Kinetics and Mechanism of Isobutene Formation from *T*-Butanol in Hot Liquid Water

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Isobutene is the only product of the uncatalyzed and acid-catalyzed dehydration of tert-butanol in compressed liquid water at 250°C. The uncatalyzed dehydration reaction is fast: equilibrium is established after about 30 s. Only one of many chemically-motivated kinetic models is able to fit all the experimental data. This model presumes a heterolytic dehydration mechanism that involves protonated alcohol, carbocation, di-tert-butyl ether, and protonated ether as intermediates. The model permits tert-butanol to dissociate as both an Arrhenius acid and a Bronsted acid while catalyzing its dehydration to isobutene. The pK_a of tert-butanol at 250°C is predicted to be about 9, whereas its value at normal temperature and pressure is 18. This 10^9 increase in the K_a value of tert-butanol hints of the promising new world of reaction chemistry in near- and supercritical water.

Introduction

Popular literature (Shaw et al., 1991) evidences a strong interest by chemical engineers and chemists in supercritical water as a novel solvent medium for practicing a wide variety of chemical reactions. In most cases, the water/solute mixture is heated from ambient temperature to the supercritical condition; thus, chemical reactions which occur in hot, compressed liquid or near-critical water play an important role in "setting the stage" for the higher temperature chemistry. Reactions in hot, compressed liquid water reflect the influence of the solvent's relatively high dielectric constant (Franck, 1970; Uematsu and Franck, 1980) and its large K_w (Quist et al., 1965; Marshall and Franck, 1981), which result from the high density of the liquid (relative to steam). These physical properties enable hot, compressed liquid water to stabilize the formation of polar and/or charged transition states, thereby enabling heterolytic (ionic) reactions to proceed at much higher rates than homolytic (free radical) reactions under the same conditions (Antal et al., 1987).

Unfortunately, few studies exist concerning chemical reactions in the near-critical solvent. Nevertheless, studies in dense supercritical water of the acid-catalyzed dehydration of the primary alcohols ethanol (Antal, et al., 1987; Ramayya et al., 1987; Xu et al., 1990, 1991) and 1-propanol (Narayan and Antal, 1989, 1990), and the solvolysis of various ethers (Townsend and Klein, 1985; Townsend et al., 1988) clearly demonstrate the role of ionic intermediates in the reaction chemistry. Since tert-butanol (*t*-BuOH) is far more reactive than the primary alcohols we had investigated earlier, we identified it as a promising candidate reactant for studies of heterolytic, acid-catalyzed dehydration reactions in hot, compressed liquid water. Our interest in this compound was strengthened by the fact that its dehydration mechanism has been the subject of much study at lower temperatures (see below), and that findings concerning tert-butanol could be relevant to the synthesis of ethyl tert-butyl ether (ETBE) in near-critical water-ethanol mixtures (Xu, 1992).

There is good agreement that an acid-catalyzed E1 mechanism (see steps 2, 4 and 5 of Figure 1a) governs the dehydration of tert-butanol in water at temperatures below 100°C (Taft et al., 1955; Purlee and Taft, 1956; Riesz et al., 1957; Boyd et al., 1960). The distinguishing feature of the E1 mechanism is the role of the carbocation intermediate $(CH_3)_3C^+$ in steps 4 and 5 of Figure 1a. Note, however, that Whalley (1966) and Baliga and Whalley (1965) reported an activation volume of -11.5 cm^3/mol for the acid-catalyzed hydration of isobutene at 35°C. This result led them to conclude that a molecule of water is bound in the transition state of the reaction; thereby supporting an E2 type mechanism. Far less is known about the dehydration reaction at higher temperatures. Ogi et al.

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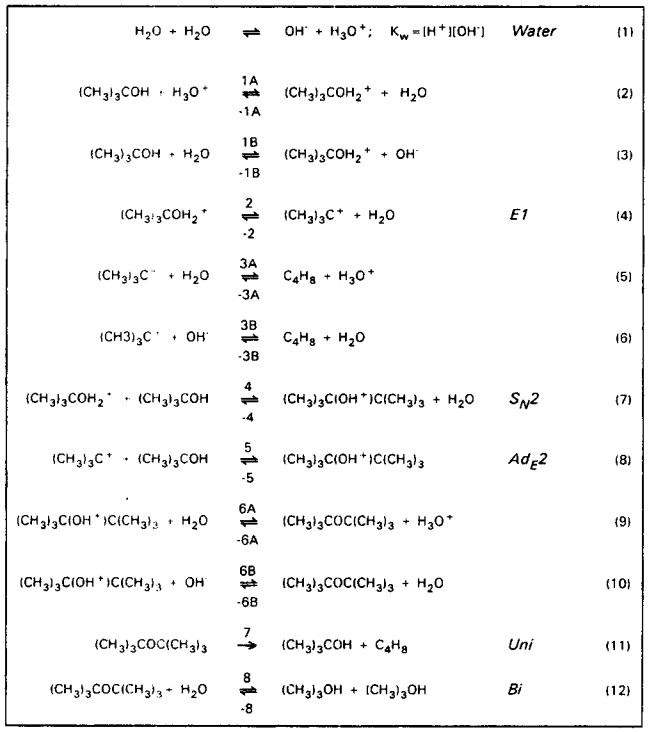

Figure 1a. Water/E1/S_N2/Ad_E2/Uni/Bi model for the dehydration of tert-butanol in near-critical water at 250°C, 34.5 MPa.

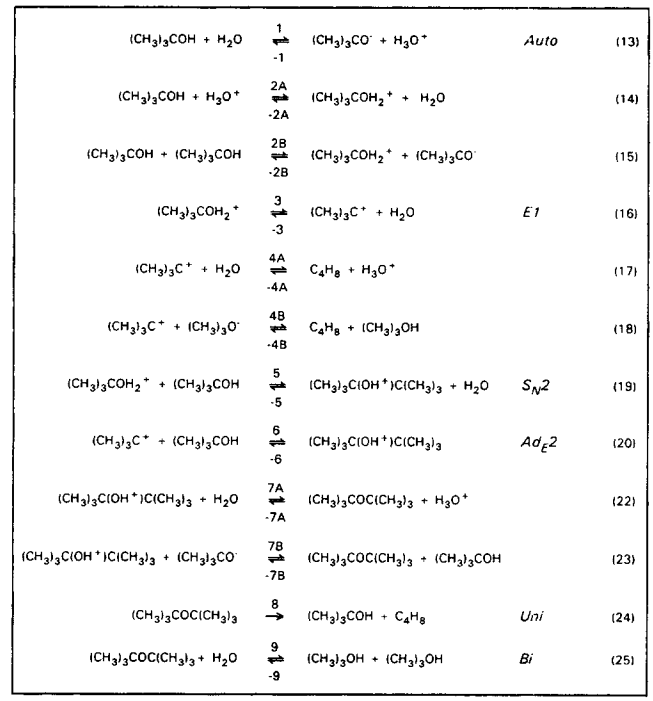

Figure 1b. Auto/E1/S_N2/Ad_E2/Uni/Bi model for the dehydration of tert-butanol in near-critical water at 250°C, 34.5 MPa.

(1990) reported a 70% conversion of tert-butanol to isobutene in compressed liquid water at 275°C and 9 MPa *without* acid catalyst. To our knowledge, this was the first observation of the uncatalyzed dehydration of tert-butanol in hot liquid water. One objective of our work was to develop a mechanistic understanding of this uncatalyzed reaction using kinetics.

A second objective of our work was to use the experimental data we acquired to make a critical examination of the extent to which kinetics can be used to reliably detail mechanism. This is a controversial subject. Some chemical engineers believe that "with the flexibility given by these (rate) constants it is not hard to get a good fit of data to a mathematical expression." In the words of one of my colleagues, " 'with six constants you can fit a charging rhinoceros' " (Hill, 1977). On the other hand, chemists are taught that "the most important single tool for mechanistic investigation is probably kinetics. Measurements of reaction rates are made for the purpose of verifying the consistency of the proposed pattern of reaction steps through dependence of rates on concentration, and also in order to derive activation parameters, ..." (Lowry and Richardson, 1987). In what follows we carefully examine the ease with which our data can be fit by various reasonable patterns of reaction steps, that are called "mechanisms."

Apparatus and Experimental Procedures

Two plug-flow (see Appendix I) reactors fabricated from Hastelloy C276 tubing were used in this work. The larger, annular flow reactor (with a metal shell surface-to-volume ratio of 17 cm^{-1}, and a sintered alumina inner annulus surface-to-volume ratio of 29 cm^{-1}) conveniently provides residence times of 20 to 100 s; whereas the capillary tube flow reactor (with a surface-to-volume ratio of 53 cm^{-1}) enables studies involving residence times of 10 s or less. Figure 2 shows the annular flow reactor. Earlier Antal et al. (1990) and Xu et al. (1992) described in detail these reactors and their associated product sampling systems.

Typically, two samples of the products exiting the reactor were taken in each of two different sampling systems for every reaction condition. Qualitative analysis of unknown liquid and gaseous products was accomplished using a Hewlett-Packard model 5790A gas chromatograph (GC) coupled to a Hewlett-Packard model 5970A mass selective detector. Quantitative analysis of the liquid products and reactant was performed using a high-performance liquid chromatograph (HPLC) composed of a Waters model 600A solvent delivery system, a Perkin-Elmer LC 600 autosampler, a Waters R-400 differential refractometer, and a Hewlett-Packard HPLC chemstation. An Alltech C18 column effected the necessary separations, using deaerated, deionized water as the solvent with a flow rate of 0.7 mL/min. Repeated injections of many standards revealed peak height calibration to be more reproducible than calibration by peak area. Typical ratios of the sample standard deviation of a peak height measurement to its mean value were less than 3.2%, whereas the comparable ratio based on peak area were as much as 16.6% and evidenced considerable scatter. Consequently, all HPLC quantitative analyses reported here were based on peak height. Typically, two injections were analyzed by HPLC per product sample. Gas products were analyzed with a Hewlett-Packard model 5840 GC equipped with a thermal conductivity detector and a flame ionization detector. Separations were effected using a Poropak Q column

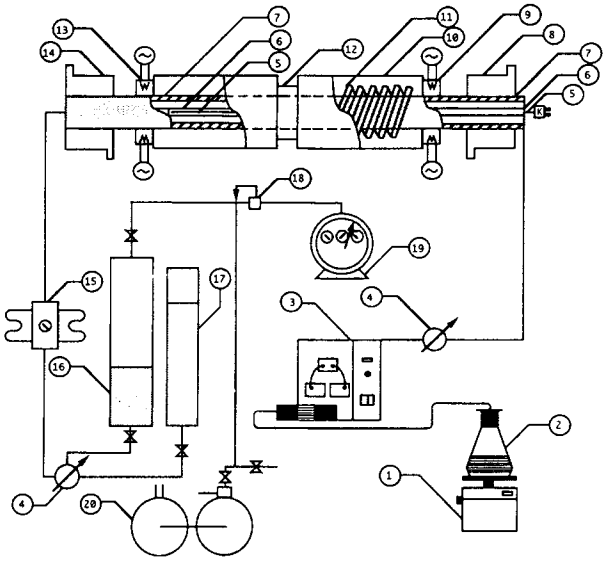

Figure 2. Annular flow reactor.

(1) Mettler balance; (2) flask with filtered and deaerated deionized water; (3) HPLC pump; (4) bypass 3-way valve; (5) probe thermocouple (type K); (6) alumina annulus; (7) Hastelloy C-276 tube; (8) entrance cooling jacket; (9) entrance heater; (10) quartz gold plated I.R. mirror; (11) furnace coil; (12) window (no coils); (13) guard heater; (14) outlet cooling jacket; (15) ten port dual loop sampling valve; (16) product accumulator; (17) drain tank; (18) back pressure regulator; (19) outflow measuring assembly; (20) air compressor.

operating at 200°C with nitrogen as a carrier gas, and a Carbosieve column operating with a temperature program of 4.2 min at 35°C, followed by a 15°C/min ramp to 227°C using helium as a carrier gas.

Laboratory grade tert-butanol from Hawaii Chemical & Scientific was used as the reactant. No impurities were detected in this reagent by either HPLC or GC analysis. Fisher certified grade 10 N sulfuric acid was used as catalyst. Isobutene (Aldrich Chemical Co.) and air standards were used to calibrate the GC.

Modeling Procedures

The application of the law of mass action to each reaction step composing a mechanism defines the set of coupled, nonlinear, stiff ordinary differential equations (ODEs) which govern the time-dependent behavior of all the species involved in the reaction network. For example, the E1 mechanism given by steps 2, 4 and 5 of Figure 1a defines a set of six ODEs governing the time-dependent behavior of tert-butanol, acid, protonated tert-butanol, water, carbocation, and alkene. The use of carbon and charge conservation make it possible to substitute two algebraic equations for two of the ODEs (see Appendix II). Because we work with dilute solutions (less than 4.3 mol%) of reactant in water, we also assume that the concentration of water is constant and equal to its value at the inlet of the reactor. Thus (in this example), we simulate the reaction chemistry by numerically integrating the remaining three ODEs, which describe the time-dependent concentration of reactant, protonated reactant, and carbocation. These equations are integrated by a double precision version of Gear's method (Gear, 1971) as realized by IMSL (IMSL, 1989). In keeping with the assumption of constant water concentration, we also assume that the density of the reactant mixture does not change as the reaction progresses; therefore, the velocity of the fluid is constant down the length of the reactor. More detailed examples of this approach have been given by Narayan and Antal (1989), Xu et al. (1990, 1991), and Xu (1992).

Additional approximations (Appendix II) are made to define the initial conditions associated with the ODEs:

(1) The initial concentration of the water solvent at normal temperature and pressure (NTP) is approximated by assuming that the reactant mixture behaves as an ideal solution at NTP.

(2) The concentrations of tert-butanol and water at reaction temperature and pressure (RTP) are given by their concentrations at NTP multiplied by the specific gravity of pure water at RTP.

(3) The only charged species present at the entrance of the reactor are H_3O^+ and HSO_4^-. We assume that H_2SO_4 fully dissociates under our conditions, but that HSO_4^- does not dissociate. This latter assumption was verified by establishing the inability of $NaHSO_4$ to catalyze the dehydration of 2-propanol at RTP.

(4) No reaction occurs during heatup prior to the entrance to the reactor. This was verified by various lower temperature, short residence time experiments.

Rate constants which give a best fit of the model to the experimental data are determined by an in-house, double precision line search algorithm (Antal and Anderson, 1992). This algorithm minimizes the objective function $\chi^2 = \Sigma(e_j/\sigma)^2$, where the residual $e_j = (y_j^{exp} - y_j^{mod})$, y_j is the yield of tert-butanol at each reaction condition j, as measured experimentally (exp) or calculated by the model (mod), and σ is the sample standard deviation associated with the yield measurement (Bevington, 1969). Replicate experiments, conducted over a period of months, indicate the ratio σ/y_j^{exp} to be about 0.04. This is in good agreement with the precision of the HPLC measurement of the tert-butanol yield. The nonlinear, least-squares line search algorithm we now employ is more reliable and faster than the IMSL BCLSF routine that we used in our earlier work (Narayan and Antal, 1989; Xu et al., 1990; 1991). (All our codes are available for public use at no cost.) Further details concerning the governing ODEs are given by Xu (1992).

Results and Discussion

Table 1 lists 38 experimental measurements of the fractional yield of tert-butanol exiting the reactor at 250°C and 34.5 MPa in the absence and presence of sulfuric acid catalyst. Error bars given in Table 1 represent an estimate of the 95% confidence interval using Student's t distribution (Benedict, 1984) based on peak height calibration. Isobutene was the only product detected by GC, GC-MSD (mass-selective detector), and HPLC analysis. No light gases, such as hydrogen, carbon monoxide, or carbon dioxide were detected. A typical carbon balance at a given condition was $99.6 \pm 2.6\%$, where the $\pm$ value indicates the sample standard deviation. Consistent with the earlier work of Ogi et al. (1990), large conversions of tert-butanol were observed in the absence of acid. Because no light gases were detected, and recognizing the catalytic influence of acid on the results displayed in Table 1, we concluded that the

Table 1. Experimental and Calculated Fractional Yields of *t*-BuOH at 250°C, 34.5 MPa Using Auto/E1/Ad_E2/Uni/Bi Model

Date	*t*-BuOH Conc. mol/dm³	H_2SO_4 Conc. mmol/dm³	Res. Time, s	tert-Butanol Yield Exp.	Calc.
10/23/91	0.1	0	1.5	0.97±0.049	0.97
10/23/91	0.1	0	2.9	0.93±0.047	0.94
10/23/91	0.1	0	5.7	0.91±0.046	0.89
10/23/91	0.1	0	12	0.77±0.039	0.80
10/15/91	0.1	0	20	0.70±0.035	0.73
09/10/91	0.1	0	28	0.68±0.034	0.68
09/12/91	0.1	0	42	0.64±0.032	0.63
09/12/91	0.1	0	85	0.58±0.029	0.60
09/11/91	0.05	0	5.5	0.92±0.046	0.90
10/30/91	0.1	0	5.7	0.91±0.046	0.89
10/30/91	0.5	0	5.9	0.89±0.045	0.86
10/30/91	1	0	5.8	0.85±0.043	0.85
10/30/91	2	0	5.8	0.81±0.041	0.82
07/05/91	0.05	0	29	0.70±0.035	0.69
09/10/91	0.1	0	27	0.69±0.035	0.69
09/10/91	0.2	0	29	0.68±0.034	0.66
09/10/91	0.5	0	28	0.65±0.033	0.65
05/25/90	1	0	30	0.60±0.030	0.61
10/23/91	0.1	0	2.9	0.93±0.047	0.94
11/27/91	0.5	0	2.9	0.92±0.046	0.92
11/27/91	1	0	2.9	0.90±0.045	0.91
09/10/91	0.2	0	29	0.68±0.034	0.66
10/15/91	0.2	0	20	0.69±0.035	0.71
09/18/91	0.2	0	5.4	0.90±0.045	0.88
09/12/91	0.5	0	83	0.58±0.029	0.57
06/01/90	0.5	0	44	0.61±0.031	0.60
12/18/91	0.1	0.1	5.7	0.65±0.033	0.64
12/18/91	0.1	0.5	5.7	0.62±0.031	0.63
12/18/91	1	0.1	5.8	0.67±0.034	0.67
06/10/92	0.1	0.2	1.5	0.72±0.036	0.72
06/10/92	0.1	0.2	3	0.63±0.032	0.64
06/10/92	0.1	0.2	12	0.61±0.031	0.61
06/05/91	0.1	0.2	29	0.61±0.031	0.61
06/05/91	0.1	1	29	0.69±0.035	0.67
06/05/91	0.1	5	29	0.78±0.039	0.79
06/05/91	0.1	0.2	44	0.61±0.031	0.61
07/02/92	0.1	0.1	3	0.72±0.036	0.71
07/02/92	0.1	0.01	3	0.91±0.046	0.91

* ± indicates the 95% confidence interval for variations in tert-butanol yield using the Student's *t* distribution.

reaction chemistry must involve ionic intermediates. Consequently, we attempted to model the results given in Table 1 by acid-catalyzed heterolytic mechanisms, such as given by steps 2, 4 and 5 of Figure 1a.

Such reasoning leads to an immediate problem, since no strong acids are present in many of the conditions listed in Table 1. Recognizing the fact that the value of K_w can be as large as 10^{-11} in near-critical water, several workers (Antal et al., 1987; Kersten, 1991; Baur, 1991) have speculated on the possibility of near- or supercritical water itself acting as an acid catalyst for reactions of this kind. Consequently, we attempted to fit the data given in Table 1 using a background concentration of protons provided by the solvent water with values of $-\log K_w$ in the vicinity of 11, combined with an E1 model for the dehydration chemistry. Since we assume that the dissociation of water is fast, we do not attempt to evaluate the rate constants associated with step 1 in Figure 1a. This "Water/E1" model (steps 1-6 in Figure 1a) achieves a fit to the experimental data $\chi^2_\nu = 1.43$ (Table 2), which is not good. The only other potential acid present is the reactant, tert-butanol. Although it is a very weak acid (McMurry, 1988) at room conditions (with a value $-\log K_a = 18$), the dissociation of tert-butanol is endothermic; consequently, we expect that its K_a should increase with increasing temperature. Figure 1b displays steps composing a model that involves tert-butanol as an acid, as well as the reactant undergoing acid-catalyzed dehydration via an E1 mechanism. This autocatalytic E1 (Auto/E1) model (steps 13–18) actually involves two acid catalysts: the Arrhenius acid H_3O^+ combined with its conjugate base OH^-, and *t*-BuOH acting as a Bronsted acid with acid/conjugate base pair *t*-BuOH/*t*-BuO^-. Acid-catalysis by H_3O^+ (involving reactions labeled "A" for Arrhenius acid in Figure 1b) is often referred to as "specific," whereas catalysis involving reactions labeled "B" (for Bronsted acid) as well as those labeled "A" is referred to as "general." The Auto/E1 model realized a fit $\chi^2_\nu = 1.79$, which is unacceptable.

Earlier kinetic studies of the acid-catalyzed dehydration of ethanol in supercritical water (Xu et al., 1991) revealed the role of diethyl ether and protonated diethyl ether as key intermediates in the reaction chemistry. Di-tert-butyl ether has been synthesized and its thermodynamic properties are well known (Fenwick et al., 1975); nevertheless, it is not available commercially, and it was not detected as a product in the reactor effluent. Assuming that this ether would not be stable as a product in water, we decided to examine the hypothesis that it could act as an intermediate in the reaction chemistry.

Table 2. Fit of Models to Experimental Measurements at 250°C, 34.5 MPa, and Number of Rate Constants

Model	χ^2_ν	No. Nonzero Rate Constant/Total No. Rate Constant in the Model
Water/E1	1.43	10/10
Auto/E1	1.79	8/12
Auto/E1/S_N2/Ad_E2	1.79	8/20
Auto/E1/S_N2/Ad_E2/Uni/Bi	0.34	12/23
Auto/E1/Ad_E2/Uni/Bi	0.32	11/23
Auto/E1/S_N2/Ad_E2/Uni	1.79	8/21
Auto/E1/S_N2/Ad_E2/Bi	1.79	8/22
Water/E1/S_N2/Ad_E2/Uni/Bi	1.31	10/21
Auto/E1/S_N2/Ad_E2/Uni/Bi (with omission of reactions labeled B)	0.55	9/17
Auto/E2/S_N2/Ad_E3/Uni/Bi	0.69	13/21

Two pathways are expected to account for the formation of the ether. The first involves an S_N2 mechanism with tert-butanol and protonated tert-butanol as reactants; whereas the second follows an Ad_E2 mechanism with tert-butanol and carbocation ($C_4H_9^+$) as reactants. Figure 1b summarizes the elementary reactions (steps 13-23) included in this model (Auto/E1/S_N2/Ad_E2), with tert-butanol acting as acid as well as reactant. The fit of this model to the data is given by $\chi^2_\nu = 1.79$, which represents no improvement over the Auto/E1 model value. Following our earlier work, we expanded this model further by including an Ad_E3 pathway (involving isobutene, tert-butanol, and H_3O^+ as reactants) to account for ether formation, but the fit did not improve.

Prior work revealed that diethyl ether (Xu et al., 1991), guaiacol (Lawson and Klein, 1985; Huppert et al., 1988), dibenzyl ether (Townsend and Klein, 1985; Wu et al., 1989), phenethyl phenyl ether, and benzyl phenyl ether (Townsend et al., 1988) all decompose in dense supercritical water in the absence of acid. In all cases the experimental evidence pointed to the role of elementary bimolecular (hydrolysis) reactions, as well as less well defined pyrolysis reactions, in the decomposition chemistry (Klein et al., 1990; Wu et al., 1991). In addition, our earlier work revealed ethene (as well as ethanol) to be an immediate product of the uncatalyzed decomposition of diethyl ether in dense supercritical water. Consequently, we found it necessary to include both bi- and unimolecular ether decomposition steps in the kinetic model which succeeded in fitting the experimental data describing ethanol dehydration in supercritical water (Xu et al., 1991). Reasoning that di-tert-butyl ether might also decompose via uncatalyzed unimolecular and bimolecular reactions, we attempted to use the model Auto/E1/S_N2/Ad_E2/Uni/Bi given by steps 13-25 in Figure 1b to fit the data. As indicated in Table 2, this model realizes an exceptionally good fit, achieving a value $\chi^2_\nu = 0.34$. Moreover, the least-squares algorithm indicates that 11 of the rate constants (parameters) in the model are zero. Thus, the fit is achieved using only 12 rate constants.

We were prepared to publish the results based on the Auto/E1/S_N2/Ad_E2/Uni/Bi model described above, but during the review process Maitland Jones, Jr. (Princeton University) and one of the two anonymous reviewers both expressed skepticism concerning the presumed role of an S_N2 reaction (step 19) in forming ether from tert-butanol. As is well known, the three methyl groups should shield the protonated alcohol from a backside attack by a nucleophile. Nevertheless, our numerical methods seemed to indicate that step 19 played an important role in the chemistry. Following the chemist's edict, we removed the S_N2 pathway from the model, and were surprised to find that this new 11 parameter Auto/E1/Ad_E2/Uni/Bi model realizes a better fit with $\chi^2_\nu = 0.32$. Figure 3 displays the accord of the Auto/E1/Ad_E2/Uni/Bi model values with experimental yield measurements. In all cases the model values lie within the 95% confidence interval of the experimental result. Some of the experimental measurements exhibit unexpected trends (see Figure 4). After many replications, we included these strange results in our modeling work, and discovered that the Auto/E1/Ad_E2/Uni/Bi model naturally mimics the strange behavior. Finally, we note that the experimental data displayed in Table 1 was acquired using two reactors with considerably different surface-to-volume ratios. The fact that the model fits all the data is consistent with our assumption

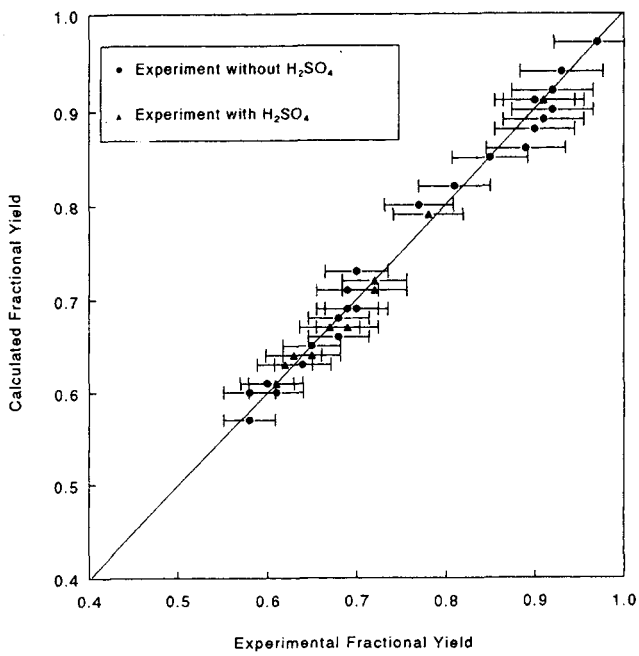

Figure 3. Calculated vs. experimental yields of tert-butanol using Auto/E1/Ad_E2/Uni/Bi model at 250°C, 34.5 MPa.

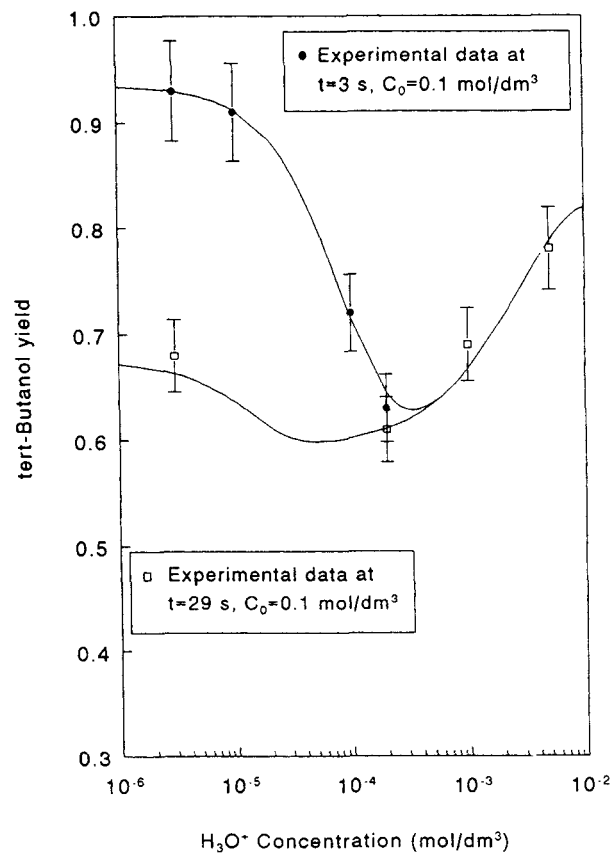

Figure 4. Tert-butanol yield vs. initial sulfuric acid concentration using Auto/E1/Ad_E2/Uni/Bi model at 250°C, 34.5 MPa.

that the reaction chemistry is governed by liquid phase, heterolytic mechanisms involving no wall effects.

In spite of the good accord of the model with the data, a skeptic might argue that the fit is fortuitous and possesses little physical significance because the model employs a relatively large number of free parameters. To examine this issue, we tested the ability of a variety of closely related models to fit the data. As indicated in Table 2, neither an Auto/E1/S_N2/Ad_E2/Uni (steps 13-24 in Figure 1b) nor an Auto/E1/S_N2/Ad_E2/Bi (steps 13-23 and 25 in Figure 1b) model was able to achieve a good fit to the data. Likewise, a Water/E1/S_N2/Ad_E2/Uni/Bi model (steps 1-12 in Figure 1a) was unable to fit the data. An abbreviated, specific acid-catalyzed Auto/E1/S_N2/Ad_E2/Uni/Bi model, which omitted all reactions labeled B in Figure 1b, achieved a fit $\chi^2_\nu = 0.55$. Evidently, the Bronsted reactions do not play a critical role in the reaction chemistry.

Earlier work (Narayan and Antal, 1989, 1990; Xu et al., 1990, 1991) with primary alcohols achieved good fits employing models based on E2 type mechanisms, which do not involve bare carbocations as intermediates (Figure 5). We attempted to use such a model (Auto/E2/S_N2/Ad_E3/Uni/Bi) to fit the data, but the result (Table 2) was not as good as the Auto/E1/Ad_E2/Uni/Bi model. As displayed in Figure 6, at least two model values do not lie within a 95% confidence interval of the experimental result, and several other values lie at the edge of the confidence interval. In our experience this situation is typical of the ability of models representing E1 and E2 type mechanisms to fit high quality experimental data. Usually one model can fit the data very well, while the other realizes an adequate, but less impressive fit. Obviously, the ability of a kineticist to discriminate between models (mechanisms) rests squarely on the quality of the available experimental data. If the data lacks precision, many models will be able to offer values that lie somewhere within the large error bar. Similarly,

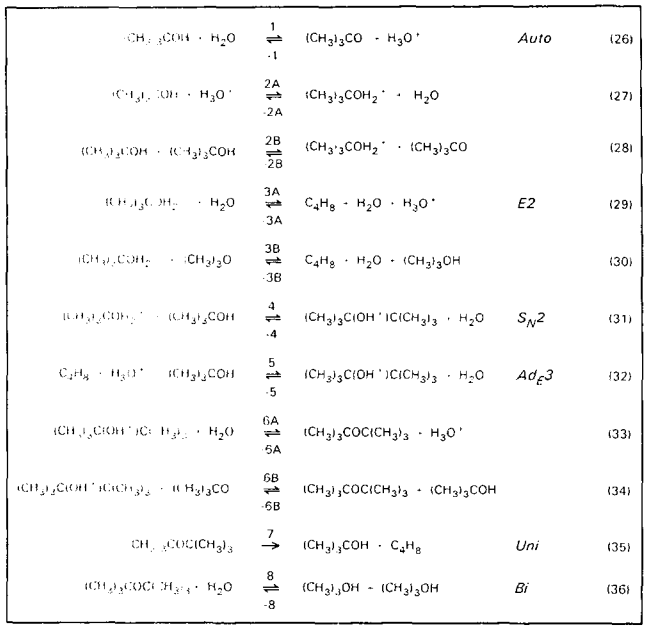

Figure 5. Auto/E2/S_N2/Ad_E3/Uni/Bi model for the dehydration of tert-butanol in near-critical water at 250°C, 34.5 MPa.

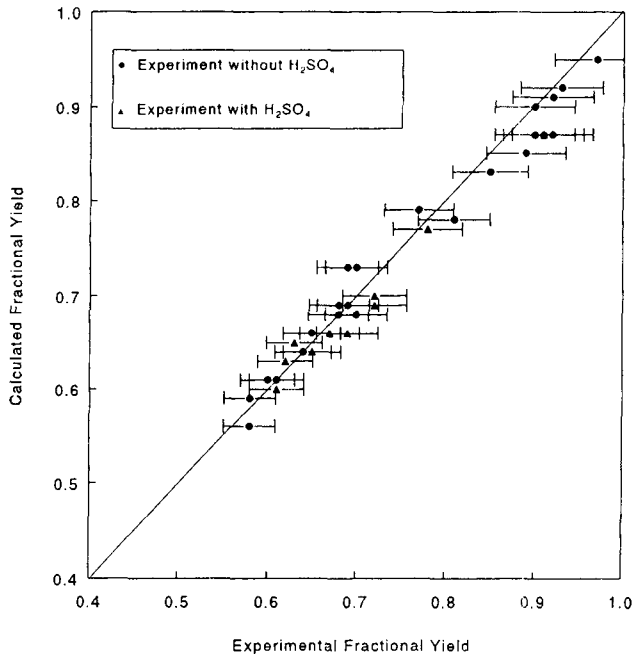

Figure 6. Calculated vs. experimental yields of tert-butanol using Auto/E2/S_N2/Ad_E3/Uni/Bi model at 250°C, 34.5 MPa.

if the data does not span a sufficiently large range of reactant concentrations and conversions, it is probable that more than one model will be able to mimic the experimental trends. Because we are unable to propose any other likely models to describe the dehydration chemistry of tert-butanol, we conclude that the agreement of the Auto/E1/Ad_E2/Uni/Bi model with the data is nontrivial.

Table 3 lists nonzero values of the rate constants which give a best fit of the Auto/El/Ad_E2/Uni/Bi model to the data. The listed best fit values of k_1 and k_{-1} result in a predicted value of 9.0 for the pK_a of tert-butanol in compressed liquid water at 250°C. This value is comparable to the acidity of *m*-chlorophenol in water at room conditions. In Table 3 we also list alternative sets of rate constants which give nearly as good a fit to the data. These *k*s are the "endpoints" which result from three different initial guesses of the rate constants; conse-

Table 3. Elementary Rate Constants for Auto/E1/Ad_E2/Uni/Bi Model and Sensitivity of χ^2_ν to Changes in Best Fit Rate Constants at 250°C, 34.5 MPa

Rate Constant	Run 1, $\chi^2_\nu = 0.32$	Run 2, $\chi^2_\nu = 0.34$	Run 3, $\chi^2_\nu = 0.36$
k_1/(dm³/mol·s)	2.81×10^{-4}	3.36×10^{-3}	1.86×10^{-5}
k_{-1}/(dm³/mol·s)	1.27×10^{7}	2.26×10^{7}	6.44×10^{4}
k_{2A}/(dm³/mol·s)	5.96×10^{4}	2.32×10^{4}	1.22×10^{4}
k_{2B}/(dm³/mol·s)	4.68×10^{-2}	8.67×10^{-2}	5.06×10^{-3}
k_3/(1/s)	8.93×10^{4}	7.94×10^{4}	2.25×10^{4}
k_{-4A}/(dm³/mol·s)	1.36×10^{4}	3.89×10^{3}	4.31×10^{3}
k_6/(dm³/mol·s)	2.54×10^{4}	3.51×10^{6}	1.62×10^{5}
k_{7A}/(dm³/mol·s)	3.30×10^{2}	4.08×10^{2}	3.69×10^{2}
k_{7B}/(dm³/mol·s)	1.59×10^{8}	2.34×10^{9}	1.46×10^{7}
k_8/(1/s)	9.60×10^{0}	1.31×10^{1}	1.22×10^{1}
k_9/(dm³/mol·s)	1.39×10^{0}	2.62×10^{0}	1.13×10^{0}

Note: Unlisted *k*s have a value of zero.

quently, they give some indication of the uncertainty associated with each value. Although the values of k_1 and k_{-1} vary, the related pK_a values remain relatively constant with values ranging between 7.8 and 9.0. This finding suggests that our predicted value of the pK_a of tert-butanol may be reasonably precise. Figure 7 displays the temporal behavior (for reaction times exceeding 0.1 s) of the reactant, intermediates, and product as predicted by the Auto/E1/Ad_E2/Uni/Bi model. Di-tert-butyl ether is the only intermediate which attains a significant concentration. Nevertheless, its concentration remains two orders of magnitude below those of tert-butanol and isobutene. As displayed in Figure 7, the concentration of carbocation significantly exceeds that of protonated alcohol when the rate constants listed under "run 1" of Table 3 are used to simulate the reaction chemistry. We remark that the rate constants associated with the other two "runs" result in concentrations of carbocation that are approximately equal to, and are less than the concentration of protonated alcohol.

Perhaps the most surprising prediction of the model concerns the mechanism of formation of isobutene (Figure 8). According to the model, reaction pathways +4A and +4B are not active (Table 3); thus, the bare carbocation is not the main source of isobutene. Instead, the carbocation reacts with tert-butanol to create the protonated ether. Isobutene is formed by the unimolecular decomposition of unprotonated di-tert-butyl ether. This reaction network (see Figure 8) explains the strange results given in Figure 4. An increase in the concentration of sulfuric acid catalyst increases the concentration of carbocation, which reacts with alcohol to form ether. Two reactions compete to consume ether. The first forms isobutene and tert-butanol; whereas the second regenerates tert-butanol alone. Thus, only a fraction of the ether is able to form alkene. Consequently, an increase in acid concentration eventually leads to a decrease in the yield of isobutene.

This unexpected result has some foundation in the earlier literature. Both Taft and coworkers (Taft, 1952; Taft et al., 1955; Levy et al., 1953) and Dostrovsky and Klein (1955) concluded that the rate determining steps for tert-butanol dehydration and isobutene hydration are different. These groups concurred that the transition state of the rate determining step

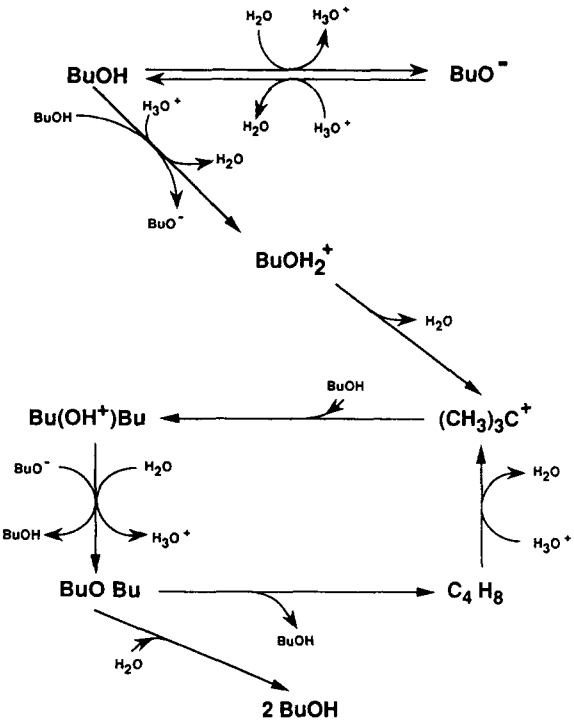

Figure 8. Acid-catalyzed reactions of tert-butanol (BuOH) in hot water.

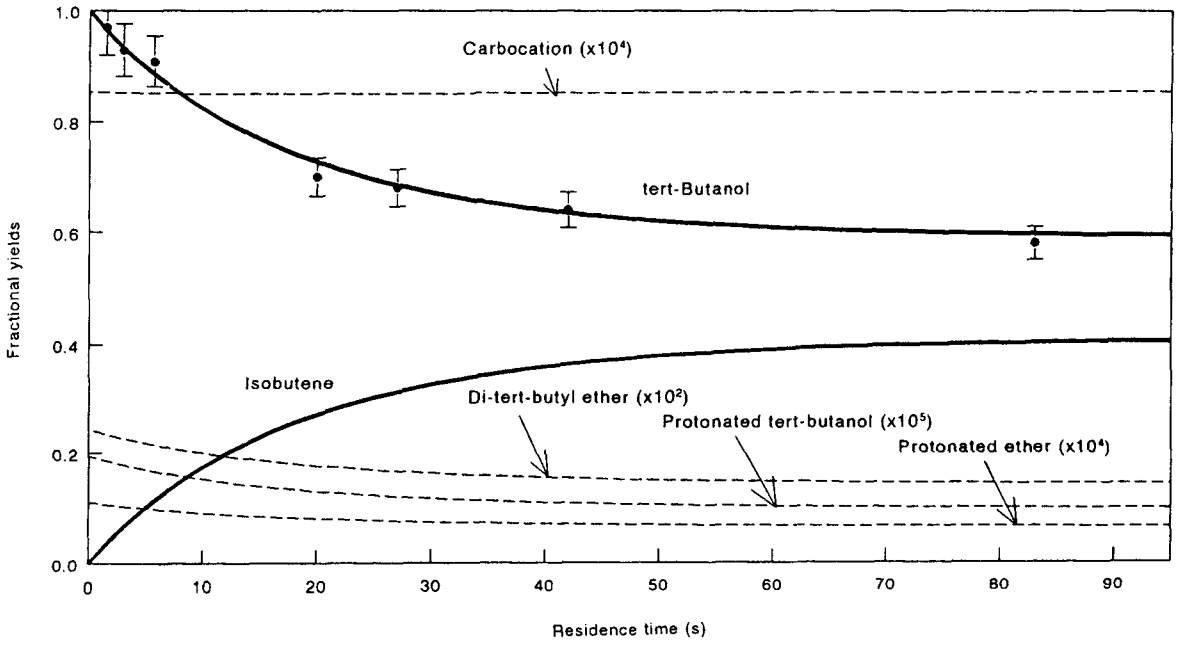

Figure 7. Fractional yields of tert-butanol, isobutene, and intermediates vs. residence time using Auto/E1/Ad_E2/Uni/Bi model at 250°C, 34.5 MPa (0.1 mol/dm³ tert-butanol at NTP without sulfuric acid).

for isobutene hydration involves only carbocation, which is in accord with the Auto/E1/Ad_E2/Uni/Bi model, and the rate constants given in Table 3. The relatively slow rate of tert-butanol dehydration observed by both groups is consistent with our model's prediction that isobutene forms via the unimolecular decomposition of di-tert-butyl ether. No earlier workers have considered the potential role of the ether in the dehydration chemistry of tert-butanol.

One may wonder how Figure 8 provides for the formation of tert-butanol from isobutene in the absence of alcohol, when the formation of tert-butanol from isobutene is evidently autocatalytic in tert-butanol. Note that although the Auto/E1/Ad_E2/Uni/Bi model achieves a good fit to the data with some rate constants set to zero, the actual values of these rate constants are probably very small, but not zero. Thus, we suppose that a trace amount of alcohol would be formed from the carbocation by reaction -3 in Figure 1b, and this would be enough to initiate the autocatalytic formation of tert-butanol, as displayed in Figure 8.

Conclusions

(1) In compressed liquid water at 250°C tert-butanol rapidly reacts to form an equilibrium mixture of itself with isobutene. No other products are detected. The rate of reaction is enhanced by the addition of trace amounts of sulfuric acid. These findings lead us to conclude that the dehydration chemistry involves heterolytic reactions characterized by ionic intermediates.

(2) tert-Butanol plays three distinct roles in the reaction chemistry. As the reactant it suffers acid-catalyzed dehydration to form isobutene. As a conventional Arrhenius acid it dissociates in water to form the catalytic acid/conjugate base pair H_3O^+/H_2O. It also acts as a Bronsted acid with catalytic acid/conjugate base pair t-BuOH/t-BuO^-. The pK_a of tert-butanol in compressed liquid water at 250°C is calculated to be about 9.

(3) The kinetic data presented in this article can all be well described by the Auto/E1/Ad_E2/Uni/Bi model (see Figure 1b) which involves protonated alcohol, carbocation, ether, and protonated ether as intermediates. Isobutene formation occurs via an uncatalyzed, unimolecular decomposition of the ether. In the presence of acid, isobutene protonates irreversibly to form carbocation, which is the key intermediate in the formation of either ether or tert-butanol.

(4) A wide variety of other mechanistic models are not consistent with the experimental data.

(5) The results of this study confirm the chemist's point of view that kinetic models can offer considerable insight into mechanism, providing that accurate experimental data are available for a wide range of reactant and catalyst concentrations, and conversions.

These conclusions include several surprising predictions which can be verified. An electrochemical determination of the pK_a of tert-butanol in hot, compressed liquid water would offer insight into our hypothesis that pK_a values associated with some weak acids can decrease dramatically as the temperature of the liquid water solvent increases. At the present time, little is known about the influence of temperature on the pK_a of many common acids above 100°C. Such an electrochemical study could offer many insights into reaction chemistry in water above 100°C. A kinetic study of the acid-catalyzed formation of tert-butanol from isobutene in near-critical water could help to confirm the autocatalytic mechanism displayed in Figure 8. Similarly, an in situ spectroscopic determination of the concentration of di-tert-butyl ether at reaction conditions would help to establish its role as an intermediate in the dehydration chemistry of tert-butanol. Such studies could have important commercial implications relative to the synthesis of ETBE and other oxygenates from isobutene.

Acknowledgments

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Appendix I: Plug-Flow Idealization of Tubular Flow Reactor Data

Criteria which assure the legitimate use of the plug-flow idealization of tubular flow reactor data are well established (Cutler et al., 1988). These criteria are based on various characteristic times from which the nondimensional numbers that represent flow in the reactor can be calculated. Three types of criteria are available. These assure negligible axial diffusion, negligible Poiseuille flow, and constant temperature within the reactor. Table A1 displays representative values of the characteristic times and nondimensional numbers for the two reactors employed in this work. Table A2 summarizes values of the various criteria which legitimatize our use of the plug-flow idealization. As is obvious from the table and the footnotes, all the relevant criteria are satisfied. Radial species diffusion plays an important role in rationalizing our neglect of Poiseuille flow within the reactor. Nevertheless, we note that in the extreme case where no radial species diffusion exists to smear the parabolic velocity profile within a laminar flow reactor, the error introduced in the calculation of rate constants by the misuse of the plug-flow idealization is small (Ramayya and Antal, 1989).

Table A1. Characteristic Times and Nondimensional Numbers for tert-Butanol Experiments at 250°C, 34.5 MPa

		Values* (s)	
	Formula	Annular Reactor	Capillary Reactor
Characteristic Time			
$\tau_{fc,R}$	R/u	1.12×10^{-1}	8.45×10^{-3}
$\tau_{fc,L}$	L/u	3.10×10^{1}	5.80×10^{0}
$\tau_{sd,R}$	R^2/D	1.41×10^{2}	7.59×10^{0}
$\tau_{sd,L}$	L^2/G	3.26×10^{2}	2.13×10^{2}
τ_{td}	R^2/α_{td}	1.50×10^{1}	8.06×10^{-1}
τ_{md}	R^2/ν	1.95×10^{1}	1.05×10^{0}
τ_{ck}	k^{-1}	1.67×10^{2}	1.67×10^{2}
Nondimensional Number			
Re	$\tau_{md}/\tau_{fc,R}$	1.75×10^{2}	1.24×10^{2}
Pr	τ_{td}/τ_{md}	7.71×10^{-1}	7.71×10^{-1}
Sc	$\tau_{sd,R}/\tau_{md}$	7.26×10^{0}	7.26×10^{0}
Pe_{sd}	$\tau_{sd,R}/\tau_{fc,R}$	1.27×10^{3}	8.99×10^{2}
Pe_{td}	$\tau_{td}/\tau_{fc,R}$	1.35×10^{2}	9.54×10^{1}
Da	$\tau_{sd,R}/\tau_{ck}$	8.48×10^{-1}	4.55×10^{-2}

*Values listed are calculated using the data from tert-butanol dehydration experiments with flow rates of 6.0 cm^3/min and 1.0 cm^3/min for the annular and capillary flow reactors respectively.

Table A2. Criteria for Validity of the Plug-Flow Idealization for tert-Butanol Experiments at 250°C, 34.5 MPa

Author*	Formula	Criteria: Annular Reactor	Criteria: Capillary Reactor		No.
Negligible Axial Diffusion					
Dickens et al. (1960)	$\tau_{fc,R}^2\tau_{ck}^{-1}\tau_{sd,R}^{-1}$	5.28×10^{-7}	5.64×10^{-8}	<0.1	(1)
Azatyan (1972)		same as above		$\ll1$	
Howard (1979)		same as above		<0.1	
Furue and Pacey (1980)		same as above		<0.1	
Mulcahy and Pethard (1963)	$\tau_{fc,L}\tau_{sd,L}^{-1}$	9.50×10^{-2}	2.73×10^{-2}	<0.06	(2)**
Dang and Steinberg (1980)	$\tau_{fc,R}\tau_{sd,R}^{-1}$	7.89×10^{-4}	1.11×10^{-3}	<0.02	(3)
Furue and Pacey (1980)	$\tau_{fc,R}^2\tau_{ck}^{-1}\tau_{sd,R}^{-1}+\tau_{sd,R}\tau_{ck}^{-1}/48$	1.77×10^{-2}	9.49×10^{-4}	$\ll1$	(4)†
	or $\tau_{fc,L}\tau_{ck}^{-1}$	1.86×10^{-1}	3.48×10^{-2}	$\ll2$	
Negligible Poiseuille Flow					
Walker (1961)	$\tau_{sd,R}\tau_{fc,R}^{-1}$	1.27×10^{3}	8.99×10^{2}	<100	(5)‡
Brown (1978)		same as above		<100	
Cleland and Wilhelm (1956)	$\tau_{sd,R}\tau_{fc,L}^{-1}$	4.56×10^{0}	1.31×10^{0}	<0.5	(6)#
Mulcahy and Pethard (1963)		same as above		<14	
Walker (1961)	$\tau_{sd,R}\tau_{ck}^{-1}$	8.48×10^{-1}	4.55×10^{-2}	<1	(7)‡
Vignes and Trambouze (1962)		same as above		<1	
Poirier and Carr (1971)		same as above		<2	
Ogren (1975)		same as above		<1	
Lede and Villermaux (1977)		same as above		<1	
Brown (1978)	$\tau_{fc,R}\tau_{ck}^{-1}$	6.69×10^{-4}	5.07×10^{-5}	<0.05	(8)
Isothermality					
Gilbert (1958)	$\tau_{td}\tau_{fc,L}^{-1}$	4.84×10^{-1}	1.39×10^{-1}	$\ll3.7$	(9)
Mulcahy and Pethard (1963)		same as above		$\ll3.7$	
Furue and Pacey (1980)		same as above		$\ll1$	

* See references of Cutler et al. (1988).
** Criteria 2 should not be emphasized (Cutler et al., 1988).
† The smaller of the two criteria should be employed.
‡ Criteria 5 and 7 should be applied together, however, criteria 5 is not strong for this work since there are no wall reactions in our experiments (Cutler et al., 1988).
# Criteria 6 reflects calculated departures of true concentration profiles from idealized profiles. It should not be emphasized relative to criteria 7 and 8 (Cutler et al., 1988).

Appendix II: Model Formulation

The E1 mechanism given by steps 2, 4, and 5 in Figure 1a defines a set of six ODEs governing the time-dependent behavior of tert-butanol ($(CH_3)_3COH$), acid (H_3O^+), protonated tert-butanol ($(CH_3)_3COH_2^+$), carbocation ($(CH_3)_3C^+$), alkene (C_4H_8), and water (H_2O). The six ODEs are listed below:

$$d[(CH_3)_3COH]/dt = -k_{1A}[(CH_3)_3COH][H_3O^+] + k_{-1A}[(CH_3)_3COH_2^+][H_2O]$$

$$d[H_3O^+]/dt = -k_{1A}[(CH_3)_3COH][H_3O^+] + k_{-1A}[(CH_3)_3COH_2^+][H_2O] + k_{3A}[(CH_3)_3C^+][H_2O] - k_{-3A}[C_4H_8][H_3O^+]$$

$$d[(CH_3)_3COH_2^+]/dt = k_{1A}[(CH_3)_3COH][H_3O^+] - k_{-1A}[(CH_3)_3COH_2^+]][H_2O] + k_{-2}[[(CH_3)_3C^+]][H_2O] - k_2[(CH_3)_3COH_2^+]$$

$$d[(CH_3)_3C^+]/dt = k_2[(CH_3)_3COH_2^+] - k_{-2}[[(CH_3)_3C^+]][H_2O] - k_{3A}[(CH_3)_3C^+][H_2O] + k_{-3A}[C_4H_8][H_3O^+]$$

$$d[C_4H_8]/dt = k_{3A}[(CH_3)_3C^+][H_2O] - k_{-3A}[C_4H_8][H_3O^+]$$

$$d[H_2O]/dt = k_{1A}[(CH_3)_3COH][H_3O^+] - k_{-1A}[(CH_3)_3COH_2^+]][H_2O] - k_{-2}[[(CH_3)_3C^+]][H_2O] + k_2[(CH_3)_3COH_2^+] - k_{3A}[(CH_3)_3C^+][H_2O] + k_{-3A}[C_4H_8][H_3O^+]$$

To avoid unnecessary integrations, we employ three algebraic equations to reduce the number of ODEs from six to three. Carbon conservation results in the following expression for isobutene:

$$[C_4H_8] = [(CH_3)_3COH]_0 - [(CH_3)_3COH] - [(CH_3)_3COH_2^+] - [(CH_3)_3C^+]$$

where $[(CH_3)_3COH]_0$ is the initial concentration of tert-butanol. Charge balance offers the following equation:

$$[H_3O^+] + [(CH_3)_3COH_2^+] + [(CH_3)_3C^+] = [OH^-] + [HSO_4^-] + [(CH_3)_3CO^-].$$

Since H_2SO_4 fully dissociates into H_3O^+ and HSO_4^- at the conditions discussed in this article, and HSO_4^- does not further dissociate, we have $[HSO_4^-] = [H_2SO_4]_0$. Employing the relationship $K_w = [H_3O^+][OH^-]$, we find:

$$[H_3O^+] = \frac{1}{2}\left(-S + \sqrt{S + 4K_w}\right)$$

where

$$S = [(CH_3)_3COH_2^+] + [(CH_3)_3C^+] - [(CH_3)_3CO^-] - [H_2SO_4]_0$$

Finally, we assume that the concentration of water remains constant throughout the reaction with a value given by:

$$[H_2O] = (1 - \text{mole fraction of tert-butanol}) \times 55.55 \times \frac{\rho_{H_2O,RTP}}{\rho_{H_2O,NTP}}$$

where $\rho_{H_2O,NTP}$ is the density of water at 0.1 MPa and 25°C, and $\rho_{H_2O,RTP}$ is the density of water at reaction temperature and pressure (RTP).

The initial conditions ($t = 0$) are as follows:

$$[(CH_3)_3COH]_0 = (\text{NTP concentration of tert-butanol}) \times \frac{\rho_{H_2O,RTP}}{\rho_{H_2O,NTP}}$$

$$[C_4H_8]_0 = [(CH_3)_3COH_2^+]_0 = [(CH_3)_3C^+]_0 = 0$$

$$[H_3O^+]_0 = \frac{1}{2}\left([H_2SO_4]_0 + \sqrt{4K_w - [H_2SO_4]_0}\right)$$

$$[H_2O]_0 = (1 - \text{mole fraction of tert-butanol}) \times 55.55 \times \frac{\rho_{H_2O,RTP}}{\rho_{H_2O,NTP}}$$

In order to calculate the residence time of the reactant at RTP, the density of tert-butanol solution is assumed to be that of pure water at the same conditions. To check the validity of this assumption, we used HYSIM software (HYSIM, 1992) to estimate the ratio of density of 1.0 M tert-butanol at RTP to that of pure water at RTP. The calculated value of this ratio, 0.98, results in a 2% decrease in the residence time and a 2% decrease in the RTP concentration of reactant entering the reactor. Modeling results indicate that the 2% changes in species concentration and residence time result in less than a 1% change in the model prediction.

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