Reaction of Anisole with Carbon Monoxide under High Pressure*

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Summary: A kinetic study has been made of the synthesis of *o*- and *p*-anisaldehyde from anisole-BF₃ complex and CO in hydrogen fluoride solution.

In the preliminary investigation a new white complex was obtained below -60°C, the composition of which was 1 mole anisole-2 moles BF₃-1 mole HF with a m.p. of -60°C. The apparent equilibrium constant for the complex formation has been determined to be 219 at 0°C on the assumption of the existence of *o*- and *p*-complex of σ -type.

As to the reaction of anisole with CO, the conditions enabling the liquid phase reaction rate-determining were found to be: a charge ratio of Anisole/HF < 30, a stirring speed above 750 rpm and an operational temperature below 60°C; the latter being essential to prevent side reactions leading to the formation of tarry matter.

The rate of each *o*- and *p*-aldehyde formation is of the first order with respect to the dissolved CO and the complex respectively. The apparent rate constants are 6.67×10^{-3} (kg⁻¹ cm²·min⁻¹) for *o*- and 4.23×10^{-3} for *p*-aldehyde formation at 40°C and the apparent activation energies 9 kcal·mole⁻¹ for both products.

Compared with the rates of the same reaction with toluene and *m*-xylene, the rate constant of anisaldehyde formation is much smaller.

Introduction

The Gatterman-Koch reaction to synthesize aromatic aldehydes from aromatic hydrocarbons and carbon monoxide with the catalyst such as AlCl₃-HCl¹⁾, is of interest from the viewpoint of reaction kinetics and the formation of aromatic hydrocarbon complex with catalysts.

In earlier papers the authors have reported this reaction with the substrates such as toluene and *m*-xylene in the HF-BF₃ system as catalyst^{2),3)}.

In the present study, anisole has been taken as a substrate as a next step in order to assess the effect of a substituent group. The equilibrium constant of the resulting complex formation and the rate equation which explains the effects of reaction variables on the formation of anisaldehyde have been determined,

No paper seems available on this reaction.

Experimental

Materials

HF: Manufactured by Daikin Kogyo Co. Ltd. (purity > 99.7% as determined by electric conductivity measurement),

BF₃: Manufactured by Baker and Adamson Works (U.S.A.) (purity 99.5% as determined by chemical analysis⁴⁾),

C₆H₅OCH₃: Purified by distillation of the c.p. reagent, (purity 98% by gas chromatography),

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

Procedure

A measured amount of HF gas was led from the HF bomb into a polyethylene cylinder which contained a fixed amount of anisole and then liquefied at a dry ice-methanol

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temperature. This mixture was then discharged into an evacuated autoclave of 117 cc capacity made of stainless steel and equipped with a magnetic stirrer and baffle.

After the autoclave had attained the experimental temperature the required quantity of BF_3 gas was introduced, via a weighing vessel, to the autoclave under stirring to establish the dissolution equilibrium; the quantity charged being determined from the weight decrease of the weighing vessel. Subsequently, CO gas was added. The reaction took place whilst stirring at a fixed speed and maintaining a constant total pressure by a continuous supply of CO.

At the desired reaction time, the autoclave was cooled immediately with ice water and after exhausting the CO and BF_3 gases the reaction product was poured onto a crushed

ice-benzene mixture.

Analysis

The following methods were adopted to analyze anisole, *o*- and *p*-anisaldehyde in the solution extracted with benzene from the above-mentioned reaction product.

1) Total amount of aldehydes: Determined by alkali titration of freed HCl in the oxime formation⁵⁾,

2) The respective amounts of *o*- and *p*-aldehyde: Determined by gas chromatography; column PEG 20 M, 2 m, temp. 220°C, carrier gas N_2 , one example of the retention time being: t_R 4.5 min for *o*-anisaldehyde, t_R 5.0 min for *p*-anisaldehyde.

Fig. 1. Dissolution of BF_3 in HF solution of anisole.

Table 1. Calculation of BF_3 dissolution.

Condition	BF_3 Pressure (kg/cm^2)	Dissolved BF_3 $(\text{BF}_3)_1/a$	BF_3 combined with An $(\text{BF}_3)_A/a$	Calculation of Eqs. (7) and (8)			
				C/a	$(C/a)/(1-(C/a))$	$(C/a)/P_{\text{BF}_3}[1-(C/a)]$	$K_o + K_p$
0°C, Charge mole ratio $\text{HF}/\text{An} = 32.6$	0	0.301	0.301	—	—	—	—
	0	0.470	0.470	—	—	—	—
	0.37	1.42	1.35	0.35	0.538	1.46	248
	1.10	1.76	1.55	0.55	1.22	1.11	188
	3.50	2.50	1.82	0.82	4.56	1.30	221
40°C, Charge mole ratio $\text{HF}/\text{An} = 33$	1.80	1.43	1.26	0.26	0.352	0.195	66.1
	2.30	1.53	1.29	0.29	0.408	0.177	60.0
	2.70	1.57	1.33	0.33	0.493	0.182	61.7
	4.20	1.70	1.41	0.41	0.695	0.165	55.9
	6.30	2.14	1.56	0.56	1.27	0.202	68.4
	8.20	2.44	1.57	0.57	1.33	0.163	55.3
	14.2	3.02	1.70	0.70	2.34	0.165	55.9
	26.1	4.26	1.83	0.83	4.88	0.188	63.8

3) Residual amount of anisole: Determined by subtraction of the total amount of aldehydes from the total amount of the MeO-group analyzed by the Zeisel method⁶⁾,

Result

Anisole- BF_3 -HF complex formation

In order to examine the formation of the anisole (hereafter abbreviated as An) complex with HF and BF_3 , the dissolution of BF_3 gas in the solution of HF-An was measured under these conditions: Charge mole ratio HF/An = 32, temperature $0^\circ\text{--}40^\circ\text{C}$ and BF_3 pressures up to 26 kg/cm^2 . The results are shown in Fig. 1 and Table 1. In Fig. 1, a , $(\text{BF}_3)_1$ and $(\text{BF}_3)_A$ denote the charged amount of An, the total amount of the dissolved BF_3 and the amount of BF_3 combined with An, respectively. The value $(\text{BF}_3)_A/a$ is calculated by Eq. (1), assuming that the Henry's constant of the dissolution of BF_3 in free HF can be adopted here on account of the large dilution of anisole with HF.

$$\frac{(\text{BF}_3)_A}{a} = \frac{(\text{BF}_3)_1}{a} - \left(\frac{b}{a}\right) H_{\text{BF}_3} P_{\text{BF}_3}, \quad (1)$$

where the Henry's constant H_{BF_3} is $5.89 \times 10^{-3} (\text{kg/cm}^2)^{-1}$ at 0°C and $2.95 \times 10^{-3} (\text{kg/cm}^2)^{-1}$ at 40°C , as calculated from the data by E. C. Hughes⁷⁾, with b as the charged mole of HF.

In Fig. 1 we see that the BF_3 pressure is not detectable for $(\text{BF}_3)_A/a < 1$, while $(\text{BF}_3)_A/a$ asymptotically approaches a mole ratio value of 2 with increasing BF_3 pressure.

These facts may be explained as follows: BF_3 reacts with the methoxy group of An to form a stable addition compound⁸⁾ according to Eq. (2), which then forms a complex with HF and BF_3 similarly to methyl benzenes, the resultant composition thus being An:HF: BF_3 = 1:1:2.

The above can be supported by the observation that when 2 moles of BF_3 were introduced into the solution consisting of 1 mole An and 1 mole HF at about -60°C under atmospheric pressure, a new white solid was obtained which melted at -60°C to produce a yellow liquid (for reference, the m.p. of the toluene-HF- BF_3 (1:1:1) complex is -65°C (yellow green) and that of the *m*-xylene-HF- BF_3 (1:1:1) complex is -55°C (yellow)⁹⁾).

Thus, on the assumption that this complex exists as a σ -complex,

in analogy with the well-studied methyl benzene-HF- BF_3 complex^{9),10)} and that both the *o*- and *p*-type are present in the complex, which is partly suggested by the presence of *o*- and *p*-isomers in the anisaldehyde produced (see later), the equilibrium constant of the complex formation can be calculated.

Assuming the moles of the *o*- and *p*-complex are C_o and C_p at the equilibrium, the equilibrium constant for the *o*-complex formation reaction, K_o , can then be expressed as:

$$K_o = \frac{C_o}{a - C_o - C_p} \cdot \frac{[\text{HF}]_e}{a + b} \cdot \frac{H_{\text{BF}_3} P_{\text{BF}_3} [\text{HF}]_e}{a + b}, \quad (4)$$

where $[\text{HF}]_e$ denotes the moles of free HF at equilibrium. Since the charge ratio HF/An ($\equiv b/a$) is nearly equal to 30, we have $[\text{HF}]_e \approx b$ and $b/(a+b) \approx 1$, and Eq. (4) becomes

$$K_o = \frac{C_o}{H_{\text{BF}_3}(a - C_o - C_p) P_{\text{BF}_3}}. \quad (5)$$

Similarly, the expression for the equilibrium constant of the *p*-complex formation, K_p , can be stated as:

$$K_p = \frac{C_p}{H_{\text{BF}_3}(a - C_o - C_p) P_{\text{BF}_3}}. \quad (6)$$

Combining Eqs. (5) and (6), we find:

$$K_o + K_p = \frac{(C/a)}{H_{BF_3} P_{BF_3} [1 - (C/a)]}, \quad (7)$$

where $C = C_o + C_p$ calculable by

$$\frac{C}{a} = \frac{(BF_3)_A}{a} - 1. \quad (8)$$

Unfortunately, it is impossible to determine K_o and K_p separately from the present measurements but the value of $(K_o + K_p)$ can be obtained from Eqs. (7) and (8).

As shown in Table 1, the average values of $(K_o + K_p)$ are 61.1 at 40°C and 219 at 0°C, from which the apparent heat of reaction is calculated to be 6 kcal·mole⁻¹ (exothermic) and the interpolated values of $(K_o + K_p)$ needed later are 100 at 22°C and

75.9 at 32°C.

Kinetic Measurement

In Table 2 the results are given of the preliminary experiments carried out in order to find the most suitable conditions for the investigation.

Operation at temperatures higher than 60°C is undesirable because of the occurrence of side reactions leading to the formation of tarry matter.

As can be seen in column (B) of Table 2, a stirring speed above 750 rpm does not significantly affect the rate under the given conditions, *i.e.* the rate is determined solely by the reaction in the liquid phase.

Thus, the following conditions were chosen for the kinetic measurements: Charge HF

Table 2. Preliminary experiments.

	Charge mole ratio An/HF/BF ₃	Temp. (°C)	Time (min)	max. P_{CO} (kg/cm ²)	Stir. speed (rpm)	Ald. yield (M%)	Nature of the mixture after reaction
(A)	1/19/2	100	50	220	1,100	—	very viscous and black tarry matter
	1/45/2	100	60	230	1,100	37	dark brown solution with tarry matter
	1/42/3	65	60	230	1,100	55	brown solution
	1/31/3	41	90	260	1,100	68	brown solution
(B)	1/32/3	41	20	185	535	13.9	brown solution
					750	30.7	
					995	31.8	
					1,445	28.6

Charge mole ratio HF/An=32, 40.6°C,
BF₃ pressure 12.8 kg/cm², 1,000 rpm.

Fig. 2. Effect of CO pressure.

22.1°C, P_{CO} 185 kg/cm², 1,000 rpm,
charge mole ratio HF/An=31.

Fig. 3. Effect of BF₃ pressure.

Table 3. Temperature effect.

Conditions	40.6°C, P_{BF_3} 12.8 $\frac{kg}{cm^2}$			31.7°C, P_{BF_3} 10.5 $\frac{kg}{cm^2}$			22.1°C, P_{BF_3} 8.5 $\frac{kg}{cm^2}$	
Time (min)	5	10	20	5	10	20	10	20
Total-Ald. yield (M%)	10.4	16.9	25.8	7.1	11.3	16.1	8.1	12.5
<i>o</i> -Ald. yield (M%)	6.3	11.5	15.8	4.6	6.9	9.6	4.9	7.3
<i>p</i> -Ald. yield (M%)	4.1	6.4	10.0	2.5	4.4	6.5	3.2	5.2
Yield ratio <i>o</i> -Ald./ <i>p</i> -Ald.	1.5	1.8	1.6	1.8	1.6	1.5	1.5	1.4

Fixed conditions: $P_{CO}=185\sim190$ kg/cm², charge mole ratio HF/An=31.

/An=32, reaction temperature below 60°C and a stirring speed above 750 rpm.

The effects of CO pressure, BF₃ pressure and temperature are given in Figs. 2 and 3 and Table 3, respectively, each under the specified conditions.

It is interesting to note that the ratio between the yields of *o*- and *p*-aldehyde is approximately 1.6 and independent of the reaction temperature.

In order to determine if the aldehyde formed can isomerize, the addition compound of BF₃-aldehyde, prepared previously at room temperature, was kept for some time under the conditions of kinetic study but without CO. No evidence of isomerization could be detected, as shown in Table 4.

Table 4. Examination of rearrangement.

	Initial charge of aldehyde-BF ₃ complex	After 20 min*
<i>o</i> -Ald.	0.77	0.76
<i>p</i> -Ald. (mole ratio)	1.00	1.00

* Conditions: 40°C, P_{BF_3} 12 kg/cm², charge mole ratio HF/aldehyde=31.

Discussion

The rate equation has been composed on the basis of the following considerations:

1) Both the *o*- and *p*-complex of σ -type are assumed to result separately from An and BF₃ in HF medium.

2) Anisaldehyde is produced by the reaction of the complex with the dissolved CO, *i.e.*,

and the rate is proportional to the CO fugacity and the concentration of the complex.

3) The kinetic discussion is limited only to the initial stage of the reaction.

Thus, the initial rates are

$$v_A = k_A H_{CO} \left(\frac{100C}{a} \right) f_{CO} \quad \text{for total aldehyde formation,} \quad (11)$$

$$v_o = k_o H_{CO} \left(\frac{100C_o}{a} \right) f_{CO} \quad \text{for } o\text{-aldehyde formation,} \quad (12)$$

and

$$v_p = k_p H_{CO} \left(\frac{100C_p}{a} \right) f_{CO} \quad \text{for } p\text{-aldehyde formation,} \quad (13)$$

where v represents the initial rate (M% · min⁻¹), k the rate constant [(kg/cm²)⁻¹ min⁻¹], f_{CO} the fugacity of CO (kg/cm²), H_{CO} the Henry's constant of CO (kg/cm²)⁻¹, a the charged An (mole), and C the initial concentration of the complex.

From the previous expressions, (5), (6) and (7), we have

$$\frac{C}{a} = \frac{H_{BF_3}(K_o + K_p)P_{BF_3}}{1 + H_{BF_3}(K_o + K_p)P_{BF_3}}, \quad (14)$$

$$\frac{C_o}{a} = K_o H_{BF_3} P_{BF_3} \left(1 - \frac{C}{a} \right), \quad (15)$$

and

$$\frac{C_p}{a} = K_p H_{BF_3} P_{BF_3} \left(1 - \frac{C}{a} \right). \quad (16)$$

Substituting (15) in (12) and (16) in (13), we finally obtain

$$v_o = k_o' \left[P_{BF_3} \left(100 - 100 \frac{C}{a} \right) \right] f_{CO}, \quad (17)$$

$$v_p = k_p' \left[P_{BF_3} \left(100 - 100 \frac{C}{a} \right) \right] f_{CO}, \quad (18)$$

Table 5. Examination of kinetic measurements.

Effect	Condition				Experimental equation						Initial values of complex		Calculation of rate constants						
	T	P_{BF_3}	P_{CO}	f_{CO}	Total-Aldehyde		o-Aldehyde		p-Aldehyde		$\frac{100C}{a}$	$P_{BF_3} \left(100 - 100 \frac{C}{a} \right)$	$k_A H_{CO}$	k'_o	k'_p	$\frac{k_o H_{CO}}{\times K_o}$	$\frac{k_p H_{CO}}{\times K_p}$	$\frac{k_o}{k'_p}$	
	(°C)	$\left(\frac{kg}{cm^2} \right)$	$\left(\frac{kg}{cm^2} \right)$	$\left(\frac{kg}{cm^2} \right)$	$\frac{-A}{\times 10^{-2}}$	B	$\frac{-A}{\times 10^{-2}}$	B	$\frac{-A}{\times 10^{-2}}$	B	(M%)	$\left(M\% \cdot \frac{kg}{cm^2} \right)$	$\left(\frac{kg}{cm^2} \right) \frac{1}{min^{-1}}$	$\frac{1}{min^{-1}}$	$\frac{1}{min^{-1}}$	$\frac{(kg/cm^2)^{-1}}{min^{-1}}$	$\frac{(kg/cm^2)^{-1}}{min^{-1}}$	$\frac{k_o}{k'_p}$	
CO Pressure	40.6	12.8	80	79	1.93	0.962	1.30	0.60	0.57	0.35	70	383	From tangent in Fig. 4						
			185	190	5.75	2.44	3.10	1.41	2.64	0.928			1.75×10^{-4}	1.95×10^{-5}	1.24×10^{-5}	6.67×10^{-3}	4.23×10^{-3}	1.57	
			290	304	8.45	3.56	5.00	2.20	3.55	1.39									
BF ₃ Pressure		1.0			0	0.274	0	0.150	0	0.100	35.0	65.0	From tangent in Fig. 5						
	22.1	3.9	185	182	0.275	0.525	0.240	0.314	0.040	0.214	61.0	152	4.72×10^{-5}	1.17×10^{-5}	0.75×10^{-5}	2.94×10^{-3}	1.88×10^{-3}	1.56	
		8.5			0.412	0.690	0.375	0.422	0.100	0.270	76.5	200							
Temp.	31.7	10.5	190	192	3.37	1.47	2.18	0.916	1.19	0.563	73.0	283.5	1.056×10^{-5}	1.65×10^{-5}	1.04×10^{-5}	4.96×10^{-3}	3.07×10^{-3}	1.58	

Note. H_{BF_3} (kg/cm^2)⁻¹: 2.95×10^{-3} (40.6°C), 3.39×10^{-3} (31.7°C), 3.98×10^{-3} (22.1°C)⁷.

$K_o + K_p$: 61.1 (40°C), 75.9 (32°C), 100 (22°C).

Experimental equation: $y = At^2 + Bt$, where y = (Produced total-Aldehyde, o-or p-Aldehyde/Charged An) $\times 100$,
 t = time (min) and A, B = constants.

Initial velocity: $(dy/dt)_0 = B$.

and

$$v_A = v_o + v^p, \quad (19)$$

where $k'_o = k_o H_{CO} K_o H_{BF_3}$, $k'_p = k_p H_{CO} K_p H_{BF_3}$ and (C/a) can be calculated by Eq. (14).

Now, with the rate equations thus obtained, the results will be examined. The values of the initial rates are obtained by differentiating the experimental quadratic equations which fit the observation, as listed in Table 5.

As can be seen in Fig. 4, there exists a

40.6°C, P_{BF_3} 12.8 kg/cm^2 , 1,000 rpm,
 charge mole ratio HF/An=32.

Fig. 4. Examination of CO pressure effect.

linear relationship between the respective initial formation rates and CO fugacity, as can be expected from the rate equations.

Results of the examinations of the BF_3 pressure effect on the rates of formation of total aldehydes, o- and p-aldehyde are shown in (a), (b) and (c) of Fig. 5, in each of which a linear relationship can be seen between the initial rate and the calculated value corresponding with the initial concentration of each complex. It should be noted, however, that the term $P_{BF_3} [100 - 100(C/a)]$ in the abscissa of (b) and (c) does not represent directly the initial concentration of the o- or p-complex. As mentioned before, we cannot obtain the separate values of K_o and K_p , but since C_o/C_p should be constant in the complex formation equilibrium at a fixed temperature the above term can be taken as a measure proportional to the concentration of each complex.

Thus, the rate equations arrived at in the above are considered adequate to explain the observed facts.

The calculated rate constants at different temperatures are given in Table 5 and their Arrhenius plots in Fig. 6.

The ratio of k'_o/k'_p , being approximately

22.1°C, P_{CO} 185 kg/cm², 1,000 rpm, charge ratio HF/An=31.

Fig. 5. Examination of BF_3 pressure effect.

Fig. 6. Arrhenius plot.

1.5, is independent of temperature and the apparent activation energies are 9 kcal·mole⁻¹ for both the *o*- and *p*-aldehyde formation, which involves the heat of dissolution of CO in HF and the heat of complex formation.

At the present stage where K_o and K_p are not known, it is impossible to discuss in detail the effect of a substituent group on CO addition to aromatics in comparison with the same reaction of toluene, *m*-xylene and phenol

investigated previously^{2,3}.

However, when comparing the corresponding values for toluene, *m*-xylene and phenol obtained by us (Table 6), we may say that unless K_o does not differ considerably from K_p , the k_o or k_p is much smaller than those for toluene or *m*-xylene; *e.g.*, if $K_o = K_p$, $k_o H_{CO} = 8.7 \times 10^{-4}/109 = 8 \times 10^{-6}$ [(kg/cm²)⁻¹ min⁻¹] and $k_p H_{CO} = 5.5 \times 10^{-4}/109 = 5.1 \times 10^{-6}$ [(kg/cm²)⁻¹ min⁻¹] (at 0°C, calculated from the data at 22°C and $E=9$ kcal·mole⁻¹), which are lower than $(kH_{CO})_{\text{toluene}}$ by a factor of 10^{-4} and even if $K_o/K_p=100$ or $1/100$, either $k_p H_{CO}$ or $k_o H_{CO}$ is ca. 10^{-2} of $(kH_{CO})_{\text{toluene}}$.

Mechanistic discussion of the effects of substituents will be published later.

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Table 6. Comparison with results of other aromatics.

Aromatics	<i>m</i> -Xylene ³⁾	Toluene ²⁾	Phenol*	
Product	2,4-dimethylbenzaldehyde	<i>p</i> -tolualdehyde	<i>p</i> -hydroxybenzaldehyde	<i>o</i> -hydroxybenzaldehyde
Rate constant** (0°C)	2.5×10^{-2}	8.1×10^{-2}	7.6×10^{-7}	1.3×10^{-6}
Conditions which give comparable formation speeds	Temp., 0°C P_{BF_3} , 5 kg/cm ² P_{CO} , 5 kg/cm ² Speed, $\frac{35 \text{ M\%}}{5 \text{ min}}$	Temp., 0°C P_{BF_3} , 5 kg/cm ² P_{CO} , 1 kg/cm ² Speed, $\frac{40 \text{ M\%}}{5 \text{ min}}$	Temp., 50°C P_{BF_3} , 5 kg/cm ² P_{CO} , 300 kg/cm ² Speed, $\frac{23 \text{ M\%}}{5 \text{ min}}$	Temp., 50°C P_{BF_2} , 5 kg/cm ² P_{CO} , 300 kg/cm ² Speed, $\frac{8 \text{ M\%}}{5 \text{ min}}$

* Unpublished. ** Rate constant = $[kH_{CO}]$, [(kg/cm²)⁻¹ min⁻¹].

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