

Kinetic Studies on the Condensation Reaction of 2-Methylol-4-*t*-Butylphenol with 4-*t*-Butylphenol Using Acid Catalysts. I.

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Synopsis

The rates of the individual reactions of 2-methylol-4-*t*-butylphenol with 4-*t*-butylphenol were measured under varying mole ratios of reactants in the presence of different acid catalysts ($5.0 \times 10^{-3}N$ to $2.0 \times 10^{-4}N$) at five different temperatures (60, 65, 70, 75, and 80°C). In all the experiments, the reactions were found to obey second-order rate law. The values of the Arrhenius parameters and the entropy of activation for the overall reaction were calculated. The relative catalytic efficiencies of the acid catalysts followed the order $HNO_3 > HCl > H_2SO_4$.

INTRODUCTION

The kinetics of the condensation reaction of various simple methylolphenols with their parent phenols using acid catalysts have been studied by various research workers.¹⁻¹⁴ In the present work a systematic study was made on the effect of various acid catalysts on the condensation reaction of 2-methylol-4-*t*-butylphenol with 4-*t*-butylphenol. This investigation is a continuation of our findings on the alkali-catalyzed 4-*t*-butylphenol-formaldehyde reaction.¹⁵ The condensation reaction in the present communication was carried out using acid catalysts such as HCl, HNO₃, and H₂SO₄ in the concentration range of $5.0 \times 10^{-3}N$ to $2.0 \times 10^{-4}N$ and at temperatures of 60, 65, 70, 75, and 80°C.

EXPERIMENTAL

Materials

4-*t*-Butylphenol and 2-methylol-4-*t*-butylphenol were prepared as described earlier.^{16,17} Formaldehyde (37%–41% solution, BDH) containing less than 2% methanol, HCl, HNO₃, H₂SO₄, NaCl, and hydrated ferric chloride used were of BDH (AR) grade.

Kinetic Measurements

The reaction was carried out in a three-necked flask fitted with a mercury seal stirrer and a reflux condenser in the temperature range of $60-80^\circ \pm 0.1^\circ C$. The flask containing the reaction mixture was suspended in a thermostat maintained at the desired temperature. In view of the difficult solubility of 4-*t*-butylphenol in water, the reaction was carried out using a dioxane-water mixture (1:1 v/v).

Even in 50% dioxane, higher concentrations of 4-*t*-butylphenol were not completely soluble. Aliquots of the reaction mixture were taken at regular intervals and placed in an ice bath to arrest the reaction. Five-ml aliquots of the mixture were used for the spectrophotometric estimation of 2-methylol-4-*t*-butylphenol (2M4TBP).¹⁸

RESULTS AND DISCUSSION

From the experimental results (Tables I, II, and III) it is clear that the reaction is following the second-order rate law. From the kinetic observations (Table

TABLE I
Second-Order Rate Constants for Various Acid Catalysts at 80°C^a

Run no.	Name and concentration of catalyst	Time; min	Amount of 2M4TBP consumed, $X \times \text{m/l} \times 10^{-3}$	Second-order rate constant, l/mole-sec	Average
1	HCl (0.006 <i>N</i>)	10	2.12	2.584	2.675×10^{-2}
		20	3.76	2.707	
		30	4.94	2.727	
		40	5.89	2.774	
		50	6.53	2.712	
2	HNO ₃ (0.006 <i>N</i>)	10	2.60	3.319	3.30×10^{-2}
		20	4.35	3.351	
		30	5.53	3.301	
		40	6.37	3.224	
		50	7.12	3.264	
3	H ₂ SO ₄ (0.006 <i>N</i>)	10	1.73	2.070	2.206×10^{-2}
		20	3.10	2.119	
		30	4.33	2.263	
		40	5.24	2.305	
		50	5.89	2.270	
		60	6.38	2.208	

^a 4TBP = 0.0125*M*; 2M4TBP = 0.0125*M*; ionic strength = 0.02; solvent = 50% dioxane; temperature = 80 ± 0.1°C

TABLE II
Second-Order Rate Constants for Various Acid Catalysts at Different Temperatures^a

Temperature, °C	$k \times 10^2$, l/mole-sec		
	HCl	H ₂ SO ₄	HNO ₃
60	0.493	0.176	0.538
65	0.669	0.3316	1.27
70	1.115	0.794	1.342
75	1.369	1.319	1.411
80	2.560	2.526	3.301

^a 4TBP = 0.0125*M*; 2M4TBP = 0.0125*M*; ionic strength = 0.02; solvent = 50% dioxane; catalyst concentration = 0.006*N*.

TABLE III
Second-Order Rate Constants for Various Concentrations of Acid Catalysts^a

Concentration, $\times 10^4 N$	$k \times 10^2$, l/mole-sec		
	HCl	HNO ₃	H ₂ SO ₄
60	2.560	3.301	2.526
100	4.055	5.573	2.526
150	5.281	8.173	3.111
200	7.515	10.633	3.855

^a 4TBP = 0.0125M; 2M4TBP = 0.0125M; ionic strength = 0.02; solvent = 50% dioxane; temperature = 80° ± 0.1°C.

I) it was concluded that the rate of the condensation reaction was dependent on the anion of the catalyst.

Effect of Temperature

The Arrhenius energy of activation for the condensation reaction with different acid catalysts and the corresponding frequency factors $\log_{10} PZ$ were calculated from the linear plot of $\log k$ against $1/T$ at five different temperatures.

The free energy of activation (ΔG), enthalpy of activation (ΔH), and the entropy of activation (ΔS) were calculated using the following equation:

$$k = (kT/h) e^{-\Delta G^\ddagger/RT} = (kT/h) e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} \quad (1)$$

ΔH^\ddagger and ΔS^\ddagger were also evaluated using eqs. (2) and (3):

$$\Delta H^\ddagger = E_a - RT \quad (2)$$

$$\Delta S^\ddagger = R \ln (Ah/kT) - R \quad (3)$$

which follow from a combination of eq. (1) with the Arrhenius equation under the assumption that E_a is temperature independent. In the direct evaluation of ΔH^\ddagger and ΔS^\ddagger from the experimental data by means of eq. (1), ΔH^\ddagger and ΔS^\ddagger are assumed to be temperature independent. It was found that the values of ΔH^\ddagger found from eqs. (1) and (2) differ very little. The various thermodynamic parameters and the frequency factor for various acid catalysts at 70°C are given in Table VIII.

TABLE IV
Relative Contribution of Acid-Catalyzed and Uncatalyzed Reaction (HCl)

$k_u \times 10^2$ (graphic value)	k_c , l ² /m ² /sec	[HCl], $\times 10^4 N$	k_c [HCl], l/m/sec	% catalyzed reaction	[HCl]/ [PTBP]	Catalyzed/ uncatalyzed, or k_c [HCl]/ k_u
1.8	659	50	3.30	64.71	0.4	1.83
1.8	659	60	3.95	68.70	0.48	2.19
1.8	659	80	5.27	74.54	0.64	2.93
1.8	659	100	6.59	78.55	0.80	3.66
1.8	659	150	9.89	84.60	1.2	5.49
1.8	659	200	13.18	87.98	1.6	7.32

TABLE V
Relative Contribution of Acid-Catalyzed and Uncatalyzed Reaction (HNO₃)

$k_u \times 10^2$ (graphic value)	k_c , l ² /m ² /sec	[HNO ₃], $\times 10^4 N$	k_c [HNO ₃], l/m/sec	% catalyzed reaction	[HNO ₃]/ [PTBP]	Catalyzed/ uncatalyzed or k_c [HNO ₃]/ k_u
2.4	832	50	4.16	63.4	0.4	1.73
2.4	832	60	4.99	67.52	0.48	2.08
2.4	832	80	6.66	73.51	0.64	2.78
2.4	832	100	8.32	77.61	0.8	3.47
2.4	832	150	12.48	83.87	1.2	5.2
2.4	832	200	16.64	87.39	1.6	6.93

TABLE VI
Relative Contribution of Acid-Catalyzed and Uncatalyzed Reaction (H₂SO₄)

$k_u \times 10^2$ (graphic value)	k_c , l ² /m ² /sec	[H ₂ SO ₄], $\times 10^4 N$	k_c [H ₂ SO ₄], l/m/sec	% catalyzed reaction	[H ₂ SO ₄]/ [PTBP]	k_c [H ₂ SO ₄]/ k_u
1.9	419	50	2.10	52.5	0.4	1.11
1.9	419	60	2.51	56.92	0.48	1.32
1.9	419	80	3.35	63.81	0.64	1.76
1.9	419	100	4.19	68.80	0.80	2.21
1.9	419	150	6.29	76.80	1.2	3.31
1.9	419	200	8.38	81.52	1.6	4.41

Effect of Catalyst Concentration

The condensation reaction between 2-methylol-4-*t*-butylphenol and 4-*t*-butylphenol could not be studied over a wider range of pH in view of the fact that increase in pH brings about a very rapid condensation reaction. Hence, the catalyst concentration was varied in the range of $2.0 \times 10^{-3} N$ to $5.0 \times 10^{-4} N$, and the rate of the reaction was found to increase with increase in the concentration of the acid catalyst (Table III).

Relative Contribution of Acid-Catalyzed and Uncatalyzed Reaction

The relative reactivities of the acid catalysts in the condensation reaction were calculated as follows: The rate of the condensation reaction is

$$-\frac{d[2M4TBP]}{dt} = k_u [4TBP][2M4TBP] + k_c [4TBP][2M4TBP][\text{acid catalyst}]^n \quad (4)$$

where n is the order in the acid-catalyzed part of the reaction, and k_c and k_u are the rate constants for the acid-catalyzed and the uncatalyzed reactions, respectively. This shows that the condensation reaction is proceeding in two paths—one catalyst dependent and the other catalyst independent.

On rearranging eq. (1), we obtain

$$\frac{-d[2M4TBP]/dt}{[4TBP][2M4TBP]} = k_u + k_c [\text{acid catalyst}]^n \quad (5)$$

TABLE VII
 Relative Reactivities of Acid Catalysts^a

Catalyst	$k_u \times 10^2$, l/m/sec, (graphic value)	k_c , l ² /m ² /sec	Relative reactivity
H ₂ SO ₄	1.9	419	1.0
HCl	1.8	659	1.6
HNO ₃	2.4	832	2.0

^a 2M4TBP = 0.0125M; 4TBP = 0.0125M; solvent = 50% dioxane; temperature = 80 ± 0.1°C.

 TABLE VIII
 Thermodynamic Parameters and Frequency Factor for Various Acid Catalysts at 70°C

<i>E</i> , kcal/mole	ΔH , kcal/mole	ΔG , kcal/mole	ΔS , e.u.	log ₁₀ <i>pZ</i>
H ₂ SO ₄	28.26	27.58	23.13	14.34
HCl	21.25	20.57	23.26	-5.86
HNO ₃	20.53	19.85	23.49	-7.59

$$k_c = k_u + k_c [\text{acid catalyst}]^n \quad (6)$$

If $n = 1$, then

$$k_0 = k_u + k_c [\text{acid catalyst}] \quad (7)$$

The values of k_u and k_c were obtained from the slope and the intercept respectively of the linear plot of k_0 versus [catalyst]. The values of k_u obtained graphically from the plot of k_0 versus [catalyst] were in fairly good agreement with the values found experimentally in the absence of catalysts. The relative efficiency of the acid-catalyzed and the uncatalyzed parts of the condensation reaction were determined by employing the values of k_u and k_c . The results are recorded in Tables IV, V and VI. The % overall reaction taking place via the catalyzed path was calculated using the following equation:

$$\% \text{ catalyzed reaction} = \frac{k_c [\text{catalyst}]}{k_u + k_c [\text{catalyst}]} \times 100$$

The relative reactivities of the acid-catalyzed condensation reaction of 2M4TBP-4TBP are given in Table VII. From Table VII, it was noticed that the relative catalytic efficiencies of the three acid catalysts are in the following order:



CONCLUSIONS

1. The condensation reaction between 2-methylol-4-*t*-butylphenol and 4-*t*-butylphenol followed a second-order rate law in the presence of acid catalysts.
2. The condensation reaction was dependent on the anion of the catalyst.

References

1. K. Oshima and E. Imoto, *Chem. High Polym. (Jpn.)*, **3**, 51 (1946)
2. E. Imoto and T. Kumura, *J. Chem. Soc. (Jpn.) Ind. Chem. Sec.*, **53**, 9 (1950)
3. H. Kakiuchi, *Chem. High Polym. (Jpn.)*, **8**, 33 (1952); **9**, 333 (1952).
4. H. Kammerer and M. Grossman, *Angew. Chem.*, **65**, 263 (1953).
5. H. Kammerer, *Makromol. Chem.*, **8**(1), 85 (1952).
6. M. Imoto and T. Tanigaki, *Kogyo Kagaku Zasshi*, **59**, 712 (1956).
7. Dakshinamurthy and M. Santappa, *J. Org. Chem.*, **27**, 1844 (1962).
8. L. M. Yeddanapalli, A. K. Kuriakose, N. Ramasubramanian, and D. Joseph Francis, *Makromol. Chem.*, **55**, 74 (1962)
9. J. H. Freeman, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem., Prepr.*, **27**(1), 84 (1967).
10. C. P. Eapen and L. M. Yeddanapalli, *Makromol. Chem.*, **119**, 4 (1968).
11. D. J. Francis and L. M. Yeddanapalli, *Makromol. Chem.*, **119**, 17 (1968).
12. D. J. Francis and L. M. Yeddanapalli, *Makromol. Chem.*, **125**, 119 (1969).
13. R. Natesan and L. M. Yeddanapalli, *Indian J. Chem.*, **11**, 1007 (1973).
14. H. C. Malhotra, and Avinash, *J. Appl. Polym. Sci.*, **20**, 2461 (1976).
15. B. Siva Rami Reddy, S. Rajadurai, and M. Santappa, *Indian J. Chem.*, **15A**, 424 (1977).
16. B. Siva Rami Reddy, S. Rajadurai, and M. Santappa *Leather Sci.*, **22**, 180 (1975).
17. B. Siva Rami Reddy, S. Rajadurai, and M. Santappa, *Curr. Sci.*, in press.
18. B. Siva Rami Reddy, S. Rajadurai, and M. Santappa, *Indian J. Chem.*, **15A**, 255 (1977).

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