A Comprehensive Kinetic Study of Acid-catalysed o-Cresol – Acetone Reaction

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The kinetics of the reaction between o-cresol and acetone was studied at 30, 35, 40 and 45±0.05° in 100% benzene. The different hydrochloric acid concentrations used were 0.0176, 0 0314, 0.0512 and 0.0727 M. The reaction was investigated with and without a promoter thioglycollic acid and taking into account the functionality (n) of o-cresol. The reaction was found to follow second order rate law and the rate of the reaction was found to increase with an increase in catalyst concentration. The activation parameters for the overall reactions have been calculated. The reaction was investigated in various solvents like benzene, chlorobenzene and methanol. The overall rate constant was resolved into step rate constants. The results have been compared with those of o-cresol – formaldehyde reaction.

BISPHENOLS formed by the condensation of various phenols with carbonyl compounds in presence of acid catalyst find a large number of applications. A thorough review of literature reveals that comprehensive kinetic studies have been carried out on the phenol and substituted-phenol – formaldehyde[1-7] reactions, but not even a single kinetic study has been carried out on o-cresol – acetone reaction, taking into account the functionality of phenol. Present paper deals with the kinetic study of o-cresol – acetone in presence of acid catalyst considering the functionality of o-cresol. The reaction has been investigated at temperature 30, 35, 40 and 45±0.05° and at hydrochloric acid concentrations 0.0176, 0.0314, 0.0512 and 0.0727 M using thioglycollic acid as a promoter.

Experimental

o-Cresol (Thomas Baker), acetone (E. Merck), hydroxylamine hydrochloride, NaOH (both B.D.H.) and benzene (Glaxo) were used. All other chemicals were either of C.P. or A.R. grade. o-Cresol was distilled twice before use. An immersion type thermostat (German model NBE) was employed for the rate studies.

Solutions of o-cresol in benzene (0.9586 – 0.9607 M) and acetone in benzene (0.3341 – 0.3350 M) were prepared. Dry hydrochloric acid gas was bubbled for different time intervals through the acetone solution before use. The dissolved hydrochloric acid concentration was determined by dissolving an aliquot of the solution in water and titrating against a standard solution of sodium hydroxide. The concentration of HCl was varied by adjusting the time interval for which hydrochloric acid gas was passed through the acetone solution. In a particular run o-cresol (50 ml) and acetone (50 ml) solution were separately placed in thermostat for a few minutes to obtain the temperature of thermostat. Reaction mixture was prepared by taking o-cresol (20 ml), acetone (20 ml) and thioglycollic acid (0.042 M; 2 ml) and refluxed at the desired temperature in the thermostat. After 2 – 3 min an aliquot (5 ml) of the reaction mixture was placed in an ice-bath to freeze the reaction. 2 ml of this solution was used for estimating acetone and 1 ml for the estimation of o-cresol. Acetone was estimated by hydroxylamine hydrochloride method and o-cresol was estimated spectrophotometrically using diazotised p-nitroaniline as an indicator.

Results and Discussion

Results of the kinetic investigation carried out at different temperatures and acid concentrations are reported in Table 1. The overall reaction was found to obey a second order rate law. This is confirmed from a plot of $\log \frac{a}{b}\left(\frac{b-y}{a-1.82y}\right)$ vs time (Fig. 1). The various activation parameters (Table 2) for the overall reaction were obtained from the plot of $\log k/T$ vs $1/T$ (Fig. 2).

It has been observed that the energy of activation as well as entropy of activation decrease with increase in acid concentration confirming that the reaction is catalysed by H+ ion. The kinetic investigation was also carried out without using any promoter at 45±0.05° and an acid concentration of 0.0727 M. These rate constants have been compared in Table 3.

The reaction was also carried out at 45±0.05° and 0.0727 M HCl using benzene, chlorobenzene and methanol as solvents (Table 4). The rate of the reaction was found to vary in various solvents in the following order : benzene 〉 chlorobenzene 〉

methanol. This can be explained by the following arguments. This particular reaction became fast in the absence of water molecule. The methanol being the most polar solvent of the three and methyl group being a very good electron donor, can donate a pair of electrons to the oxygen of the OH⁻ group. This helps oxygen acquire a negative charge which can form a hydration sphere around the CH_3OH molecule by a strong hydrogen bonding with water. Thus, water molecules keep up their dominance when methanol is used as a solvent ; so the reaction became very slow as determined

TABLE 1—RESULTS OF KINETIC STUDY OF o-CRESOL–ACETONE REACTION

[HCl] $\times 10^3$ M	Initial [CH$_3$COCH$_3$] M	Time s	[CH$_3$COCH$_3$] reacted mol dm^{-3}	[o-Cresol] reacted mol dm^{-3}	Second order rate const. dm^3 mol^{-1} s^{-1}	Average value of rate const. dm^3 mol^{-1} s^{-1}
		Initial [o-Cresol]=0.4570 M, [Promoter]=0.002 M Temp.=30±0.05°				
17.6	0.189 2	3 000	0.006 3	0.011 4	4.59×10^{-5}	
		7 200	0.014 2	0.026 1	4.44×10^{-5}	$(4.57 \pm 0.09) \times 10^{-5}$
		10 800	0.023 8	0.043 5	4.68×10^{-5}	
		18 000	0.031 5	0.056 5	4.59×10^{-7}	
31.4	0.189 0	3 600	0.009 7	0 017 8	5.95×10^{-5}	
		6 600	0.016 2	0.029 6	5.67×10^{-5}	$(5.69 \pm 0.24) \times 10^{-5}$
		12 000	0.027 0	0.049 6	5.40×10^{-5}	
		18 000	0.040 5	0.078 7	5.82×10^{-5}	
51.2	0.188 7	3 600	0.012 1	0.022 1	7.48×10^{-5}	
		7 200	0.025 3	0.038 9	8.91×10^{-5}	$(8.31 \pm 0.13) \times 13^{-5}$
		14 400	0.045 4	0 083 0	8.28×10^{-5}	
		19 800	0 057 4	0.105 6	8.35×15^{-5}	
72.7	0.189 5	3 600	0.026 7	0.048 8	1.78×10^{-4}	
		7 200	0.041 5	0.075 9	1.50×10^{-4}	$(1.51 \pm 0.18) \times 10^{-4}$
		10 800	0.052 6	0.096 2	1.35×10^{-4}	
		14 400	0.067 4	0.125 0	1.43×10^{-4}	
		Initial [o-Cresol]=0.4576 M, [Promoter]=0.002 M Temp.=35±0 05°				
17.6	0.188 7	3 600	0.008 7	0.015 8	5.30×10^{-5}	
		7 200	0.017 6	0.032 3	5.61×10^{-5}	$(5.68 \pm 0.29) \times 10^{-5}$
		14 400	0.034 3	0.062 7	5.96×10^{-5}	
		18 600	0.041 7	0.076 3	5.88×10^{-5}	
31.4	0.188 9	3 600	0.018 3	0.018 9	6.34×10^{-5}	
		7 200	0.019 7	0.036 0	6.34×10^{-5}	$(6.46 \pm 0.26) \times 10^{-5}$
		14 400	0.036 0	0.066 2	6.31×10^{-5}	
		18 000	0.046 1	0.033 9	6.85×10^{-5}	
51.2	0.188 5	3 600	0.016 9	0 030 9	1.34×10^{-4}	
		7 200	0.037 4	0.068 4	1.32×10^{-4}	$(1.41 \pm 0 10) \times 10^{-4}$
		12 000	0.061 8	0.112 4	1.52×10^{-4}	
		16 800	0.076 4	0.139 8	1.49×10^{-4}	
72.7	0.189 0	3 600	0.033 0	0.060 0	2.28×10^{-4}	
		7 200	0.058 0	0.106 7	2.32×10^{-4}	$(2.25 \pm 0.16) \times 10^{-4}$
		10 800	0.070 0	0.127 4	2.02×10^{-4}	
		14 400	0.093 0	0.170 1	2.39×10^{-4}	
		Initial [o-Cresol]=0.4576 M, [Promoter]=0.002 M Temp.=40±0.05°				
17.6	0.188 9	3 600	0.019 1	0.035 3	1.22×10^{-4}	
		7 200	0.037 1	0.068 2	1.30×10^{-4}	$(1.36 \pm 0.12) \times 10^{-4}$
		12 000	0.059 6	0.108 4	1.43×10^{-4}	
		18 000	0.079 8	0.146 0	1.49×10^{-4}	
31.4	0.188 2	3 600	0.024 7	0.045 2	1.64×10^{-4}	
		7 200	0.040 9	0.074 4	1.48×10^{-4}	$(1.70 \pm 0.18) \times 10^{-4}$
		10 800	0.065 6	0.118 7	1.83×10^{-4}	
		16 200	0.085 9	0.157 1	1.87×10^{-4}	
51.2	0.188 0	3 000	0.029 3	0.054 2	2.40×10^{-4}	
		6 000	0 049 3	0.089 7	2.25×10^{-4}	$(2.52 \pm 0.25) \times 10^{-4}$
		10 800	0.081 8	0.148 8	2.59×10^{-4}	
		14 400	0.101 8	0.186 2	2.85×10^{-4}	
72.7	0.188 5	3 000	0.064 2	0.117 4	6.44×10^{-4}	
		6 000	0.098 5	0.182 2	6.41×10^{-4}	$(6.63 \pm 0.23) \times 10^{-4}$
		10 800	0.132 3	0.230 4	6.82×10^{-4}	
		14 400	0.146 0	0.287 1	6.85×10^{-4}	

(Table 1 contd.)

Initial [*o*-Cresol] = 0.4565 *M*, [Promoter] = 0.002 *M*
Temp. = 45 ± 0.05°

|						
17.6	0.188 5	3 000	0.044 8	0.081 5	3.97×10^{-4}	
		8 400	0.088 5	0.161 0	3.80×10^{-4}	$(3.92 \pm 0.14) \times 10^{-4}$
		12 600	0.113 5	0.205 4	4.06×10^{-4}	
		19 800	0.137 3	0.249 8	4.14×10^{-4}	
31.4	0.188 0	3 600	0.066 8	0.120 9	5.72×10^{-4}	
		7 800	0.105 5	0.192 0	5.66×10^{-4}	$(5.55 \pm 0.18) \times 10^{-4}$
		10 800	0.119 3	0.215 9	5.30×10^{-4}	
		16 800	0.143 0	0.261 6	5.55×10^{-4}	
51.2	0.188 6	5 400	0.106 0	0.192 9	8.22×10^{-4}	
		7 200	0.119 8	0.215 6	8.01×10^{-4}	$(8.43 \pm 0.39) \times 10^{-4}$
		10 800	0.144 8	0.280 6	8.91×10^{-4}	
		18 000	0.163 5	0.295 4	8.59×10^{-4}	
72.7	0.188 5	3 600	0.114 8	0.208 9	1.45×10^{-3}	
		6 600	0.136 0	0.244 8	1.11×10^{-3}	$(1.25 \pm 0.18) \times 10^{-3}$
		9 600	0.151 0	0.303 3	1.25×10^{-3}	
		14 400	0.168 5	0.303 3	1.25×10^{-3}	
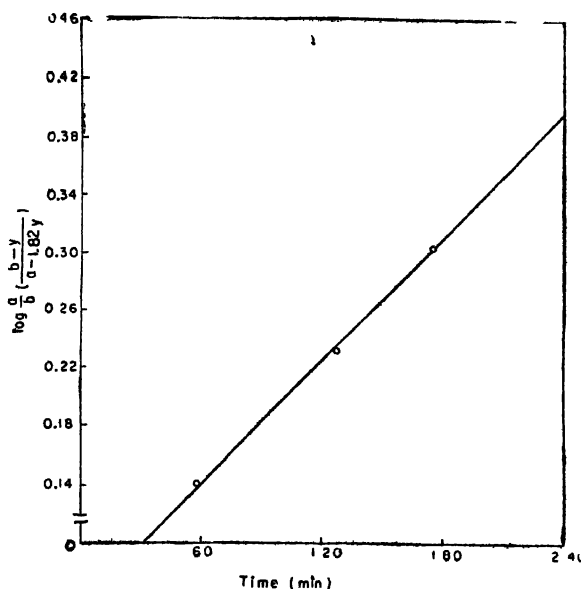
Fig. 1. Plot of $\log \frac{a}{b} \left(\frac{b-y}{a \ 1 \ 82y} \right)$ vs time for acid-catalysed *o*-cresol − acetone reaction ; [HCl] = 72.7 × 10⁻³ *M*, temp. = 45 ± 0.05°.
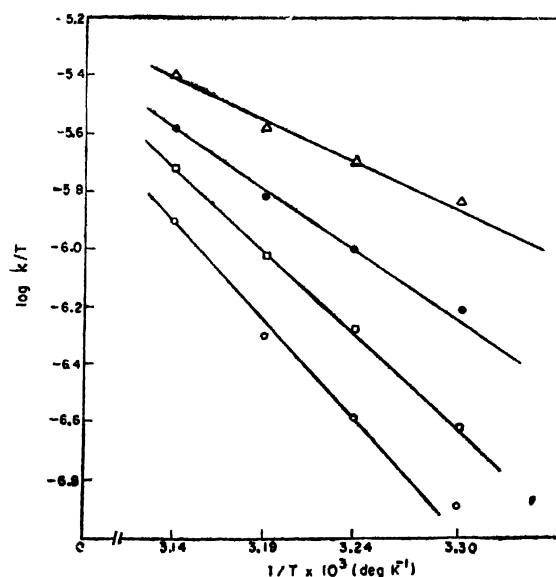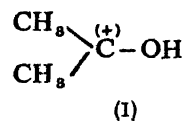

Fig. 2. Plot of log k/T vs $1/T$ for acid-catalysed -cresol − acetone reaction ; [HCl] : (△) 72.7×10⁻³, (●) 51.2×10⁻³, (□) 31.4×10⁻³ and (O) 17 6× 0⁻³ *M*.

experimentally. The chlorobenzene is less polar than methanol and it absorbs smaller number of water molecules than methanol and hence higher rate of reaction than that in methanol. In benzene the reaction is fastest due to the fact that benzene is a non-polar solvent and cannot absorb water molecule and the reaction proceeds smoothly. Finally, a comparative study of overall rate constants for *o*-cresol − acetone has been made with *o*-cresol − formaldehyde[6,8] reaction. The rate of the reaction was found to be higher in the case of *o*-cresol − acetone reaction. This is because in acetone two methyl groups which are electron donating, help oxygen acquire a partial negative charge and carbon atom a partial positive charge

TABLE 2—ACTIVATION PARAMETERS FOR
o-CRESOL − ACETONE REACTION

[HCl] *M*	*E* kcal mol⁻¹	log *A*	Δ*S* e.u.
0.017 6	38.29	20.68	42.23
0.031 4	25.50	11.86	7.10
0.051 2	22.77	10.19	−0 49
0.072 7	15.66	5.46	−21.97

thereby helping the formation of carbonium ion (I) in the presence of H⁺ ion faster than in the case of formaldehyde,

$$\begin{array}{c} CH_3 \\ CH_3 \end{array} \!\!\!\! \begin{array}{c} {}^{(+)} \\ C - OH \end{array}$$

(I)

TABLE 3—COMPARISON OF OVERALL RATE CONSTANT WITH AND WITHOUT USING PROMOTER

$[HCl] = 0.0727\ M$, Temp. $= 45 \pm 0.05°$

Initial $[CH_3COOH_3]$ $b\ (M)$	Initial $[o\text{-Cresol}]$ $a\ (M)$	Time s	$[CH_3COOH_3]$ reacted mol dm^{-3}	$[o\text{-Cresol}]$ reacted mol dm^{-3}	Second order rate const. dm^3 mol^{-1} s^{-1}	Average rate const. dm^3 mol^{-1} s^{-1}
			[Promoter] = 0.0020 M			
0.188 5	0.456 5	3 600	0.114 8	0.208 9	1.45×10^{-3}	
		6 600	0.136 0	0.244 8	1.11×10^{-3}	$(1.25 \pm 0.18) \times 10^{-3}$
		9 600	0.151 0	0.274 8	1.16×10^{-3}	
		14 400	0.168 5	0.368 3	1.25×10^{-3}	
			without using promoter			
0.188 2	0.457 0	3 600	0.060 2	0.104 5	1.67×10^{-4}	
		7 200	0.084 4	0.154 4	1.53×10^{-4}	$(1.66 \pm 0.08) \times 10^{-4}$
		12 000	0.109 1	0.200 7	1.72×10^{-4}	
		16 800	0.121 5	0.219 9	1.72×10^{-4}	

TABLE 4—REACTION CARRIED OUT IN VARIOUS ORGANIC SOLVENTS

$[HCl] = 0.0727\ M$, [Promoter] $= 0.002\ M$ Temp. $= 45 \pm 0.05°$

Solvent	Time s	Initial $[CH_3COOH_3]$ M	Initial $[o\text{-Cresol}]$ M	$[CH_3COOH_3]$ reacted mol dm^{-3}	$[o\text{-Cresol}]$ reacted mol dm^{-3}	Second order rate const. dm^3 mol^{-1} s^{-1}	Average value of rate const. dm^3 mol^{-1} s^{-1}
Benzene	3 600	0.188 5	0.456 5	0.114 8	0.208 9	1.45×10^{-3}	$(1.25 \pm 0.18) \times 10^{-3}$
	6 600			0.136 0	0.244 8	1.11×10^{-3}	
	9 600			0.151 0	0.274 8	1.16×10^{-3}	
	14 400			0.168 5	0.308 3	1.25×10^{-3}	
Chlorobenzene	3 600	0.188 9	0.457 0	0.108 2	0.188 8	4.90×10^{-4}	$(4.76 \pm 0.26) \times 10^{-4}$
	6 000			0.118 7	0.216 0	4.40×10^{-4}	
	9 600			0.137 9	0.253 7	4.72×10^{-4}	
	15 600			0.154 8	0.284 8	5.02×10^{-4}	
Methanol	3 600	0.188 5	0.457 0	0.092 1	0.168 5	3.73×10^{-4}	$(3.65 \pm 0.04) \times 10^{-4}$
	6 000			0.110 2	0.200 5	3.55×10^{-4}	
	10 800			0.131 5	0.238 0	3.73×10^{-4}	
	16 800			0.141 9	0.270 2	3.61×10^{-4}	

Calculation of step rate constants :

$$(H_3C)C_6H_4(OH) + CH_3COCH_3 \xrightarrow{k_1}$$
$$(H_3C)C_6H_3(OH)C(OH)(CH_3)_2 \quad (A)$$

$$(H_3C)(C_6H_3)(OH)C(OH)(CH_3)_2$$
$$+ (H_3C)(C_6H_4)(OH) \xrightarrow{k_2}$$
$$(H_3C)C_6H_3(OH)C(CH_3)_2(OH)C_6H_3(CH_3) \quad (B)$$
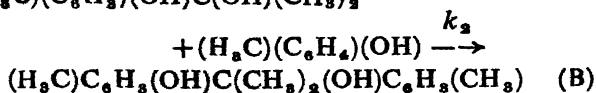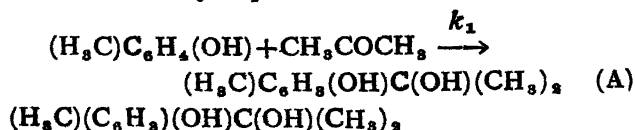
The overall second order rate expression for the formation of product is

$$\frac{dx}{dt} = k(a-x)(b-y) \quad (1)$$

where, a is initial concentration of o-cresol, b the initial concentration of acetone, x the amount of o-cresol reacted in mol dm^{-3} in time t s, and y the amount of acetone reacted in mol dm^{-3} in time t s.

From equations (A) and (B) it is obvious that o-cresol is being used in both the steps. Therefore, at any stage in the reaction the amount of the o-cresol consumed will be more than that of acetone. This can be verified from Table 1. The average proportion of o-cresol and acetone reacted was actually found to be $x = 1.82y$. Substituting the

values of x in equation (1) and on integration we get expression for overall rate constant,

$$k = \frac{2.303 \times 1.82}{t\,(1.82b-a)} \log \frac{a}{b}\left(\frac{b-y}{a-1.82y}\right) \quad (2)$$

From equations (A) and (B) the rate of formation of 4-[1,1-dimethylmethane-1-ol]-2-methylphenol is

$$\frac{dy}{dt} = k_1(na-y-r)(b-y) \quad (3)$$

where, $(a-x)$, $(b-y)$ and $(y-r)$ are the concentrations of o-cresol, acetone and tertiary alcohol derivative respectively at time t and x, y and r are the respective amounts of o-cresol, acetone and tertiary alcohol reacted at time t, and n is the functionality of o-cresol. The rate of formation of 4,4-isopropylidenebis(2-methylphenol) is

$$\frac{dr}{dt} = k_2(na-y-r)(y-r) \quad (4)$$

where, $(na-y-r)$ is concentration of o-cresol at any time t. The amount of o-cresol reacted at any stage of the reaction is equal to the sum of acetone and 4-[1,1-dimethylmethane-1-ol]-2-methyl-

phenol reacted at any time t, i.e.

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dr}{dt} \tag{5}$$

From equations (3), (4) and (5),

$$\frac{dx}{dt} = nk_1(a-x)(b-y) + nk_2(a-x)(y-r) \tag{6}$$

From equations (1) and (6),

$$k(a-x)(b-y) = nk_1(a-x)(b-y) + nk_2(a-x)(y-r) \tag{7}$$

$$\text{or} \quad k = nk_1 + nk_2\left(\frac{y-r}{b-y}\right) \tag{8}$$

Now, $(y+r) = x$ or $r = (x-y)$ and the functionality of o-cresol $(n) = 1$.

$$\text{Therefore,} \quad k = k_1 + k_2\left(\frac{2y-x}{b-y}\right) \tag{9}$$

Substituting the values of x, y and k (from Table 1) at two different time intervals, two simultaneous equations for k_1 and k_2 at given temperature and HCl concentration were obtained. These equations were then solved for k_1 and k_2 and are reported in Table 5. As is clear from Table 5, the rate of formation of 4,4-isopropylidene-bis(2-methylphenol) is $16-21$ times the rate of formation of tertiary alcohol, $k_2/k_1 = 16-21$. An attempt was also made

TABLE 5—STEP RATE CONSTANT AT DIFFERENT TEMPERATURE AND [HCl]

[HCl] M	k_1 dm³ mol⁻¹ s⁻¹	k_2 dm³ mol⁻¹ s⁻¹	k_2/k_1
Temp.=30±0.05°			
0.017 6	3.68×10^{-5}	6.69×10^{-4}	18.2
0 031 4	4.35×10^{-5}	8.23×10^{-4}	18.9
0.051 2	7.18×10^{-5}	1.49×10^{-3}	19.2
0.072 7	1.02×10^{-4}	1.92×10^{-3}	18.8
Temp.=35±0.05°			
0.017 6	4.80×10^{-5}	9.79×10^{-4}	20.4
0.031 4	5.45×10^{-5}	1.04×10^{-3}	19.2
0.051 2	7.72×10^{-5}	1.50×10^{-3}	19.5
0.072 7	1.29×10^{-4}	2.47×10^{-3}	19.1
Temp.=40±0.05°			
0.017 6	1.00×10^{-4}	2.05×10^{-3}	20.3
0.031 4	1.12×10^{-4}	2.23×10^{-3}	19.8
0.051 2	$1 62 \times 10^{-4}$	3.23×10^{-3}	19.9
0.072 7	2.43×10^{-4}	4.84×10^{-3}	19.5
Temp.=45±0.05°			
0.017 6	2.02×10^{-4}	3.49×10^{-3}	17.3
0.031 4	2.17×10^{-4}	3.58×10^{-3}	16.8
0.051 2	2.50×10^{-4}	4.07×10^{-3}	16.3
0.072 7	4.4×10^{-4}	7.08×10^{-3}	16.8

to evaluate the ratio k_2/k_1 from purely theoretical considerations of acid-catalysed o-cresol$-$acetone reaction as suggested by Ryabukhin[9]. From equations (3) and (4),

$$\frac{d(y+r)}{dt} = k_1(b-y)(na-y-r) + k_2(y-r)(na-y-r) \tag{10}$$

Dividing equation (10) by (6),

$$\frac{d(y+r)}{dx} = \frac{k_1(b-y)(na-y-r) + k_2(y-r)(na-y-r)}{nk_1(a-x)(b-y) + nk_2(a-x)(y-r)} \tag{11}$$

or

$$\frac{d(y+r)}{dx} = \frac{na-y-r}{n(a-x)}$$

or

$$\frac{d(y+r)}{na-y-r} = \frac{1}{n} \cdot \frac{dx}{a-x} \tag{12}$$

Integrating, we obtain,

$$\log (na-y-r) = \frac{1}{n} \log (a-x) + \log c \tag{13}$$

At $t=0$, $y=0$ and $r=0$,

$$\log na = \frac{1}{n} \log a + \log c = \log a^{1/n} + \log c$$

$$\log c = \log [na^{(n-1)/n}]$$

Putting the value in equation (13),

$$\log (na-y-r) = \frac{1}{n} \log (a-x) + \log na^{(n-1)/n} \tag{14}$$

$$na-y-r = na^{(n-1)/n} \cdot (a-x)^{1/n} \tag{15}$$

$$y+r = na - na^{(n-1)/n} \cdot (a-x)^{1/n} \tag{16}$$

To determine the ratio between reacted o-cresol and acetone equation (4) is subtracted from equation (3),

$$\frac{d(y-r)}{dt} = k_1(b-y)(na-y-r) - k_2(y-r)(na-y-r) \tag{17}$$

Dividing equation (17) by equation (3),

$$\frac{d(y-r)}{dy} = 1 - \frac{k_2}{k_1}\left(\frac{y-r}{b-y}\right) \tag{18}$$

or

$$\frac{d(y-r)}{dy} = 1 - u\left(\frac{y-r}{b-y}\right) \tag{19}$$

where, $u = k_2/k_1$.

Integrating we get,

$$\frac{y-r}{(b-y)^u} = -\frac{1}{1-u} \frac{1}{(b-y)^{u-1}} + c \tag{20}$$

At $t=0$, $y=0$ and $r=0$,

$$c = \frac{1}{1-u} \cdot b^{1-u}$$

Putting the value of c in equation (20),

$$\frac{y-r}{(b-y)^u} = \frac{1}{1-u} \cdot b^{1-u} - \frac{1}{1-u}(b-y)^{1-u}$$

$$(y-r) = \frac{1}{1-u} \cdot b^{1-u}(b-y)^u$$

$$- \frac{1}{(1-u)} \cdot (b-y)^{1-u} \cdot (b-y)^u$$

$$y-r = \frac{1}{u-1}(b-y) - \frac{1}{u-1} b^{1-u} (b-y)^u \tag{21}$$

Adding equations (16) and (21),

$$2y = na - na^{(n-1)/n} (a-x)^{1/n} + \frac{1}{u-1}(b-y)$$

$$- \frac{1}{u-1} \cdot b^{1-u} (b-y)^u \quad (22)$$

which can be solved for x,

$$x = a - \left[\frac{a^{(1-n)/n}}{n} \left\{ na - 2y + \frac{1}{u-1}(b-y) \right. \right.$$

$$\left. \left. - \frac{1}{u-1} \cdot b^{1-u}(b-y)^u \right\} \right]^n \quad (23)$$

u can be obtained from equation (23) by the amount of x and y at a given time interval. We have actually calculated the values of u at temperatures 35 and 45° and at concentration of HCl 0.0572 M. These values of u obtained at different time intervals are given in Table 6.

TABLE 6—CALCULATED VALUES OF k_2/k_1

Time s	Calculated $k_2/k_1 = u$	Average value
Temp.=35±0.05°, [HCl]=0.0512 M		
3 600	19.30	
7 200	19.45	19.32
12 000	18.90	
16 800	19.64	
Temp.=40±0.05°, [HCl]=0.0372 M		
3 000	19.80	
6 000	19.65	19.82
10 800	19.72	
14 400	20.12	

In obtaining the values of k_2/k_1 (Table 6) the relation $x = 1.82y$ has no where been used, whereas, the ratio k_2/k_1 given in Table 5 involves indirectly the relation $x = 1.82y$. The average calculated values of k_2/k_1 (Table 6) are in good agreement with the experimental values (Table 5). This confirms the approximation used in obtaining the second order

rate expression regarding the proportion of o-cresol and acetone reacted at a given time interval. Finally, a comparison has been made (Table 7) of the values of overall rate constants obtained purely from theoretical considerations of the reaction by using equation (24),

$$k = k_1 + \frac{k_2}{u-1} \left[1 - \left(\frac{b-y}{b} \right)^{u-1} \right] \quad (24)$$

TABLE 7—COMPARISON OF OVERALL RATE CONSTANTS

Temp. ±0.05°	[HCl] M	Average value of overall rate const. ×10⁴ dm³ mol⁻¹ s⁻¹	
		From eqn. (2)	From eqn. (25)
35	0.051 2	1.41	1.44
40	0.051 2	2.52	3.28

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