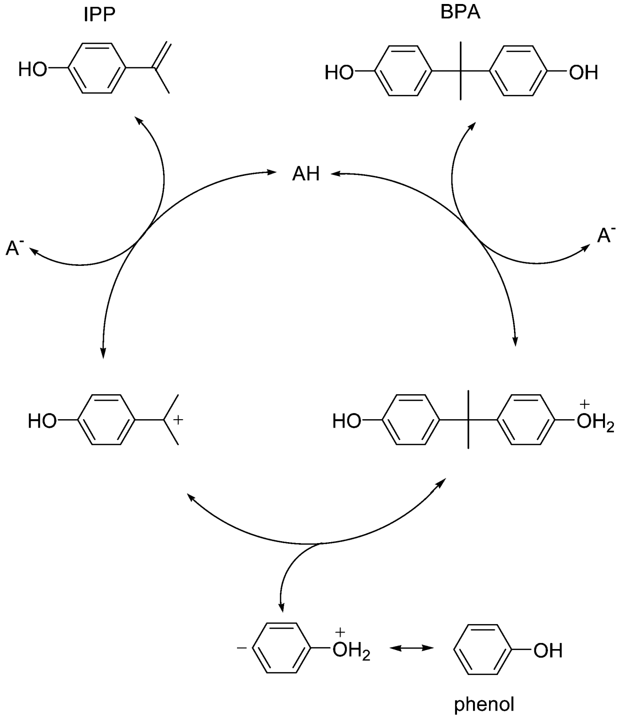
Another possible acid-catalyzed mechanism is given in Scheme 3. In this mechanism, the aromatic ring, rather than the oxygen, is protonated. This protonation step is facilitated by the presence of the oxygen, which serves to stabilize the resulting cation via electron delocalization. Cleavage then occurs as the reverse of electrophilic aromatic substitution, yielding phenol directly and the isopropylphenol cation. As in Scheme 2, the isopropylphenol cation forms IPP while liberating a β-hydrogen.

The key difference between the base-catalyzed mechanism and the two acid-catalyzed mechanisms is the location of the bond that breaks during cleavage. In either acid-catalyzed mechanism, the bridging carbon is cleaved from the reactive phenol group involved in the initial step

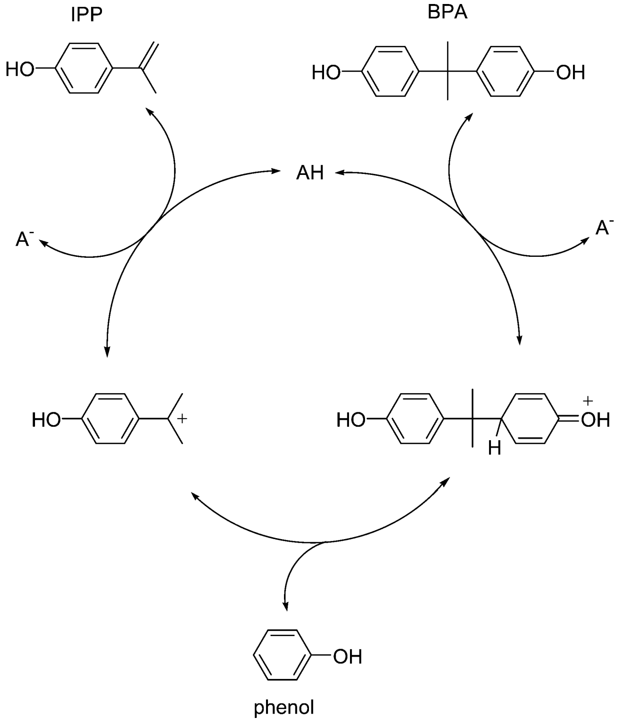
---

(31) Lyman, W. J.; Reehl, W. F.; Rosenblatt, D. H. *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*; McGraw-Hill: New York, 1982.

SCHEME 2. Acid-Catalyzed Mechanism for BPA Cleavage in HTW via Protonation of the Hydroxyl Group[5]



SCHEME 3. Acid-Catalyzed Mechanism for BPA Cleavage in HTW via Protonation of the Aromatic Ring



of the reaction. By contrast, in the base-catalyzed mechanism, the bridging carbon is retained by the reactive phenol group. Hence, IPP appears as a result of the second step in the base-catalyzed cycle, whereas it is not formed until the final step of the acid-catalyzed cycles. Thus, for unsymmetrical methylene bridge-containing diaryls with only one hydroxyl group on an aromatic ring, products resulting from acid catalysis may be different from those that form via base catalysis.

Inspection of Schemes 1−3 enables identification of key structural features required for methylene bridge cleavage through acid or base catalysis in HTW. Schemes 2 and 3 suggest that both an aromatic hydroxyl group and a β-hydrogen are necessary for cleavage by acid catalysis. In both acid-catalyzed mechanisms, the hydroxyl group is involved in the initial step, and the β-hydrogen is needed for an intermediate step. Considering Scheme 2, Schnell and Krimm[5] suggest that protonation of the hydroxyl group in BPA results in weakening of the bond between the bridging carbon and the protonated phenol group. We speculate that this weakening is due to an electron-withdrawing inductive effect of the protonated hydroxyl group. The existence of this effect should be independent of the position of the hydroxyl group. In contrast, Scheme 3 implies that the role of the hydroxyl group is to enable protonation of the aromatic ring. Because the attacking proton must add to the ipso position, only *ortho*/*para*-hydroxy-substituted diaryls linked by a methylene bridge can cleave according to Scheme 3. Hence, acid-catalyzed cleavage will occur for methylene-linked diaryls that are hydroxy-substituted ortho or para to the linking carbon according to Schemes 2 and 3, whereas those hydroxy-substituted at the meta position may be cleaved only according to Scheme 2. In fact, the reactivity of a 3,3′-bisphenol in HTW at acidic pH may provide a means of discriminating between Schemes 2 and 3.

The β-hydrogen is needed to provide a facile reaction path for the carbocation formed during acid-catalyzed cleavage. After cleavage, a positive charge exists on the formerly bridging carbon atom. If a β-hydrogen is present, the carbocation can undergo β-scission to regenerate the acid catalyst and form a double bond. For true methylene ($-CH_2-$) bridges, which lack a β-hydrogen, cation stabilization and proton regeneration may be possible via charge migration to the oxygen atom; however, instability of the primary carbocation likely precludes its formation. In either scenario, unsubstituted bishydroxyarylmethanes, which contain true methylene bridges, are not reactive by acid catalysis in HTW. However, bishydroxyarylmethane derivatives, with symmetric or unsymmetric carbene ($-CR_2-$) bridges containing at least one hydrogen β to the linking carbon, can undergo acid-catalyzed cleavage.

Scheme 1 indicates that methylene bridges can be cleaved in HTW through base catalysis only if there is a hydroxyl group in the ortho or para position and if there is a good leaving group attached to the methylene bridge. Again, the hydroxyl group is necessary for reaction initiation, and the leaving group is required during an intermediate step. Scheme 1 suggests that both *ortho*- and *para*-hydroxy-substituted phenyl groups linked by methylene bridges can react in HTW through the base-catalyzed formation of an *ortho*- or *para*-quinone methide. However, this reactivity may not exist for *meta*-hydroxy-substituted phenyl groups. Electron displacement throughout a meta-substituted phenoxide anion would not result in cleavage of the methylene group but rather would lead to resonance stabilization of the anion.

Further, the portion of the methylene bridge-containing diaryl that is cleaved from the methylene group develops a negative charge after cleavage, and hence the reactivity of the methylene group is related to the stability of the cleaved anion. This is analogous to the concept of the leaving group in nucleophilic substitution reactions. Hence, as the basicity of the cleaved anion decreases, the reactivity of the diaryl increases.

Additionally, there is no β-hydrogen required for base-catalyzed cleavage. Thus, both carbene bridges and true methylene bridges may be cleaved according to Scheme 1, whereas only carbene bridges react via acid catalysis.

The mechanisms presented in Schemes 1−3 can account for the reactivity observed for different methylene bridges under hydrothermal conditions. If an aromatic hydroxyl group is not present and the aromatic rings are unsubstituted, methylene bridge-containing diaryls will be stable under hydrothermal conditions. For example, diphenylmethane and 1-benzylnaphthalene were stable after 1 h in water at 460 °C.[18] Similarly, di-*p*-tolylmethane did not react after 1 h in water at 430 °C.[19] The hydroxyl substituent is required for both acid- and base-catalyzed cleavage, and its presence may enable methylene bridge cleavage in HTW. In addition to bisphenol A, 4,4′-dihydroxydiphenylmethane and 2,2′-dihydroxydiphenylmethane are cleaved in HTW at temperatures below 350 °C.[19]

The effect of added acid and base on the hydrothermal reactivity of methylene bridges can also be explained by Schemes 1−3. For example, cleavage of 4,4′-dihidroxydiphenylmethane in HTW is accelerated by added base but not by added acid.[19] Acid-catalyzed cleavage would yield an energetically unfavorable cresol primary cation. Despite the presence of the hydroxyl group, the instability of the primary carbocation that needs to form and the lack of a fast reaction path for this intermediate (no β-hydrogen) militate against acid-catalyzed cleavage. Thus, one would not expect added acid to accelerate the reaction. Base catalysis, however, is permitted by the presence of the para hydroxyl group and the phenoxide leaving group. Hence, added base should and does accelerate the reaction.

This explanation can also be used to account for the reactivity of phenol resin prepolymers in HTW. These prepolymers are structurally similar to 4,4′-dihydroxydiphenylmethane, as they consist of several substituted phenols linked by true methylene bridges. Again, added base accelerated the decomposition of these prepolymers, but added acid did not.[32]

The effect of the leaving group is demonstrated when considering that BPA is readily cleaved in HTW at 250 °C, whereas 4-cumylphenol did not react even after 1 h at this temperature. The fragment cleaved from BPA through base catalysis is an isomeric phenoxide, which rearranges to give the phenoxide anion. The fragment that would be cleaved from 4-cumylphenol via base catalysis is the benzene anion. Benzene is clearly a much weaker acid than phenol, and hence the benzene anion is a much stronger base than the phenoxide anion. Thus, because the phenoxide anion is a better leaving group than the benzene anion, bisphenol A should be, and is, more reactive than 4-cumylphenol through base catalysis in HTW.

Conclusion

The synthesis of *p*-isopropenylphenol via bisphenol A cleavage in HTW is first order in bisphenol A. BPA cleavage occurs by specific acid catalysis, specific base catalysis, and general catalysis with water acting as a general catalyst. The primary mechanism for BPA cleavage in neutral HTW is general catalysis by water. The existence of specific acid- and base-catalyzed mechanisms suggests that water can act as both a general acid and a general base for the cleavage reaction. General base catalysis by water is more significant than general acid catalysis by water and therefore the dominant mechanism in neutral HTW. A detailed kinetics model built upon a water-catalyzed mechanism was quantitatively consistent with the experimental data and accurately predicted the experimental acetone yields.

The results of this work allow one to predict the reactivity of methylene bridge-containing diaryls under hydrothermal conditions. If a hydroxyl group is present on an aromatic ring, then hydrothermal cleavage may be possible. Base-catalyzed cleavage is possible when the hydroxyl group is located ortho or para to the bridging carbon. Additionally, the portion of the molecule cleaved from the methylene bridge must be a good leaving group, such as the phenoxide anion, or base-catalyzed cleavage is not likely to occur. Cleavage may occur via an acid-catalyzed path when the aromatic ring is hydroxy-substituted at the ortho or para position and there exists a hydrogen β to the bridging carbon. Acid-catalyzed cleavage of a *meta*-hydroxy-substituted diaryl containing a methylene cross-link may also be possible if the β-hydrogen is present, provided that the reaction is initiated through protonation of the hydroxyl group. In neutral HTW, where both acid and base catalysis is possible, we expect base-catalyzed bridge cleavage to be more significant than acid-catalyzed cleavage for compounds that contain hydroxyl groups in the ortho or para positions, have good leaving groups, and are alkyl-substituted at the methylene bridge.

Experimental Section

We performed experiments using 0.6 mL batch reactors. Reactors were loaded with reactants and degassed water in a helium-filled glovebox and then sealed. The sealed reactors were then immersed in a preheated temperature-controlled fluidized sand bath for the desired reaction time. After the reaction time had elapsed, the reactors were removed from the sandbath and submersed in a bath of ambient temperature water to quench the reaction. Reactors were then further cooled for 30 min in a refrigerator and the contents subsequently collected. Reaction products were identified using GC-MS, and quantified using GD-FID. Full details of the general experimental method are available in our earlier paper.[8]

Acknowledgment. We thank Prof. M. R. DeCamp for providing mechanistic advice. Additionally, we gratefully acknowledge the NSF for providing a graduate fellowship to S.E.H. Financial support was also provided by the ACS-PRF (37603-AC9) and NSF (CTS-0218772).

JO0356964

---

[32] Suzuki, Y.; Tagaya, H.; Asou, T.; Kadokawa, J.; Chiba, K. *Ind. Eng. Chem. Res.* **1999**, *38*, 1391.