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HIGH PRESSURE SYNTHESES OF AROMATIC ALDEHYDES

BY YOSHIMASA TAKEZAKI, HIROSHI TERANISHI, NOBUYUKI SUGITA AND KIYOSHI KUDO

Kinetic studies have been made on the syntheses of aromatic aldehydes from toluene, *m*-xylene and anisole and carbon monoxide in the $HF-BF_3$ reaction system.

Rate determinations were conducted under the condition in which the liquid phase reaction was rate-determining, which could be realized by reducing the concentration of the substrate remarkably.

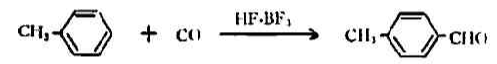
As to the liquid phase reaction of each aldehyde formation, the rate is of the first order with respect to the dissolved CO and to the complex, respectively.

The rate constants, $[min^{-1}(kg/cm^2)^{-1}]$, obtained at 0°C are 8×10^{-2} for toluene, 2.6×10^{-2} for *m*-xylene and 4.6×10^{-5} for anisole.

Introduction

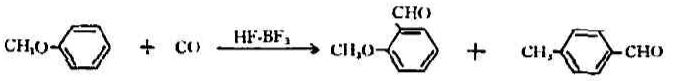
The Gatterman-Koch reaction to synthesize aromatic aldehydes from aromatic hydrocarbons and carbon monoxide with the catalyst, such as $AlCl_3-HCl$[1], is interesting from the viewpoint of reaction kinetics.

Since no kinetic study seems available on this reaction in the $HF-BF_3$ reaction system, the following kinetic studies have been made in this laboratory:



(*p*-tolualdehyde),

(2, 4-dimethylbenzaldehyde),



(*o*- and *p*-anisaldehyde)

The details of these studies reviewed here have been published as given in ref. 2).

Experimentals

Material

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1) M. H. Dilke and D. D. Eley, *J. Chem. Soc.*, 1949, 2601; H. C. Brown and H. W. Pearsall, *J. Am. Chem. Soc.*, 74, 191 (1952)

2) T. Takezaki, N. Sugita *et al.*, *J. Japan Petrol. Inst.*, 7, 564 (1964); Y. Takezaki, T. Teraoka *et al.*, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), 69, 907 (1966); Y. Takezaki, A. Inoue *et al.*, *Bull. Japan Petrol. Inst.*, 9, 45 (1967)

HF : Manufactured by Daikin Kogyo Co. Ltd. (purity>99.7 %)

BF_3: Manufactured by Baker and Adamson Works (U.S.A.) (purity 99.5 %)

CO : Generated by the decomposition of formic acid with the hot sulfuric acid (purity>98 %)

Toluene, *m*-Xylene, Anisole: Purified by distillation of the c.p. reagent (purity>98 %).

Procedure

The measured amounts of the liquefied HF and an aromatic compound were charged in an evacuated autoclave, made of stainless steel and equipped with a magnetic stirrer and baffle.

After the autoclave attained the experimental temperature, the required quantity of BF_3 gas was introduced to it under stirring to establish the dissolution equilibrium. Subsequently, CO gas was added.

The reaction took place while stirring at a fixed speed and maintaining a constant total pressure by the continuous supply of CO. At the desired reaction time, the autoclave was cooled immediately, and the gases exausted, then the produced aldehyde was analyzed by the hydroxylamine method and gas chromatography.

Kinetic Measurement

The results are given in Table 1 of the preliminary experiments carried out in order to examine the effect of stirring speed on the reaction rate.

Table 1. Fffect of stirring speed

Reaction	T (°C)	P_{CO} (kg/cm²)	P_{BF_3} (kg/cm²)	Ar/HF (mole ratio)	Time (min)	Stirring speed (rpm)	Yield of aldehyde (M%)	Controlling conditions for the liquid phase reaction
p-Tolualdehyde from toluene	0	3	3	1/60	3.0	260	4.1	charge mole ratio toluene/HF≤1/600, stirring speed ≥780 rpm
						750	18.5	
						1500	61.2	
		1	1	1/600	1.2	780	32.6	
						1420	32.0	
					3.0	780	52.5	
						1300	51.5	
2.4-Dimethylbenzaldehyde from *m*-xylene	0	3	5	1/60	5	900	22.5	charge mole ratio *m*-xylene/HF≤1/90, stirring speed ≥900 rpm
						1400	38.1	
		5	5	1/90	5	750	29.5	
						900	32.0	
						1200	32.1	
						1700	32.0	
Anisaldehyde from anisole	40	180	13	1/32	20	530	13.9	charge mole ratio anisole/HF≤1/32, stirring speed ≥750 rpm
						750	30.7	
						990	31.8	
						1500	28.6	

Note: Ar represents toluene, *m*-xylene or anisole.

In both syntheses of *p*-tolualdehyde from toluene and of 2, 4-dimethylbenzaldehyde from *m*-xylene, the gas-liquid contact was found rate determining at the concentration of 1/60 (charge mole ratio: toluene or *m*-xylene/HF). At this concentration, the effects of CO pressure on the rates for both reactions are examined under the fixed stirring speed as shown in Fig. 1. The initial rates are proportional to CO pressure under this condition as seen in Fig. 2; the diffusion of CO gas into the liquid-film is inferred to be rate-determining.

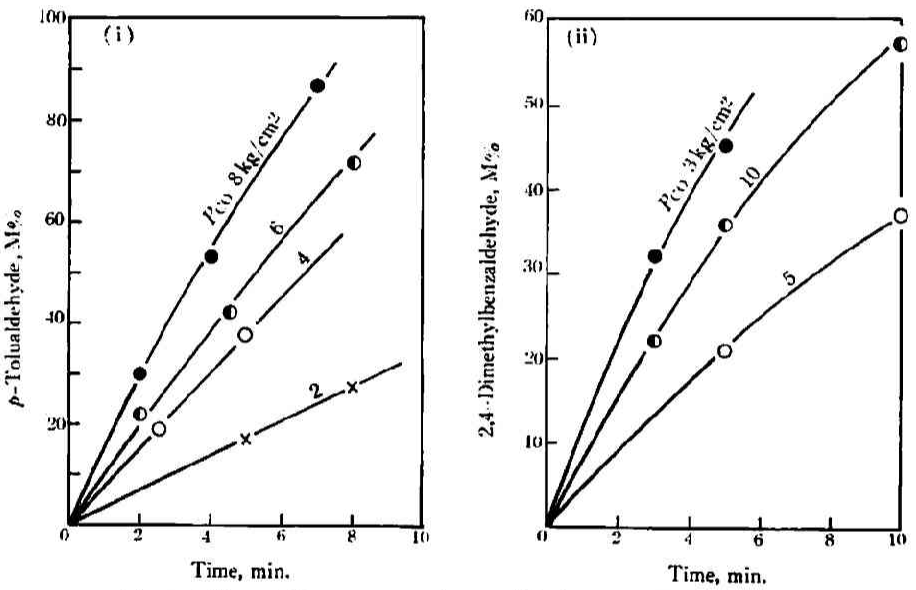


Fig. 1 Effect of CO pressure under gas diffusion-controlled condition
(i) 0°C, P_{BF_3} 3 kg/cm², stirring speed 750 rpm
(ii) 0°C, P_{BF_3} 5 kg/cm², stirring speed 1100 rpm

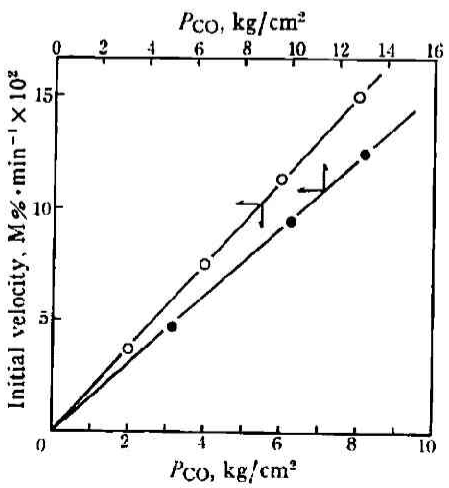


Fig. 2 Examination of CO pressure under the diffusion-controlled condition
—○— : *p*-tolualdehyde formation
—●— : 2,4-dimethylbenzaldehyde formation

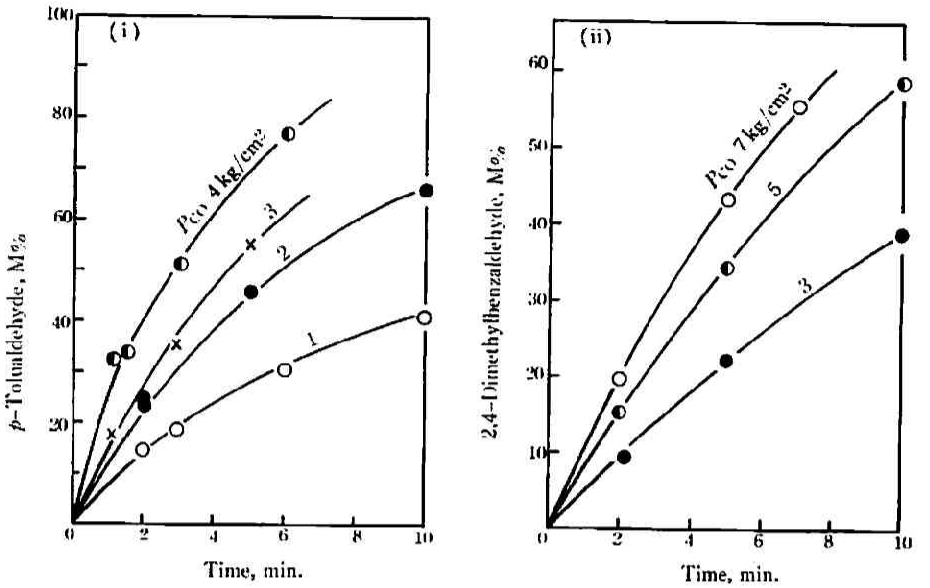


Fig. 3 Effect of CO pressure for tolu- and dimethylbenzaldehyde formation
(i) 0°C, P_{BF_3} 1 kg/cm², charge mole ratio toluene/HF = 1/600
(ii) 0°C, P_{BF_3} 5 kg/cm², charge mole ratio *m*-xylene/HF = 1/130

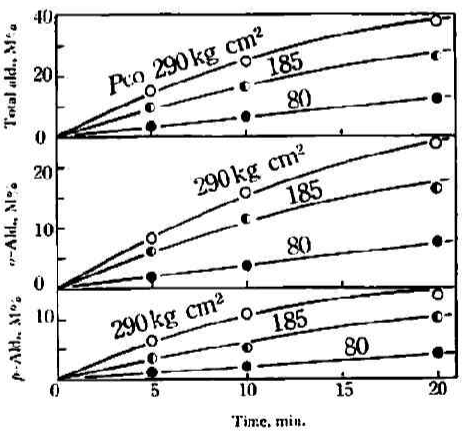


Fig. 4. Effect of CO pressmre for anisaldehydes formation
40°C, P_{BF_3} 12.8 kg/cm², charged mole ratio anisole/HF = 1/32 ald. denotes anisaldehyde.

The conditions enabling the liquid phase reaction to be rate-determining, are given in the last column of Table 1, and the kinetic studies given in this report hereafter are those made under these conditions.

The effect of CO pressure, BF_3 pressure and temperature are given in Figs. 3, 4, 5 and 6, respectively.

The syntheses of anisaldehydes require higher CO pressure and temperature than in the tolualdehyde and dimethylbenzaldehyde syntheses.

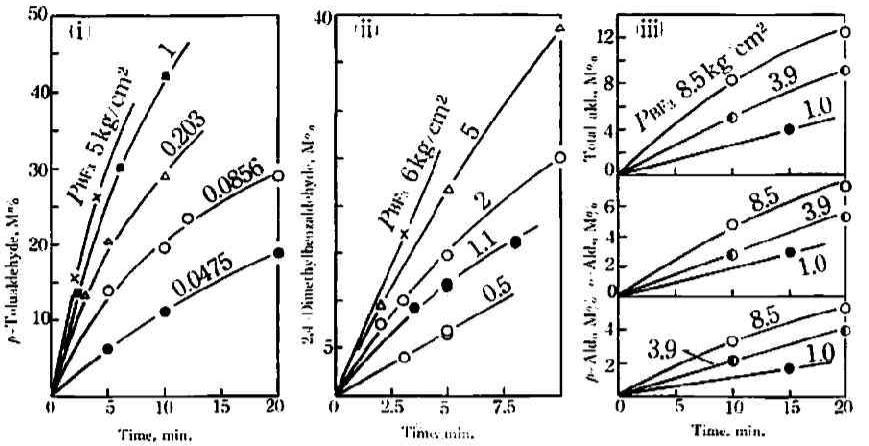


Fig. 5 Effect of BF_3 pressure

(i) 0°C, P_{CO} 1 kg/cm², charge mole ratio toluene/HF = 1/600

(ii) 0°C, P_{CO} 3 kg/cm², charge mole ratio *m*-xylene/HF = 1/130

(iii) 22°C, P_{CO} 185 kg/cm², charge mole ratio anisole/HF = 1/31, ald. denotes anisaldehyde

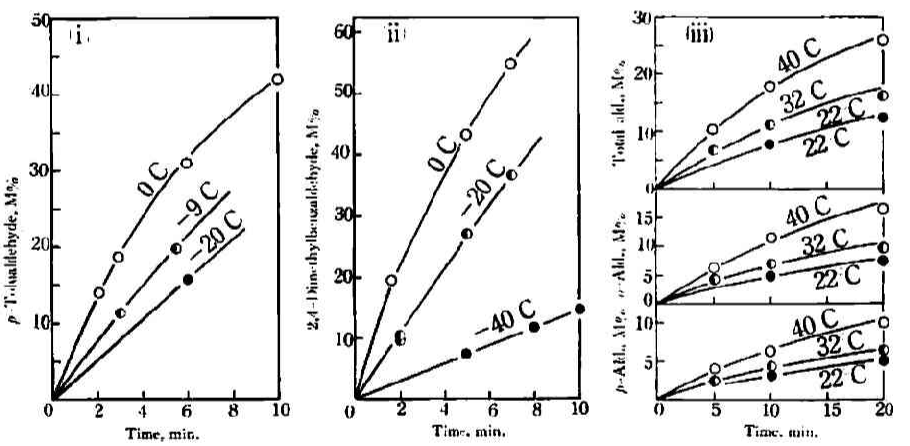


Fig. 6 Effect of temperature

(i): P_{CO} 1 kg/cm², P_{BF_3} 1 kg/cm², charge mole ratio toluene/HF = 1/600.

(ii): P_{CO} 7 kg/cm², P_{BF_3} 5 kg/cm², charge mole ratio *m*-xylene/HF = 1/130.

(iii): P_{CO} 185 kg/cm², charge mole ratio anisole/HF = 1/32

—○—: P_{BF_3} 12.8 kg/cm², —◐—: P_{BF_3} 10.5 kg/cm², —●—: P_{BF_3} 8.5 kg/cm²

Discussion

The initial rate equations have been derived from the following considerations.

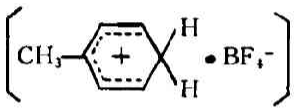
1) The respective aldehyde is produced by the reaction of the complex with dissolved CO as shown in (1) and (2), and the rate is the first order with respect to the complex and CO pressure.

$$\mathrm{Ar(d)+HF+BF_3(d)} \overset{\mathrm{BF_3\,(gas)}\ \Updownarrow H_{BF_3}\ K}{\rightleftharpoons} [\mathrm{ArH^+\cdot BF_4^-}], \tag{1}$$

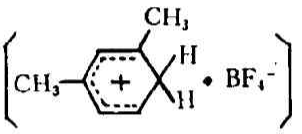
$$[\mathrm{ArH^+\cdot BF_4^-}]+\mathrm{CO(d)} \overset{\mathrm{CO\,(gas)}\ \Updownarrow H_{CO}\ k}{\longrightarrow} [\mathrm{Aldehyde\cdot H^+\cdot BF_4^-}], \tag{2}$$

where Ar(d) represents toluene, *m*-xylene or anisole, K the equilibrium constant for the complex formation, k [$(\mathrm{kg/cm^2})^{-1}\,\mathrm{min}^{-1}$] the rate constant, H_{BF_3} the Henry constant [$(\mathrm{kg/cm^2})^{-1}$] of BF_3 dissolution in HF and H_{CO} the Henry constant of CO [$(\mathrm{kg/cm^2})^{-1}$] in HF.

2) Judging from the selective formation of *p*-tolualdehyde from toluene and of 2, 4-dimethylbenzaldehyde from *m*-xylene, the complex type (I) is presumably formed from toluene, and the type (II) from *m*-xylene by (1).



(I)



(II)

The initial amount of toluene complex (I) or *m*-xylene complex (II) relative to the charged substrate, represented by C_0, is given by (3),

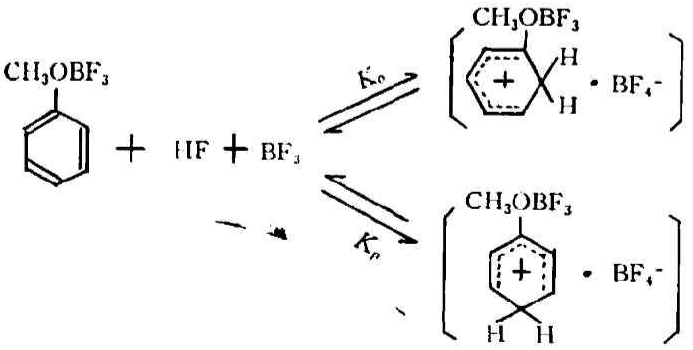
$$K=\frac{C_0}{(1-C_0)H_{BF_3}P_{BF_3}} \tag{3}$$

In this equation, the concentration of HF is omitted since the large excess amount of HF is used. Then, the initial rate, v_0, is

$$v_0=kH_{CO}C_0f_{CO}=kH_{CO}\frac{KH_{BF_3}P_{BF_3}}{1+KH_{BF_3}P_{BF_3}}f_{CO} \tag{4}$$

where f_{CO} denotes the fugacity of CO.

3) Both *o*- and *p*-anisaldehyde are produced from anisole, so the formations of both *o*- and *p*-complex of anisole are assumed, *i.e.*,



(5)

(6)

The initial amount of the o-complex ($\equiv C^o{}_0$) and the p-complex ($\equiv C^p{}_0$) are given by (7) and (8),

$$K_o=\frac{C^o{}_0}{(1-C^t{}_0)H_{BF_3}P_{BF_3}} \tag{7}$$

and

$$K_p=\frac{C^p{}_0}{(1-C^t{}_0)H_{BF_3}P_{BF_3}} \tag{8}$$

where K_o denotes the equilibrium constant for (5), K_p for (6), and $C^t{}_0=C^o{}_0+C^p{}_0$.
Then, the initial rates are

$$v^t{}_0=k_t H_{CO}C^t{}_0 f_{CO} \quad \text{for the total aldehyde formation,} \tag{9}$$

$$v^o{}_0=k_o H_{CO}C^o{}_0 f_{CO} \quad \text{for the } o\text{-aldehyde formation,} \tag{10}$$

and

$$v^p{}_0=k_p H_{CO}C^p{}_0 f_{CO} \quad \text{for the } p\text{-aldehyde formation.} \tag{11}$$

Combining these with (7) and (8), we obtain

$$v^t{}_0=k'_t\frac{(K_o+K_p)H_{BF_3}P_{BF_3}}{1+(K_o+K_p)H_{BF_3}P_{BF_3}}f_{CO}. \tag{12}$$

$$v^o{}_0=k'_o\frac{P_{BF_3}}{1+(K_o+K_p)H_{BF_3}P_{BF_3}}f_{CO}. \tag{13}$$

and

$$v^p{}_0=k'_p\frac{P_{BF_3}}{1+(K_o+K_p)H_{BF_3}P_{BF_3}}f_{CO}. \tag{14}$$

where $k'_t=k_t H_{CO}$, $k'_o=k_o K_o H_{CO}H_{BF_3}$ and

$k'_p=k_p K_p H_{CO}H_{BF_3}$.

Table 2. Equilibrium constants for the complex formation reaction and Henry constant of BF_3 gas in HF

Complex formation reaction	Equilibrium constant K	T °C	Henry constant of BF_3 gas [(kg/cm²)⁻¹]
Toluene(d)+HF+BF_3(d)	900	0	4.86×10^{-3}
	1,200	−9	6.61×10^{-3}
	1,600	−20	8.67×10^{-3}
m-Xylene(d)+HF+BF_3(d)	86.5*	0	4.86×10^{-3}
	200*	−20	8.67×10^{-3}
	590*	−40	1.58×10^{-2}
Anisole(d)+HF+BF_3(d)	61.1**	40	2.95×10^{-3}
	75.9**	32	3.30×10^{-3}
	100**	22	3.98×10^{-3}

Note: * These values are at the HF solution saturated with a complex and m-xylene.

** These values represent the equilibrium constant of (K_o+K_p), since the separate determinations of K_o and K_p are impossible.

Table 3 Examination of BF_3 pressure effect

Reaction	Condition: Fixed condition	Condition: P_{BF_3} (kg/cm²)	Observed initial rate: v_0 (mole %·min⁻¹)	Calculation: C_0* (mole %)	Calculation: Rate constant kH_{CO} [(kg/cm²)⁻¹ min⁻¹]	
p-Tolualdehyde from toluene	0°C P_{CO} 1 kg/cm²	0.0475	1.44	21.1	6.8×10^{-2}	av. 8.0×10^{-2}
		0.0860	2.71	29.6	9.2×10^{-2}	
		0.203	4.06	50.8	8.0×10^{-2}	
		1.0	6.55	81.0	8.1×10^{-2}	
		5.0	7.32	92.9	7.9×10^{-2}	
2,4-Dimethyl-benzaldehyde from *m*-xylene	0°C P_{CO} 3 kg/cm²	0.5	1.41	17.8	2.6×10^{-2}	av. 2.6×10^{-2}
		1.1	2.55	31.8	2.7×10^{-2}	
		2.0	3.54	45.4	2.6×10^{-2}	
		5.0	5.19	68.6	2.5×10^{-2}	
		6.0	5.53	71.8	2.5×10^{-2}	
o- and *p*-Anisaldehyde from anisole	Fixed condition	P_{BF_3} (kg/cm²)	v'_0 (mole %·min⁻¹)	C'_0 (mole %)	$k_t H_{CO}$ [(kg/cm²)⁻¹ min⁻¹]	
	22°C P_{CO} 185 kg/cm² (f_{CO} = 182 kg/cm²)	1.0	0.274	65.0	4.7×10^{-5}	av. 4.6×10^{-3}
		3.9	0.525	152	4.6×10^{-5}	
		8.5	0.690	200	4.8×10^{-5}	
			v_{o0} (mole %·min⁻¹)	C'** [mole % (kg/cm²)]	$k_o H_{CO} K_o$ [(kg/cm²)⁻¹ min⁻¹]	
		1.0	0.150	65.0	3.2×10^{-3}	av. 3.0×10^{-3}
		3.9	0.314	152	2.9×10^{-3}	
		8.5	0.422	200	2.8×10^{-3}	
			v_{p0} (mole %·min⁻¹)	C'** [mole % (kg/cm²)]	$k_p H_{CO} K_p$ [(kg/cm²)⁻¹ min⁻¹]	
		1.0	0.100	65.0	2.1×10^{-3}	av. 2.0×10^{-3}
		3.9	0.214	152	2.0×10^{-3}	
		8.5	0.270	200	1.9×10^{-3}	

* $C'=\dfrac{100P_{BF_3}}{1+(K_o+K_p)H_{BF_3}P_{BF_3}}$, representing the initial value for the complex

** C_0: Initial amount of the complex relative to the charged substrate

Equilibrium constants for the complex formations and Henry constant of BF_3 are reproduced in Table 2, which were reported in the previous papers[2].

Now, according to the derived rate equations, the results will be examined. As can be seen in Fig. 7, there exists a linear relationship between the respective initial rate and CO fugacity as expected from the rate equations.

Results of the examination of the BF_3 pressure on the rates are given in Table 3, showing the correctness of the derived rate equations as to the effect of BF_3 pressure.

The reaction velocity for anisaldehydes formation is much slower than those for tolualdehyde and dimethylbenzaldehyde formation.

From the temperature effect on rates, given in Tables 4 and 5, the apparent activation energies

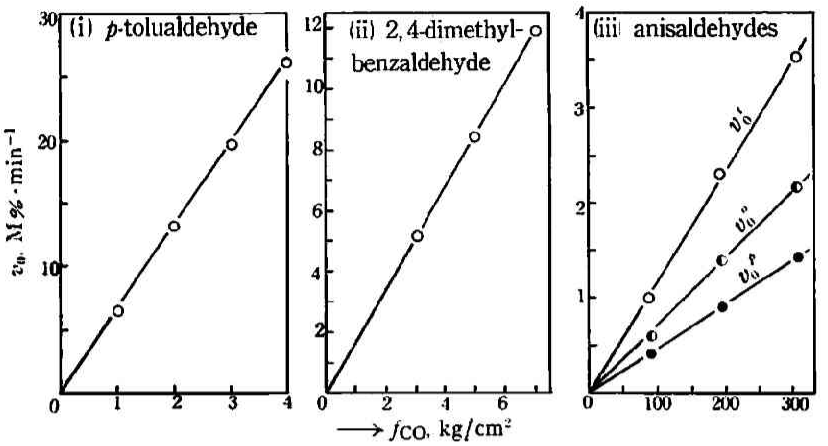


Fig. 7 Examination of CO pressure
(i): 0°C, P_{BF_3} 1 kg/cm^2. (ii): 0°C, P_{BF_3} 5 kg/cm^2. (iii): 40°C, P_{BF_3} 12.8 kg/cm^2

Table 4. Examination of temperature effect

Reaction	Fixed conitions	T °C	Initial velocity v_0 (mole %·min^{-1})	Initial amount of complex C_0 (mole %)	Rate constant $k\,H_{CO}$ [(kg/cm^2)$^{-1}$ min^{-1}]	Activation energy (kcal·mole^{-1})
p-Tolualdehyde from toluene	P_{CO}, 1 kg/cm^2	0	6.55	81.0	8.1×10^{-2}	
	P_{BF_3}, 1 kg/cm^2	−9	3.90	88.8	4.4×10^{-2}	7.6
	toluene/HF = 1/600*	−20	2.62	93.3	2.8×10^{-2}	
2,4-Dimethylbenzaldehyde from m-xylene	P_{CO}, 7 kg/cm^2	0	11.9	68.6	2.5×10^{-2}	
	P_{BF_3}, 5 kg/cm^2	−20	5.32	88.7	8.5×10^{-3}	8.1
	m-xylene/HF = 1/130*	−40	1.51	98.0	2.2×10^{-3}	

* charge mole ratio

Table 5. Examination of temperature effect

Reaction	P_{CO} (kg/cm^2)	f_{CO} (kg/cm^2)	P_{BF_3} (kg/cm^2)	T °C	Initial rate [mole %·min^{-1}]	C'' [mole % (kg/cm^2)]	Rate constant [(kg/cm^2)$^{-1}$ min^{-1}]	Activation energy (kcal·mole^{-1})
o-Anisaldehyde from anisole	185	190	12.8	40	v^o_0 1.41	383	$k_oH_{CO}K_o$ 6.7×10^{-3}	
	190	192	10.5	32	0.92	284	4.9×10^{-3}	9.0
	—	—	—	22	—	—	3.0×10^{-3}*	
p-Anisaldehyde from anisole	185	190	12.8	40	v^p_0 0.93	383	$k_pH_{CO}K_p$ 4.2×10^{-3}	
	190	192	10.5	32	0.56	284	3.1×10^{-3}	9.0
	—	—	—	22	—	—	2.0×10^{-3}*	

* cf. Table 3

(kcal/mole) are obtained to be 7.6 for the formation of tolualdehyde, 8.1 for dimethylbenzaldehyde and 9 for anisaldehydes. Though the rate equations can explain the effects of reaction variables, as described above, there can be another possible mechanism such as the substitution reaction of uncom-

plexed aromatics by formyl cation. This mechanism can offer the expression of the same type as presented in this paper with respect to CO pressure and BF_3 pressure except for the value of the rate constant. More detailed discussion on the mechanism will be published later.

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Institute for Chemical Research
Kyoto University
Kyoto, Japan