

## The Effect of Organic Additives on the Autoxidation of Benzene and Toluene in the Aqueous Phase and the Kinetic Analysis<sup>\*1</sup>

Hiroshi HOTTA, Nobutake SUZUKI and Kazuo ISODA

*Japan Atomic Energy Research Institute, Takasaki-shi, Gunma*

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The effect of organic additives on the autoxidations of benzene and toluene was studied at 180°C in a ferrous sulfate aqueous solution. The additives were benzene, toluene, ethylbenzene, cumene, cyclohexene, cyclohexane, *n*-hexane, *t*-butyl alcohol, isopropyl alcohol, and ethyl alcohol. The yields of the phenol and benzaldehyde produced were measured as functions of the initial volume fraction of the additive. The yields decreased with the addition of a trace of the additive, and the yields increased still more with further addition. In order to interpret these results, the general expression for the yield of the main product was derived by the Gale-Wagner method and was analyzed numerically by using the IBM 7044. The mole fraction of the additive, corresponding to the maximum yield, can give information regarding the relative reactivity of the additive as compared with the results of the above numerical analysis. It is concluded from the present study that the experiment of the flow system for the autoxidation of toluene containing various additives is necessary to get exact kinetic information concerning these additives by using the present numerical analysis, because the equation is derived on the assumption that the concentration of the additive is constant.

It had been noted in a previous study that the yield of phenol from the autoxidation of benzene in an aqueous solution is considerably affected by impurities in benzene.<sup>1)</sup> In the present paper, the effect of organic additives on the autoxidations of benzene and toluene is investigated in considerable detail and analyzed on the basis of the numerical analysis of the equation for the yield of the product as a function of the fraction of an additive, obtained as a result of the kinetic analysis of the binary autoxidation in the aqueous phase on the assumption of the reaction scheme previously established in our laboratory.<sup>1-5)</sup>

### Experimental

As in the previous study,<sup>1)</sup> 1 cc of an organic mixture with benzene or toluene was put on 15 cc of a 0.01M ferrous sulfate aqueous solution in a hard-glass tube in a 50 cc stainless-steel reactor under an oxygen pressure of 30 atm. Then, this system was heated at 180°C for 30 min by means of a controlled heater. After

cooling, the phenol from benzene was analyzed by the measurement of the optical absorbance in ether,<sup>5)</sup> while the benzaldehyde from toluene was analyzed gas-chromatographically by using a column of PEG 6000.<sup>3)</sup> These methods were described in detail in the previous papers.

The composition of the organic mixture is represented by the volume fractions of the additives, which were ethylbenzene, cumene, cyclohexene, cyclohexane, *n*-hexane, *t*-butyl alcohol, isopropyl alcohol, and ethyl alcohol. The autoxidation was carried out by using mixtures containing these additives in fractions of 0.0002, 0.001, 0.005, 0.01, and more than 0.01. The benzene was purified by the previous method,<sup>1)</sup> and the toluene was of the spectro-grade, Merck. The additives were used without further purification.

### Results

#### The Yields of Phenol and Benzaldehyde.

The amounts of phenol and benzaldehyde produced from the mixture of benzene and toluene are plotted against the volume fraction of toluene in the original organic mixture in Fig. 1. The results for the systems containing benzene or toluene of less than a 0.05 fraction are shown in detail in Figs. 2(A) and 3(A).

The yields of phenol from the benzene mixtures and of benzaldehyde from the toluene mixtures are represented by the relative yield, namely, by the ratios of the amounts produced from these mixtures to those produced from the pure benzene or toluene, in Figs. 2 and 3. The additives are

<sup>\*1</sup> The Autoxidation of Aromatic Hydrocarbons in Aqueous Solutions. XIII.

1) N. Suzuki and H. Hotta, *This Bulletin*, **37**, 244 (1964).

2) H. Hotta, N. Suzuki and T. Abe, *ibid.*, **39**, 417 (1966).

3) N. Suzuki and H. Hotta, *ibid.*, **40**, 1361 (1967).

4) H. Hotta and N. Suzuki, *ibid.*, **41**, 1537 (1968).

5) H. Hotta, A. Terakawa, K. Shimada and N. Suzuki, *ibid.*, **36**, 721 (1963).

represented in Figs. 2 and 3 by the following symbols: a) benzene, b) toluene, c) ethylbenzene, d) cumene, e) cyclohexene, f) cyclohexane, g) *n*-hexane, h) *t*-butyl alcohol, i) isopropyl alcohol and j) ethyl alcohol.

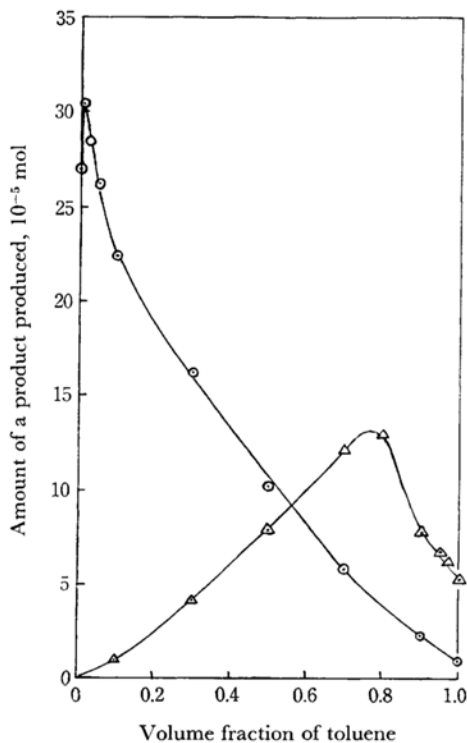


Fig. 1. Amounts of phenol (○) and benzaldehyde (△) produced from the mixture of benzene and toluene against the volume fraction of toluene.

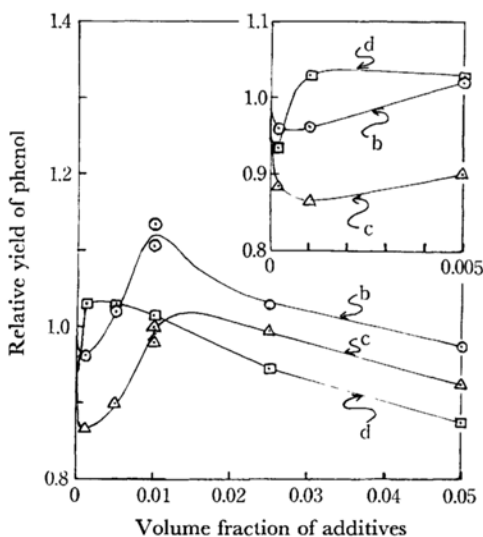


Fig. 2(A). Relative yields of phenol produced from the benzene mixture with various additives; b) toluene (○), c) ethylbenzene (△), and d) cumene (□).

In Fig. 1, the yield of benzaldehyde from the pure toluene is one-fifth as large as the yield of phenol from the pure benzene in spite of the fact that the dissociation energy of the  $\text{PhCH}_2\text{-H}$  bond is lower than that of the  $\text{Ph-H}$  bond, as has been pointed out in previous papers.<sup>3,4</sup> This may be partly attributed to the difference in the number of hydrogen atoms available for reaction. However,

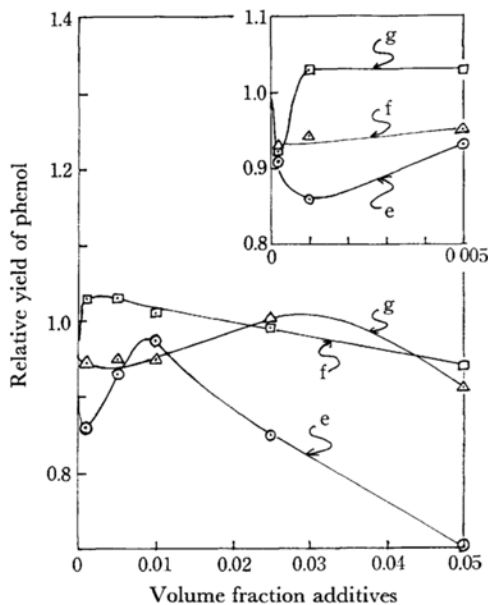


Fig. 2(B)  
e) Cyclohexene (○), f) cyclohexane (△), and g) *n*-hexane (□).

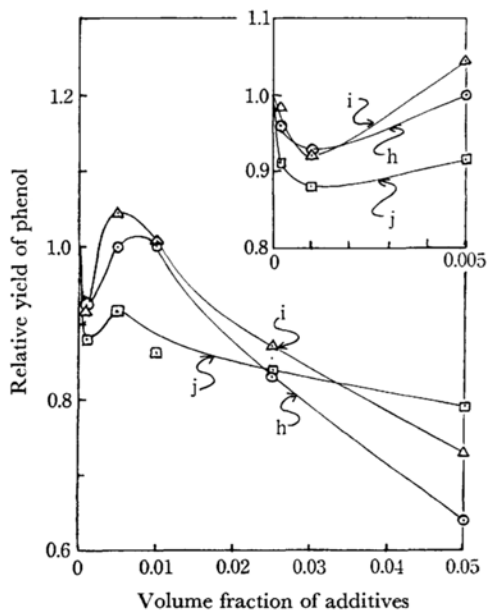


Fig. 2(C)  
h) *t*-Butyl alcohol (○), i) isopropyl alcohol (△), and j) ethyl alcohol (□).

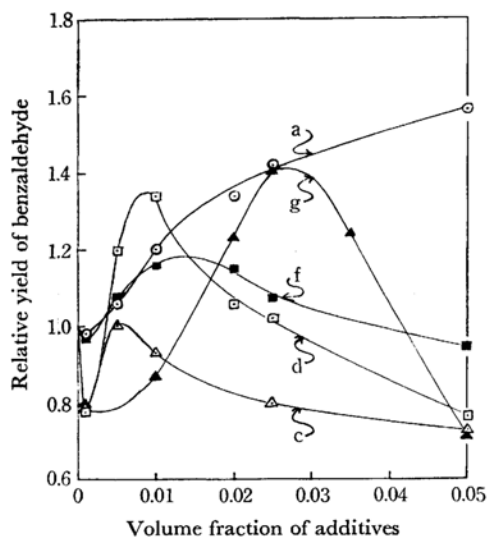


Fig. 3(A). Relative yields of benzaldehyde from the toluene mixture with various additives; a) benzene (○), c) ethylbenzene (△), d) cumene (□), f) cyclohexane (▲), and g) n-hexane (■).

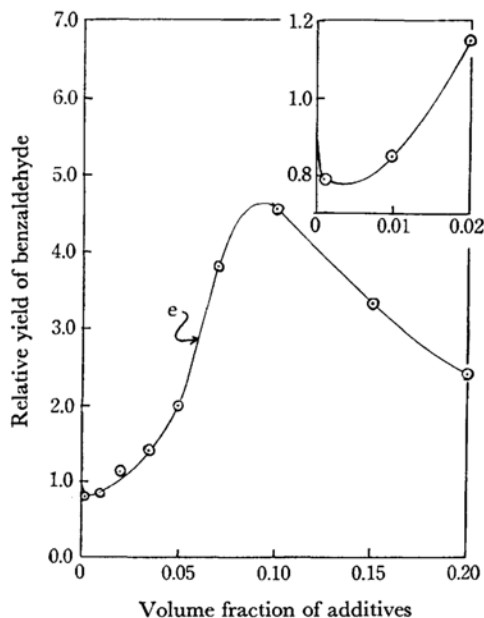


Fig. 3(B)  
e) Cyclohexene (○).

recently, the solubility of benzene and toluene in water was measured between 100°C and 200°C.<sup>6)</sup> According to these results, the main reason for the difference of their yield can be attributed to the difference in their solubility in water, which will be discussed in the following section.

**The Relative Solubility in Water.** Although the abscissas of the yield curves in Figs. 1, 2, and

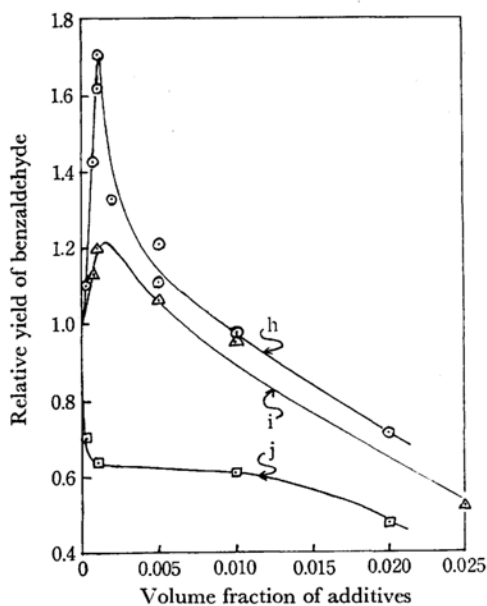


Fig. 3(C)  
h) *t*-Butyl alcohol (○), i) isopropyl alcohol (△), and j) ethyl alcohol (□).

3 represent the initial volume fractions of additives in the oil phase,  $v_B$ , it is necessary to know the mole fraction of additives to the total of the organic reactants in the aqueous phase,  $x_B$ , in order to make a kinetic analysis of these results. Although the measurement of the solubility at 180°C is not so easy, the  $x_B$  can be estimated by means of the following equation;

$$x_B = \frac{(BH)_{aq}}{(AH)_{aq} + (BH)_{aq}} \quad (1)$$

$$= \frac{y_B}{y_B + \frac{s_A}{s_B}(1-y_B)} \quad (2)$$

where AH (or A) and BH (or B) represent a host reactant (benzene or toluene) and an additive reactant respectively, and where  $s$  is the solubility of the pure AH or BH in water. If  $y_B$ , the mole fraction of an additive in the oil phase in equilibrium with  $x_B$ , is assumed to be equal to the initial one in the oil phase, it can easily be related to  $v_B$ . Furthermore, it is assumed in Eq. (2) that the ratio of the molar solubility,  $s_A/s_B$ , at 180°C is equal to that at room temperature; the figures for the latter are cited in Table I from the data of McAuliffe<sup>7)</sup> except in the case of cyclohexene.<sup>8)</sup> The solubility of benzene or toluene, measured in our laboratory, is 0.224M or 0.058M respectively at 180°C.<sup>6)</sup> This ratio (3.86) is in good agreement with that at room temperature (3.90) shown in Table I. For alcohols, since the values of  $v_B$  are very low, it is assumed

7) C. McAuliffe, *Nature*, **200**, 1093 (1963).

8) E. J. Farkas, *Anal. Chem.*, **37**, 1173 (1965).

6) H. Hotta, M. Ito and H. Murashima, unpublished.

TABLE 1. RATIO OF MOLAR SOLUBILITY  
AT ROOM TEMPERATURE

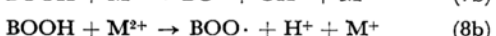
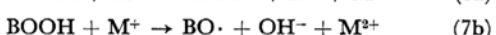
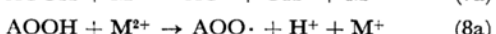
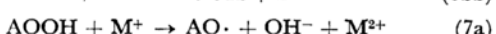
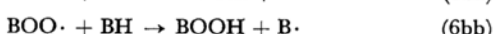
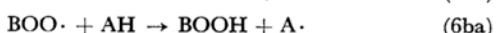
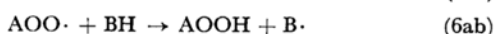
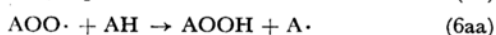
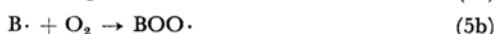
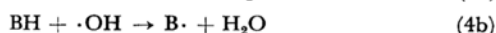
Benzene	3.90
Toluene	1.00
Cyclohexene	0.303
Ethylbenzene	0.256
Cyclohexane	0.112
Cumene	0.0758
n-Hexane	0.0190

that all the alcohols added in the oil phase are dissolved in the aqueous phase at 180°C.

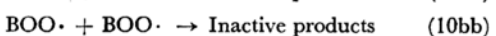
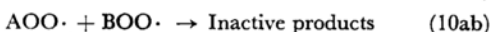
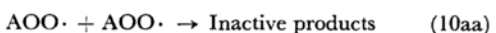
### Discussion

#### The Reaction Scheme and the Kinetic

**Analysis.** According to the previous studies,<sup>1-5</sup> the reaction scheme of the co-oxidation of AH and BH in an oxygenated aqueous solution containing metal ions ( $M^+$  and  $M^{2+}$ ) can be assumed to be as follows:



and partly:



where  $M^+$  and  $M^{2+}$  represent ferrous and ferric ions respectively for the present experiment. The rate constants of the respective reactions are represented by the subscript  $k$ ; for example,  $k_{4a}$  indicates that for reaction (4a). The general expression for the yield of the product from such a chain process can be derived in the following manner by the Gale-Wagner method.<sup>9,10</sup>

When the yield of the hydroxyl radical from reaction (3) is represented by  $Y(OH)$ , the yield of  $A\cdot$  or  $B\cdot$  from reaction (4) is expressed in the form:

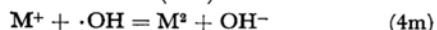
$$(A)_0 = a_0 Y(OH) \quad (11a)$$

$$(B)_0 = (1 - a_0) Y(OH) \quad (11b)$$

where:

$$a_0 = \frac{k_{4a}(AH)}{k_{4a}(AH) + k_{4b}(BH)} \quad (12)$$

It is assumed in the derivation of Eq. (11) that the contribution of reaction (4 m)



can be ignored because the hydroxyl radical usually reacts faster with organic reactants than with inorganic reactants.

After these radicals,  $A\cdot$  and  $B\cdot$ , are oxidized instantaneously to the peroxides by reaction (5), they give the hydroperoxides, AOOH or BOOH, and the equimolar radicals,  $A\cdot$  or  $B\cdot$ , by reaction (6). The relative reactivity of peroxy radicals ( $ROO\cdot$ ) toward hydrocarbons is fairly independent of the structure of R.<sup>11</sup> Recently, the dependence on the structure of R is illustrated rather finely.<sup>12</sup> When it is assumed in the present analysis that:

$$\frac{k_{4b}}{k_{4a}} = \frac{k_{6ab}}{k_{6aa}} = \frac{k_{6bb}}{k_{6ba}} = R_{b/a} \quad (13)$$

the yield of the products from reaction (6) is expressed in the forms:

$$\begin{aligned} (AOOH) = (A) &= \frac{k_{6aa}(AH)}{k_{6aa}(AH) + k_{6ab}(BH)} \times a_0 Y(OH) \\ &= a_0^2 Y(OH) \end{aligned} \quad (14aa)$$

$$\begin{aligned} (AOOH) = (B) &= \frac{k_{6ab}(BH)}{k_{6aa}(AH) + k_{6ab}(BH)} \times a_0 Y(OH) \\ &= a_0(1 - a_0) Y(OH) \end{aligned} \quad (14ab)$$

$$\begin{aligned} (BOOH) = (A) &= \frac{k_{6ba}(AH)}{k_{6ba}(AH) + k_{6bb}(BH)} \\ &\quad \times (1 - a_0) Y(OH) \\ &= a_0(1 - a_0) Y(OH) \end{aligned} \quad (14ba)$$

$$\begin{aligned} (BOOH) = (B) &= \frac{k_{6bb}(BH)}{k_{6ba}(AH) + k_{6bb}(BH)} \\ &\quad \times (1 - a_0) Y(OH) \\ &= (1 - a_0)^2 Y(OH) \end{aligned} \quad (14bb)$$

because, on the assumption of Eq. (13),

$$\begin{aligned} a_0 &= \frac{k_{4a}(AH)}{k_{4a}(AH) + k_{4b}(BH)} \\ &= \frac{k_{6aa}(AH)}{k_{6aa}(AH) + k_{6ab}(BH)} \\ &= \frac{k_{6ba}(AH)}{k_{6ba}(AH) + k_{6bb}(BH)} \\ &= \frac{1}{1 + R_{b/a} \frac{(BH)}{(AH)}} \end{aligned} \quad (15)$$

9) L. H. Gale and C. D. Wagner, *J. Am. Chem. Soc.*, **86**, 4531 (1964).

10) H. Kurihara and H. Hotta, *This Bulletin*, **40**, 719 (1967).

11) G. A. Russell and R. C. Williams, Jr., *J. Am. Chem. Soc.*, **86**, 2364 (1964).

12) B. S. Middleton and K. U. Ingold, *Can. J. Chem.*, **45**, 191 (1967).

The subscripts of Eq. (14) correspond to those of reaction (6). Therefore, the total yields of the hydroperoxides from reaction (6) are:

$$(\text{AOOH})_1 = a_0 Y(\text{OH}) \quad (16a)$$

$$(\text{BOOH})_1 = (1 - a_0) Y(\text{OH}) \quad (16b)$$

Since these hydroperoxides are decomposed by reactions (7) and (8), the amounts of the products from them by these reactions are given by:

$$\begin{aligned} (\text{AO})_1 &= \frac{k_{7a}(\text{M}^+)}{k_{7a}(\text{M}^+) + k_{8a}(\text{M}^{2+})} \times a_0 Y(\text{OH}) \\ &= a_0 m_a Y(\text{OH}) \end{aligned} \quad (17a)$$

$$\begin{aligned} (\text{AOO}) &= \frac{k_{8a}(\text{M}^{2+})}{k_{7a}(\text{M}^+) + k_{8a}(\text{M}^{2+})} \times a_0 Y(\text{OH}) \\ &= a_0(1 - m_a) Y(\text{OH}) \end{aligned} \quad (18a)$$

$$\begin{aligned} (\text{BO})_1 &= \frac{k_{7b}(\text{M}^+)}{k_{7b}(\text{M}^+) + k_{8b}(\text{M}^{2+})} \times (1 - a_0) Y(\text{OH}) \\ &= (1 - a_0) m_b Y(\text{OH}) \end{aligned} \quad (17b)$$

$$\begin{aligned} (\text{BOO}) &= \frac{k_{8b}(\text{M}^{2+})}{k_{7b}(\text{M}^+) + k_{8b}(\text{M}^{2+})} \times (1 - a_0) Y(\text{OH}) \\ &= (1 - a_0)(1 - m_b) Y(\text{OH}) \end{aligned} \quad (18b)$$

where:

$$\begin{aligned} m_a &= \frac{k_{7a}(\text{M}^+)}{k_{7a}(\text{M}^+) + k_{8a}(\text{M}^{2+})} \\ m_b &= \frac{k_{7b}(\text{M}^+)}{k_{7b}(\text{M}^+) + k_{8b}(\text{M}^{2+})} \end{aligned}$$

Equations (17) and (18) correspond to reactions (7) and (8) respectively.

The oxyradicals, given by Eq. (17), become the final products by means of reaction (9), while the peroxides regenerate the new peroxides and oxyradicals through the same cycle. When the above cycle, starting from the primary hydroxyl radical, is named the first cycle, the cycle started by these peroxides of Eq. (18) can be called the second cycles. Since the radicals,  $\text{A}\cdot$  and  $\text{B}\cdot$ , of Eq. (14) are oxidized instantaneously to the peroxides by reaction (5) the total yield of the peroxides formed during the first cycle or of the starting peroxides for the second cycle is given as the sum of Eqs. (14) and (18);

$$(\text{AOO}) = a_0(2 - m_a) Y(\text{OH}) \quad (19a)$$

$$(\text{BOO}) = (1 - a_0)(2 - m_b) Y(\text{OH}) \quad (19b)$$

However, since some of them are terminated by reaction (10), the correction coefficient,  $c$ , must be multiplied to Eq. (19) as a measure of the fraction of the peroxides carrying the chain process to the next cycle without termination reactions like:

$$\begin{aligned} (\text{AOO})_1 &= a_0(2 - m_a) c_a Y(\text{OH}) \\ &= a_1 Y(\text{OH}) \end{aligned} \quad (20a)$$

$$\begin{aligned} (\text{BOO})_1 &= (1 - a_0)(2 - m_b) c_b Y(\text{OH}) \\ &= b_1 Y(\text{OH}) \end{aligned} \quad (20b)$$

The yields of the products formed during the second cycle are expressed similarly with the first cycle as follows;

$$(\text{AOOH})_2 = a_1 Y(\text{OH})$$

$$\begin{aligned} (\text{AOO})_2 &= (\alpha a_1 + a_0 b_1) c_a Y(\text{OH}) \\ &= a_2 Y(\text{OH}) \end{aligned}$$

$$(\text{AO})_2 = a_1 m_a Y(\text{OH})$$

$$(\text{BOOH})_2 = b_1 Y(\text{OH})$$

$$\begin{aligned} (\text{BOO})_2 &= [\beta b_1 + (1 - a_0) a_1] c_b Y(\text{OH}) \\ &= b_2 Y(\text{OH}) \end{aligned}$$

$$(\text{BO})_2 = b_1 m_b Y(\text{OH})$$

where;

$$\alpha = 1 - m_a + a_0 \quad (21a)$$

$$\beta = 2 - m_b - a_0 \quad (21b)$$

Generally, the yields of the products formed during the  $n$ th cycle are expressed in the forms;

$$(\text{AOOH})_n = a_{n-1} Y(\text{OH}) \quad (22a)$$

$$\begin{aligned} (\text{AOO})_n &= (\alpha a_{n-1} + a_0 b_{n-1}) c_a Y(\text{OH}) \\ &= a_n Y(\text{OH}) \end{aligned} \quad (23a)$$

$$(\text{AO})_n = a_{n-1} m_a Y(\text{OH}) \quad (24a)$$

$$(\text{BOOH})_n = b_{n-1} Y(\text{OH}) \quad (22b)$$

$$\begin{aligned} (\text{BOO})_n &= [\beta b_{n-1} + (1 - a_0) a_{n-1}] c_b Y(\text{OH}) \\ &= b_n Y(\text{OH}) \end{aligned} \quad (23b)$$

$$(\text{BO})_n = b_{n-1} m_b Y(\text{OH}) \quad (24b)$$

Since Product A is formed from  $\text{AO}\cdot$  by reaction (9), the total yield of product A over all the cycles can be estimated in the following manner:

$$\begin{aligned} Y(\text{Product A}) &= \sum_n (\text{AO})_n \\ &= m_a Y(\text{OH}) \left( \sum_n a_n \right) \end{aligned} \quad (25)$$

$$= m_a Y(\text{OH}) (a_0 + F) \quad (26)$$

where:

$$\begin{aligned} F &= \left[ 1 + \frac{c_a c_b a_0 (1 - a_0)}{(1 - c_a \alpha)(1 - c_b \beta)} \right] \\ &\times \left[ \frac{c_a a_0 (1 - m_a)}{(1 - c_a \alpha)} + \frac{c_a c_b a_0 (1 - a_0)(1 - m_b)}{(1 - c_a \alpha)(1 - c_b \beta)} \right. \\ &\quad \left. + \frac{c_a a_0}{(1 - c_a \alpha)} \left( 1 + \frac{c_b (1 - a_0)}{(1 - c_b \beta)} \right) \right] \end{aligned} \quad (27)$$

Reaction (10) might give  $\text{AO}\cdot$ . When it is assumed that all the termination processes (reaction (10)) are the same type with the following reaction (28);



the factor,  $(1 - c_a)/c_a m_a$ , must be multiplied to Eq. (26).

Although  $\alpha$  and  $\beta$  are not always less than unity, according to the definition of Eq. (21), the termination reaction (10), i.e., the correction coefficient,  $c$ , controls the chain process like:

$$1 > c_a \alpha > 0 \text{ or } 1 > c_b \beta > 0 \quad (29)$$

It is assumed for the summation of Eq. (25) that  $c$ ,  $(M^+)/(M^{2+})$ , and  $(BH)/(AH)$  are constant for all the cycles, but they may be at least somewhat different in a few cycles at the beginning from in the later cycles.

**Numerical Analysis of Eq. (27).** Equation (27) was analyzed numerically by means of the IBM 7044 against the mole fraction of BH, namely,  $x_B$ , as defined by Eq. (1), for all the combinations of  $R_{b/a}$  (which was 0.1, 0.3, 1.0, 3.0, or 10.0),  $m_a$  and  $m_b$  (which were 0.8, 0.7, or 0.6), and  $c_a$  and  $c_b$  (which were 0.90, 0.85, 0.80, 0.75, 0.70, 0.65, or 0.60). Some examples are shown in Figs. 4—7 to illustrate the relationships between the yield of the product and these factors. In these figures, the value of  $F$  relative to  $F_0$ , which is for  $x_B=0$ , is plotted as  $F_{rel}$ . The  $F_{max}$  and  $x_{max}$  values in the following discussion mean, respectively, the maximum value of  $F_{rel}$  and the value of  $x_B$ , which gives  $F_{max}$  for certain conditions.

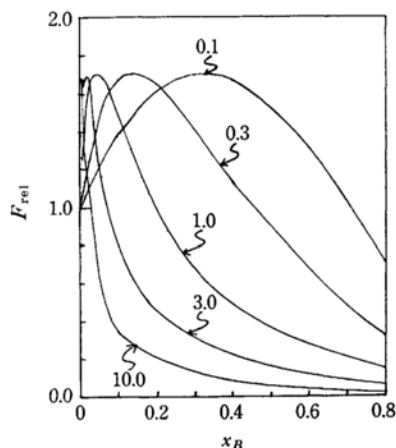


Fig. 4. The value of as  $F_{rel}$  the function of  $x_B$  for various  $R_{b/a}$  ( $m_a=m_b=c_a=c_b=0.7$ ).

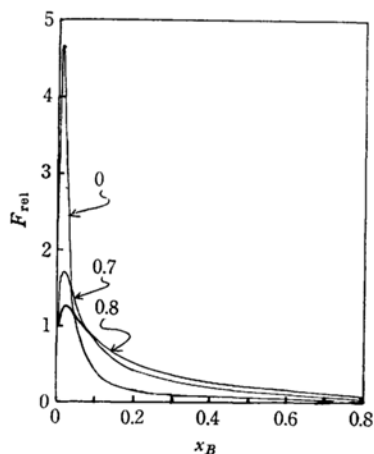


Fig. 5. The value of  $F_{rel}$  as the function of  $x_B$  for various  $m_a$  ( $R_{b/a}=3.0$ ,  $m_b=c_a=c_b=0.7$ ).

The  $F_{rel}-x_B$  curve against various  $R_{b/a}$  values is shown in Fig. 4 for  $m_a=m_b=c_a=c_b=0.7$ . This figure indicates that  $F_{max}$  is almost independent of  $R_{b/a}$  for a certain combination of other factors, while  $x_{max}$  decreases with an increase in  $R_{b/a}$ .

The  $F_{rel}-x_B$  curve against various  $m_a$  values is shown in Fig. 5 for  $R_{b/a}=3.0$  and  $m_b=c_a=c_b=0.7$ . This figure indicates that  $F_{max}$  decreases with an increase in  $m_a$ , while  $x_{max}$  does not so vary with  $m_a$ . The curve becomes concave with a decrease in  $m_a$  in spite of an increase in  $F_{max}$ . The value of  $F_{rel}$  was not so affected by  $m_b$ , as numerical analysis showed.

The  $F_{rel}-x_B$  curve against various  $c_a$  values is shown in Fig. 6 for  $R_{b/a}=3.0$  and  $m_a=m_b=c_b=0.7$ . This figure indicates that  $F_{max}$  decreases with a decrease in  $c_a$ , while  $x_{max}$  does not so vary with  $c_a$ . The curve becomes concave with an increase in  $c_a$  in spite of the increase in  $F_{max}$ .

The  $F_{rel}-x_B$  curve against various  $c_b$  values is

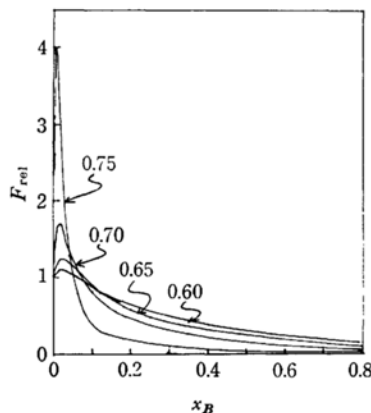


Fig. 6. The value of  $F_{rel}$  as the function of  $x_B$  for various  $c_a$  ( $R_{b/a}=3.0$ ,  $m_a=m_b=c_b=0.7$ ).

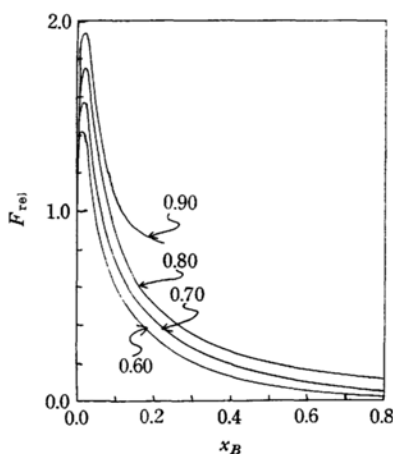


Fig. 7. The value of  $F_{rel}$  as the function of  $x_B$  for various  $c_b$  ( $R_{b/a}=3.0$ ,  $m_a=m_b=0.8$ ,  $c_a=0.75$ ).

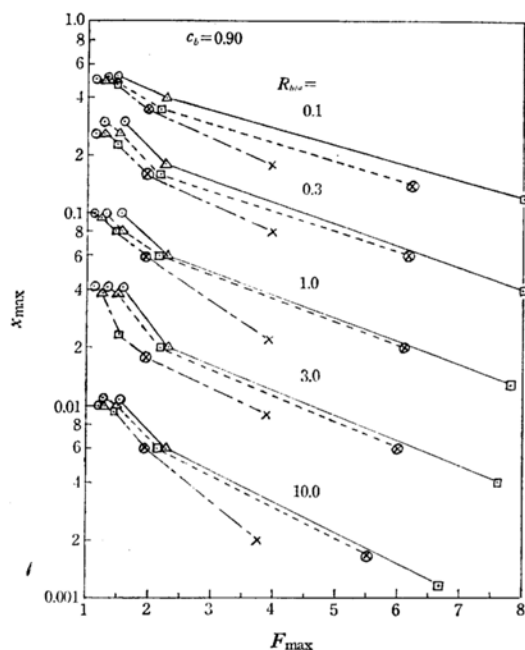


Fig. 8. Conditions for the relative peak height of the yield curve at  $c_b = 0.90$ . Figures give the value of  $R_{b/a}$ . — for  $m_a = 0.6$ , ---- for  $m_a = 0.7$ , --- for  $m_a = 0.8$ ,  $\times$  for  $c_a = 0.80$ ,  $\otimes$  for  $c_a = 0.75$ ,  $\square$  for  $c_a = 0.70$ ,  $\triangle$  for  $c_a = 0.65$  and  $\odot$  for  $c_a = 0.60$ .

shown in Fig. 7 for  $R_{b/a} = 3.0$ ,  $m_a = m_b = 0.8$ , and  $c_a = 0.75$ . This figure indicates that  $F_{\max}$  decreases with a decrease in  $c_b$ , while  $x_{\max}$  and the shape of the curve do not so vary with  $c_b$ .

These relationships are summarized in Fig. 8 for  $c_b = 0.90$  and in Fig. 9 for  $c_b = 0.60$ . Although the two figures are separated so as not to confuse the plottings, they should be overlapped in order to make the dependence on  $c_b$  clear. The  $F_{\max}$  values are plotted against  $\log x_{\max}$  for various conditions. Since the points for the respective  $R_{b/a}$  values are in a group, the value of  $R_{b/a}$  is indicated above the group. They are classified by the  $m_a$  value in the group, that is, by solid lines for  $m_a = 0.60$ , by dotted lines for  $m_a = 0.70$ , and by broken lines for  $m_a = 0.80$ . The values of  $c_a$  are indicated by the marks explained in Fig. 8.

The patterns of the points for the respective  $R_{b/a}$  values differ a little. Since the values of  $F$  were computed from point to point for  $x_B$ , the patterns are similar between the  $R_{b/a}$  groups in a close computation, as may be expected from Fig. 4. The larger  $R_{b/a}$  gives the smaller  $x_{\max}$  for the same  $F_{\max}$ , and the smaller  $c_a$  gives the smaller  $F_{\max}$ , as may be seen clearly in Figs. 8 and 9.

As may be seen in Figs. 5 and 6, the concavity or shape of the  $F_{\text{rel}}-x_B$  curve also gives kinetic information. Therefore, the values of  $x_B$ , giving  $F_{\text{rel}} = 1$  after passing  $F_{\max}$ , may be classified as in Figs. 8 and 9. Although this figure is omitted in the present

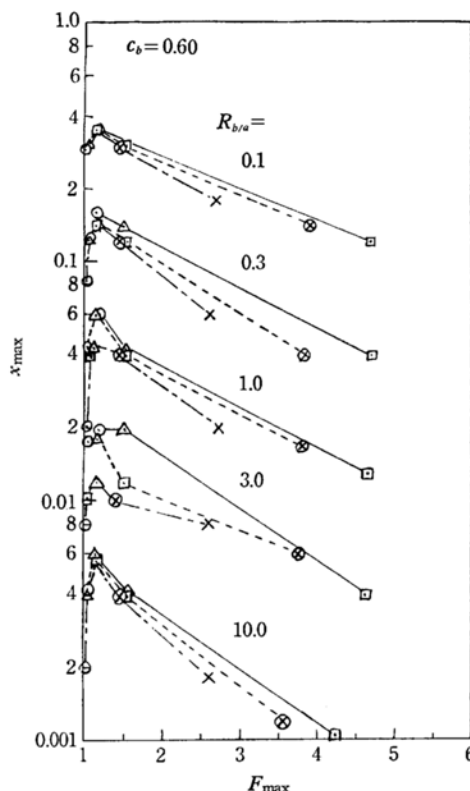


Fig. 9. Conditions for the relative peak height of the yield curve at  $c_b = 0.60$ . Figures give the value of  $R_{b/a}$ . Marks are the same as in Fig. 8.

paper, is shown a regularity similar to that of Figs. 8 and 9.

**Oxidation of Toluene Mixtures.** As may be seen in Fig. 3, the yield of benzaldehyde decreases at first with the addition of a trace of the additive, but the further addition of it causes the yield to increase to a maximum yield. The minimum or maximum relative yields ( $Y(A)_{\min}$  or  $Y(A)_{\max}$ ), the values of  $v_B$ , corresponding to them in Fig. 3, ( $v_{\min}$  or  $v_{\max}$ ), and the values of  $x_{\min}$  or  $x_{\max}$ , as estimated from these  $v$  values by means of Eq. (2) on the assumption presented above, are listed in Table 2, in which the additives are listed in the order of  $x_{\max}$ . Similar values for the yield of phenol from benzene, obtained from Fig. 2, are also listed in Table 2.

When the  $x_{\max}$  and  $Y(A)_{\max}$  for hydrocarbons added in Table 2 B) are applied to the diagram in Figs. 8 and 9, which indicate the relationship between  $x_{\max}$  and  $F_{\max}$  ( $Y(A)_{\max}$ ) as the function of  $R_{b/a}$ , the reactivities of these hydrocarbons for the reaction of the type:



are in the order of:

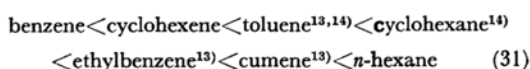


TABLE 2. THE MINIMUM OR MAXIMUM RELATIVE YIELDS AND THE CORRESPONDING COMPOSITIONS OF ADDITIVES

Additives	Minimum condition			Maximum condition		
	$v_{\min}$	$x_{\min}$	$Y(A)_{\min}$	$v_{\max}$	$x_{\max}$	$Y(A)_{\max}$
<b>A) Oxidation of Benzene</b>						
Toluene	0.001	$2 \times 10^{-4}$	0.96	0.01	$2 \times 10^{-3}$	1.12
Cyclohexane	0.005	$1 \times 10^{-4}$	0.94	0.03	$7 \times 10^{-4}$	1.01
Ethylbenzene	0.001	$5 \times 10^{-5}$	0.87	0.015	$7 \times 10^{-4}$	1.02
Cyclohexene	0.001	$7 \times 10^{-5}$	0.86	0.01	$7 \times 10^{-4}$	0.97
Cumene	$1 \times 10^{-4}$	$1 \times 10^{-6}$	0.94	0.001	$1 \times 10^{-5}$	1.03
<i>n</i> -Hexane	$1 \times 10^{-4}$	$3 \times 10^{-7}$	0.92	0.001	$3 \times 10^{-6}$	1.03
<i>t</i> -Butyl alcohol	0.001	$3 \times 10^{-3}$	0.92	0.007	$2 \times 10^{-2}$	1.01
Isopropyl alcohol	0.001	$4 \times 10^{-3}$	0.92	0.005	$2 \times 10^{-2}$	1.05
Ethyl alcohol	0.001	$5 \times 10^{-3}$	0.86	0.005	$2 \times 10^{-2}$	0.92
<b>B) Oxidation of Toluene</b>						
Benzene	0.001	$4 \times 10^{-3}$	0.99	0.2	0.54	2.6
Cyclohexene	0.001	$3 \times 10^{-4}$	0.79	0.1	0.04	4.7
Cyclohexane	0.001	$1 \times 10^{-4}$	0.78	0.027	$3 \times 10^{-3}$	1.44
Ethylbenzene	0.001	$2 \times 10^{-4}$	0.78	0.005	$1 \times 10^{-3}$	1.00
Cumene	0.001	$6 \times 10^{-5}$	0.79	0.01	$6 \times 10^{-4}$	1.34
<i>n</i> -Hexane	0.001	$2 \times 10^{-5}$	0.97	0.015	$3 \times 10^{-4}$	1.08
<i>t</i> -Butyl alcohol	n.d.	—	n.d.	0.001	0.01	1.7
Isopropyl alcohol	n.d.	—	n.d.	0.001	0.015	1.2
Ethyl alcohol	n.d.	—	n.d.	n.d.	—	n.d.

"n.d." means "not detected."

When  $R_{b/a}$  is defined as in Eq. (13). The order between toluene, cyclohexane, ethylbenzene, and cumene has been confirmed by other investigators.<sup>13-15</sup> However, cyclohexene has been expected to be more reactive than cumene.<sup>15)</sup>

The present computation of Eq. (27) gave no curve with both the minimum and maximum seen in Figs. 2 and 3 for any combination of various parameters; rather it gave a curve which has only the maximum seen in Figs. 4-7 or a curve which decreases monotonously. Since Eq. (27) is derived on the assumption that  $(BH)/(AH)$  is constant throughout the cycles, another equation was derived by the same procedure on the assumption that all amount of an additive added is consumed by the fourth cycle. This equation gave a monotonously decreasing curve for the numerical analysis over the same range of parameters as with Eq. (27), except for the combination,  $m_a=0.8$ ,  $m_b=0.6$ , and  $c_a=c_b=0.8$ , which gives both the minimum and the maximum. In the light of these results, the present curves in Figs. 2 and 3 suggest that, when  $x_b$  is very small, all of the additive is consumed within a few cycles at the beginning in a batch system like the present reactor.

13) G. A. Russell, *J. Am. Chem. Soc.*, **78**, 1047 (1956).

14) D. J. Carlson and K. U. Ingold, *ibid.*, **89**, 4891 (1967).

15) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 793 (1967).

Cyclohexene is fairly soluble in water, as may be seen in Table 1, and it would be very reactive for reaction (30).<sup>15)</sup> In fact, the oil phase after the reaction was greatly colored only in the case of cyclohexene. Therefore, the irregularity of cyclohexene in the series 31 may be concluded to be due to the shift in the maximum in Fig. 3(B), because if cyclohexene is present in the later cycles without such consumption, the value of  $x_{\max}$  would be even smaller.

Since *n*-hexane is very insoluble in water, as may be seen in Table 1, there is no trouble with the consumption, as has been mentioned above. Supporting this conclusion, the  $Y(A)_{\min}$  of *n*-hexane is nearly equal to unity. Therefore, although there has been no report about the relative reactivity of *n*-hexane for reaction (30), the  $x_{\max}$  value of *n*-hexane in Fig. 3(A) is the most reliable.

The  $v_{\max}$  values of the other additives are more or less shifted to larger values due to the consumption of the smaller  $x_b$ . Therefore, an experiment on the flow system, for which  $(BH)/(AH)$  can be kept constant, is necessary for the useful application of the diagram in Figs. 8 and 9. Furthermore, the direct measurement of the solubility without the use of Eq. (2) is necessary in order to get exact information from it. Toluene is the most suitable as the host reactant (AH), for the reaction scheme (reactions (3)-(10)) is correct for it.<sup>3,4)</sup>

Another problem is that the  $x_{\max}$  value as esti-



mated by Eq. (2), is too small, for the value of  $R_{b,a}$  obtained from it by using Figs. 8 and 9 is too large compared with the data provided by the other methods at lower temperatures.<sup>13-15</sup> It is not clear whether this discrepancy is due to reaction temperature, a characteristic of the aqueous phase, or some approximation for the derivation of Eq. (26).

The values of  $Y(A)_{max}$  for alcohols are in the order of:

$$t\text{-butyl} > \text{isopropyl} > \text{ethyl} \quad (32)$$

In the diagram of Figs. 8 and 9, the larger  $Y(A)_{max}$  or  $F_{max}$  value corresponds to the larger  $c_a$  value. This means that reaction (10) for toluene is suppressed by alcohol, which has a more complex structure or is more oxidable.

**Oxidation of Benzene Mixtures.** According to the previous studies, the autoxidation of benzene is initiated by reaction (4) with impurities in benzene, which are more reactive than benzene.<sup>1)</sup> Even though the hydroxyl radical reacts with benzene, reaction (4) may involve addition. Furthermore, more than one half of the phenol produced is formed not through  $C_6H_5O\cdot$  but through  $C_6H_5^+$ .<sup>4)</sup> Therefore, Eq. (25) must be modified for benzene to the form:

$$Y(\text{Phenol}) = \sum[(1-i)m_a + if]a_{n-1} + \sum ifb_{n-1} \quad (33)$$

where  $i$  is the fraction of phenol produced through  $C_6H_5^+$ , which can be determined by using oxygen-18, as has been seen in a previous study,<sup>4)</sup> and where  $f$ , which is not necessarily equal to  $a_0$  as defined by Eq. (12) for the case of benzene, is defined in the form:

$$\begin{aligned} f &= \frac{k_{\theta aa}(AH)}{k_{\theta aa}(AH) + k_{\theta ab}(BH)} \\ &= \frac{k_{\theta ba}(AH)}{k_{\theta ba}(AH) + k_{\theta bb}(BH)} \end{aligned} \quad (34)$$

instead of Eq. (15).

The order of the  $x_{max}$  values in Table 2A is not always the same as in series 31. This is due to the difference between benzene and toluene in the reaction mechanism, as has been mentioned above. Since the mechanism for benzene is rather complex, benzene is not a suitable standard reactant (AH) for a study of the relative reactivity using the present method. The value of  $x_{max}$  for toluene (0.002) suggests that toluene is more reactive than benzene in the series 31 in spite of the fact that the yield of phenol is larger than that of benzaldehyde in Fig. 1. This subject has already been discussed in the section on the yields of benzaldehyde in "Results."