observed in the case of *o*-substituted phenyl acetate, but the polarity of the substituents existing on the benzene ring afforded remarkable effects on the exchange rate. The electron-attracting group on the benzene ring promoted the exchange reaction. Kinetic data showed that the reaction center of the ester was the carbonyl carbon atom. The nucleophilic reactant which was formed by the preliminary reaction attacked the reaction center in the ester, followed by the bond migration which was the true exchange step and was considered to be rate-determining step. The substituents on the benzene ring gave the polar effect on the rate-determining step.

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[Chem. Pharm. Bull.
13(3) 368~378 (1965)]

UDC 547.581.2.07.02.14

50. **Yukio Akahori** : Studies on Isotopic Acyl Exchange. IV.[*1] Acyl Exchange Reaction of Subtituted Phenyl Benzoates and Related Compounds; Effect of Acyl Group on the Exchange Rate.

(*Shizuoka College of Pharmacy*[*2])

In the previous papers,[*1], [1a,b] isotopic acyl exchange between phenyl acetates and acetic acid in pyridine was studied, and it was found that the exchange reaction consisted of the preliminary reaction and the true exchange step.[1a,b] The preliminary reaction was the rapid equilibrium reaction to which the acid and pyridine contributed, and the structural changes of the base affected the equilibrium and the change of equilibrium afforded effect on the exchange rate.[1b] The structural changes of the phenolic component in the ester gave the striking effects on the exchange rate, and the effect was due to the polarity of the substituents which was related to the rate-determining step.[*1] Thus the factors which govern the exchange rate were investigated except the effect of the structural change of acyl component in the ester. Since the structure of the ester was closely related to the rate-determining step,[*1] it is predicted that the exchange rate is affected by the structural changes of acyl group in the ester. Present paper deals with the study of effects on the exchange rate caused by structural changes of the acyl group in the ester.

Experimental

1) **Materials**——Substituted phenyl benzoates : Substituted phenols were dissolved in dry pyridine and the theoretical amounts of benzoyl chloride were added into the solutions, and the mixtures were allowed

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[*1] Part Ⅲ : This Bulletin, **13**, 361 (1965).

[*2] Oshika, Shizuoka (赤堀幸男).

1) *a*) Part I. Y. Akahori, S. Fukushima : This Bulletin, **12**, 166 (1964). *b*) Part Ⅱ. Y. Akahori : *Ibid*., **13**, 352 (1965).

2) A.L. Bernoulli, A. St. Goar : Helv. Chim. Acta, **9**, 763 (1926).

3) Schiaparelli : Gazz. chim. ital., **11**, 74 (1881); Beilstein, **H**, **9**, 118 (1926).

4) Hubner : Ann., **210**, 386 (1881); Beilstein, **H**, **9**, 118 (1926).

5) Neumann : Ber., **18**, 3320 (1884); Beilstein, **H**, **9**, 119 (1926).

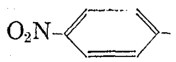
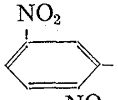
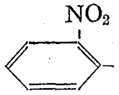
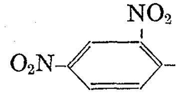
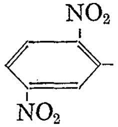
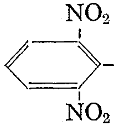
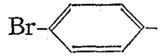
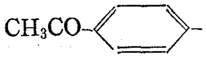
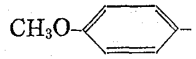
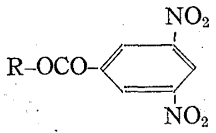
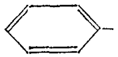
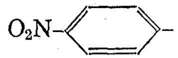
6) Kym : Ber., **32**, 1427 (1899); Beilstein, **H**, **9**, 119 (1926).

7) E. Fromm, R. Ebert : J. prak. Chem., **108**, 75 (1924); C.A., **18**, 3180 (1924).

8) E.B. Barnett, I.G. Nixon : Chem. News, **129**, 190 (1924); C.A., **19**, 260 (1925).

Table I. Properties of Phenyl Benzoates and Related Compounds

R-OCOC$_6$H$_5$

R	Cryst. form	Recryst. solvent	m.p. found	m.p. lit.	Calcd.				Found			
					C	H	N	Br	C	H	N	Br
	colorless rods	CHCl$_3$-MeOH	140	141[2)] 142[3,4)]	64.20	3.73	5.76	—	64.07	3.97	5.74	—
	colorless needles	MeOH	93	93[2)] 93~94[5)]	64.20	3.73	5.76	—	64.22	3.84	5.71	—
	colorless prisms	〃	58	55[3)] 58[4)] 59[5)]	64.20	3.73	5.76	—	64.18	3.87	5.73	—
	〃	CHCl$_3$-MeOH	128~129	132~133[6)]	54.17	2.80	9.72	—	54.20	3.02	9.84	—
	slight yellow needles	MeOH	112	—	54.17	2.80	9.72	—	54.27	3.11	9.46	—
	nearly colorless prisms	CHCl$_3$-MeOH	112	112[7)]	54.17	2.80	9.72	—	54.17	2.97	9.96	—
	colorless plates	MeOH	102.5~103	102~103[2)]	56.34	3.27	—	28.84	56.35	3.27	—	29.00
	colorless needles	CHCl$_3$-MeOH	132.5~133	—	74.99	5.03	—	—	74.71	4.99	—	—
	〃	MeOH	87~88	—	73.67	5.30	—	—	73.58	5.19	—	—
												
	colorless rod	acetone-MeOH	144	—	54.17	2.80	9.72	—	54.18	2.79	9.68	—
	colorless needles	〃	190	188[8)]	46.86	2.12	12.61	—	46.91	2.13	12.89	—

to stand at room temperature overnight. The solutions were poured into ice-water, and the resulting precipitates were dried *in vacuo*, followed by recrystallization from suitable solvents. Table I collected their properties.

Substituted phenyl 3,5-dinitrobenzoates: Phenols were acylated by means of 3,5-dinitrobenzoyl chloride and pyridine, and treated as described above. The properties of phenyl 3,5-dinitrobenzoates were shown in Table I.

Benzoic acid: Commercial benzoic acid was recrystallized from petr. ether, giving colorless needles, m.p. 121° (lit. m.p. 122.30°,[9] 122.375°[10]).

Benzoic acid (carboxyl-^{14}C): Benzoic acid (carboxyl-^{14}C) (0.7 mc./mmole) supplied from Daiichi Chem. Co. was diluted with stable benzoic acid in petr. ether, yielding colorless needles, 4.52×10^5 c.p.m./mmole, m.p. 121°.

3,5-Dinitrobenzoic acid (carboxyl-^{14}C): Benzoic acid (carboxyl-^{14}C) (4.52×10^5 c.p.m./mmole) was nitrated by the method of Brewster and Williams,[11] yielding nearly colorless prisms (from dil. MeOH), m.p. 204~206° (lit. m.p. 205~207°),[11] 4.46×10^5 c.p.m./mmole.

Pyridine and toluene were purified by the methods described in Part I.[1a)]

2) **Analytical Procedure**——a) Counting was carried out by the method described in Part I.[1a)]

b) Determination of kinetic rate was due to the method appeared in Part I.[1a)]

c) Reaction procedure: The exchange reaction was carried out in pyridine as shown in Part III.[*1] In the present study, labeled benzoic acid or labeled 3,5-dinitrobenzoic acid was used as the acid component, and the stable esters were employed.

d) Examination of the isolation method: Chemical and radiochemical purities of the reaction products were confirmed by the methods described in Part I,[1a)] and it was found that recrystallization from suitable solvents afforded the pure samples which could be used for counting.

In the case of 3,5-dinitrobenzoates, large amounts of pyridine were required to make the reaction-solution, and the recovery of the reaction product from the solution was not good.

For isolation of the reaction products, the rapid treatment was recommended to avoid troubles. No separation-induced exchange was found in all of the cases.

e) Examination of the counting method: Dinitrophenyl benzoates showed considerable quenching at higher concentrations, and the precise calibration was required for these esters. Since the quenching was quite sensitive to the concentration of the esters, the samples must be exactly weighed into the counting vials.

f) The labeled position in the reaction product was determined by the method described in Part I,[1a)] and it was confirmed that the carbonyl group in the ester was labeled.

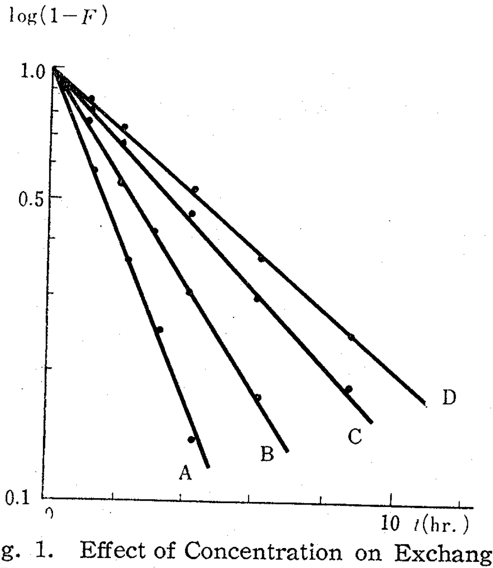
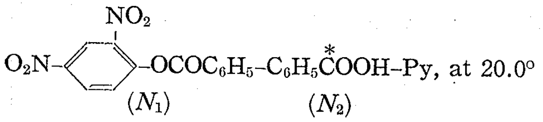


Fig. 1. Effect of Concentration on Exchange Rate


$O_2N\text{-}C_6H_3(NO_2)\text{-}OCOC_6H_5\text{-}C_6H_5\overset{*}{C}OOH\text{-}Py$, at 20.0°

(N_1) (N_2)

	N_1 (mole/L.)	N_2 (mole/L.)	$t_{1/2}$ (hr.)
A	0.622	2.590	1.6
B	0.711	1.422	2.4
C	0.771	0.771	3.4
D	0.412	0.830	4.3

Results

The observed values of specific radioactivities of the esters at equilibrium were identical with the calculated values, and

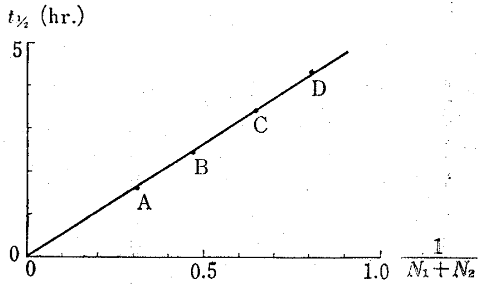
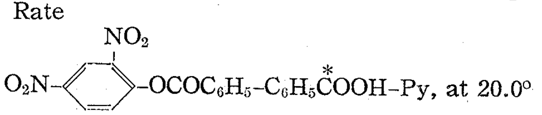


Fig. 2. Concentration Dependence of Exchange Rate


$O_2N\text{-}C_6H_3(NO_2)\text{-}OCOC_6H_5\text{-}C_6H_5\overset{*}{C}OOH\text{-}Py$, at 20.0°

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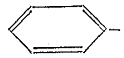
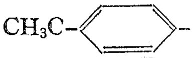
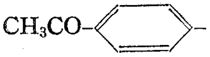
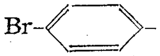
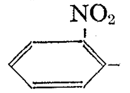
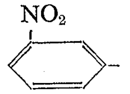
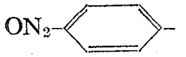
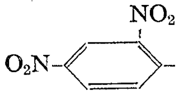
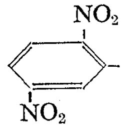
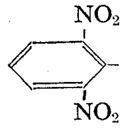
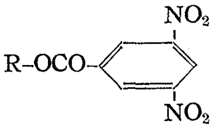
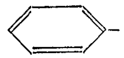
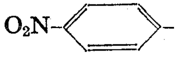
9) R.S. Jessup, C.B. Green: Bur. Stand. J. Res., **13**, 483 (1934); Beilstein, **II**, **9**, 75 (1949).
10) F.W. Schwab, E. Wichers: Bur. Stand. J. Res., **34**, 333 (1945); C. A., **39**, 4000 (1945).
11) R.Q. Brewster, B. Williams: Organic Synth., **III**, 337 (1955), Wiley.

the linearity of log $(1-F)$ *vs.* t was found in all of these cases, as shown in Fig. 1. The concentration dependency of the exchange rate was confirmed, as shown in Figs. 1 and 2, and it was concluded that the exchange rate R was dependent on concentration of the ester and that of the acid in the first order, respectively. The result was identical with the kinetic order obtained in the exchange reactions of phenyl acetates which are described in Part I[1a)] and Ⅲ.[*1] The rate constant k was calculated by the equation $R=kN_1N_2$, and the values were collected in Table Ⅱ. Phenyl benzoate and p-methoxy-, p-acetyl-, and p-bromo-phenyl benzoates showed extremely slow exchange, and their half-exchange times $t_{1/2}$ were inferred by extending the lines in diagram of log $(1-F)$ *vs.* t. Phenyl 3,5-dinitrobenzoate showed slow exchange reaction, and $t_{1/2}$ was deduced by the same method as described above. Consequently, the accurate values of k were not obtained for the five kinds of esters, and their approximate values were shown in Table Ⅱ.

Table Ⅱ. Exchange Rates of Phenyl Benzoates and Phenyl 3,5-Dinitrobenzoates

$R\text{-}OCOC_6H_5$

R	10^5k (L./mole/sec.)							E_a (Kcal./mole)
	65.0°	55.0°	45.0°	35.0°	25.0°	20.0°	17.0°	
	$<10^{-2}$	—	—	—	—	—	—	—
	$<10^{-2}$	—	—	—	—	—	—	—
	$<10^{-2}$	—	—	—	—	—	—	—
	$<10^{-2}$	—	—	—	—	—	—	—
	0.038	0.02	—	—	—	—	—	—
	10^{-2}	—	—	—	—	—	—	—
	0.054	0.03	—	—	—	—	—	—
	—	—	—	10.4	5.21	3.71	2.84	13.2
	13.9	7.35	3.58	1.67	—	—	—	14.6
	—	—	—	8.94	4.47	3.21	—	13.0
								
	$<10^{-2}$	—	—	—	—	—	—	—
	1.62	—	—	—	—	—	—	—

1) Effect of Substituents in the Phenol Ring

Increase of number of nitro group on the phenol ring afforded the promoting effect on the exchange rate. Methoxyl, acetyl and bromo groups on the phenol ring gave no promoting effect on the exchange rate. This tendency was in accordance with the results obtained in the exchange reactions of phenyl acetates, and it was concluded that the effect was due to the polarity of the substituents. No steric effect on the exchange rate caused by nuclear substituents in the phenol ring was observed in the cases of dinitrophenyl benzoates. The exchange rate of 2,4-dinitrophenyl benzoate was almost identical with that of 2,6-dinitrophenyl benzoate. The temperature dependency of the exchange rate was shown in Fig. 3, and E_a values for the reaction of these benzoates were shown in Table II, and no remarkable difference of the E_a value was found in the cases of these dinitrophenyl esters.

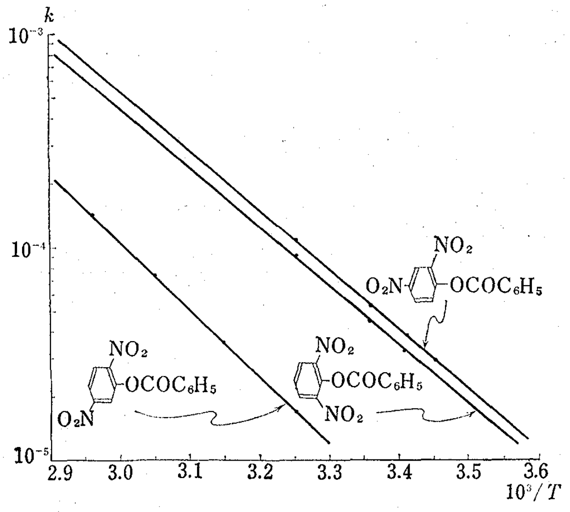


Fig. 3. Temperature Dependency of Exchange Rate of Dinitrophenyl Benzoate in Pyridine

2) Effect on the Exchange Rate of the Structure of the Acyl Group

The exchange reaction of benzoates was slower than that of the corresponding acetates, and the decreasing ratio of their exchange rates is in order of 10^{-2}. When nitro groups were introduced into the benzene ring of benzoic acid, the exchange reaction was promoted, as shown in the case of 3,5-dinitrobenzoate. The comparison of the exchange rates of acetate, benzoate and 3,5-dinitrobenzoate was illustrated in Table III.

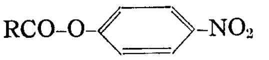
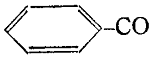
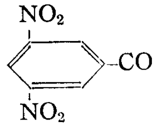
Discussion

Kinetic order of the exchange rate in the reaction of phenyl benzoates is in accordance with that of phenyl acetates, and this fact indicates the presence of the same reaction mechanism in these exchange reactions at least regarding to the rate-determining step.

The exchange reactions of phenyl acetates are faster than those of the corresponding phenyl benzoates, and the comparison of the exchange rates is shown in Table V. In the exchange reaction, the reaction center of the ester is the carbonyl carbon atom of which electropositivity may be affected by structural changes of the acyl component. Accordingly, it is expected that the rate of the exchange reaction of phenyl benzoate may be faster than that of phenyl acetate because of the stronger acidity of benzoic acid than that of acetic acid. The experimental data, however, showed the reversed result, and the reason may be attributed to the steric hindrance caused by the benzene ring. When the steric relation is kept under the same condition and the electropositivity of the carbonyl carbon atom is solely changed, the expected change of the exchange rate is observed. In the case of 3,5-dinitrobenzoate, the electropositivity of the carbonyl carbon atom is increased without accompanying any changes of steric relation with respect to this reaction center, and the increasing effect on the exchange rate due to the introduction of nitro groups is explained in the term of electropositivity. However, the increasing ratio is in order of 10^2 by introduction of two nitro groups, and the ratio is smaller than the increasing ratio caused by the introduction of nitro group into the phenol ring. The increasing ratio in the latter case is in order of 10^5 for introduction of two nitro groups, as shown in Table Ⅴ. Thus the polar effect on the exchange rate of the substituents in the benzene ring of benzoic acid is considerably smaller the effect caused by the substituents on the phenol ring. These facts are explained by the reaction mechanism described in Part Ⅲ[*1] where the rate-determining step was shown to be the bond migration step. The rate of the exchange reaction may be mainly governed by the polarity of the substituents present on the phenol ring, because lability of the ester bond which is present between the phenolic oxygen and the carbonyl carbon atom may be strongly affected by the polarity of the substituents on the phenol ring. The experimental data supports this inference.

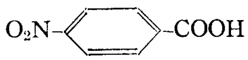
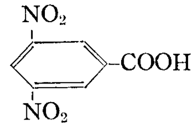
The mechanism for the exchange reaction is in part analoguous to the mechanism of base-catalyzed hydrolysis of esters, and the comparison of these two reactions affords interesting results. Table Ⅲ collected the comparison of the exchage rates of *p*-nitrophenyl esters (p-NO_2-C_6H_4-OCOR) and the rates of base-catalyzed hydrolysis of the

TABLE Ⅲ. Exchange Rates and Hydrolysis Rates

	Exchange rate 		Hydrolysis rate[b] RCO-OC_2H_5
RCO	10^5k[a]	relative rate	relative rate
CH_3CO	26. 2	485	16. 2[13]
	0. 054	1. 00	1. 00[12,14,15]
	—	—	110[12,14,15]
	1. 62	30. 0	—

a) in pyridine at 65.0°.
b) Base-catalyzed hydrolysis in 60% aq. acetone at 25°.

TABLE Ⅳ. Dissociation Constants of Carboxylic Acids

Acid	Ka[a]	References
CH_3COOH	1.77×10^{-5}	17)
C_6H_5COOH	6.31×10^{-5}	18)
	3.76×10^{-4}	19)
	1.57×10^{-3}	20)

a) at 25° in water.

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12) C. K. Ingold : "Structure and Mechanism in Organic Chemistry," p. 759 (1953), Cornell Univ. Press.
13) G. Davis, D. P. Evans : J. Chem. Soc., **1940**, 339.
14) R. L. Henbest Jr., M. E. Jacox : J. Am. Chem. Soc., **74**, 3004 (1952).
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16) C. K. Ingold : "Structure and Mechanism in Organic Chemistry," p. 754 (1953), Cornell Univ. Press.
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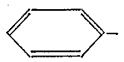
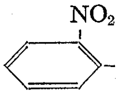
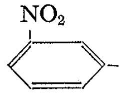
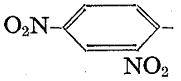
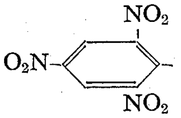
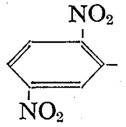
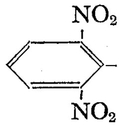
20) J. Kendall : J. Chem. Soc., **101**, 1275 (1912); C. A., **6**, 3043 (1912).

corresponding ethyl esters (C_2H_5-OCOR). Although the alcoholic components in the esters are different in these two series, their relative rates in both of the series can be compared as follows.

In the case of base-catalyzed hydrolysis of esters, it has been known that the reaction center of the ester is the carbonyl carbon atom and that the rate determining-step is the process in which the carbonyl carbon atom is attacked by hydroxyl ion.[16] In the exchange reaction, the reaction center in the ester is the same point, but the rate-determining step is different from that of hydrolysis. The rate-determining step in the exchange reaction is the bond migration step which corresponds to the leaving step in base-catalyzed hydrolysis of esters. The relation between the hydrolysis and the exchange reaction can be applied to explanation of differences appeared between the relative rates in both of the series.

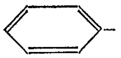
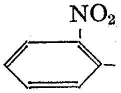
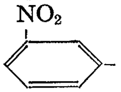
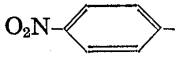
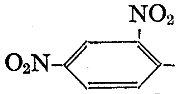
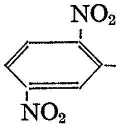
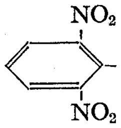
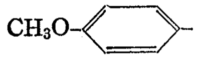
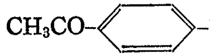
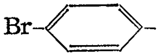
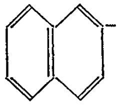
The ratio of the exchange rate of *p*-nitrophenyl acetate to that of *p*-nitrophenyl benzoate is more than thirty times as much as the ratio of the base-catalyzed hydrolysis rate of ethyl acetate to that of ethyl benzoate. The reason for the difference may be attributed to the difference of molecular sizes of the attacking groups. In the case of the exchange reaction, the attacking group is the bulky complex as described in Part II,[15] and the attacking process may be strongly affected by the steric effect. When the exchange reactions of acetates and benzoates are compared, the molecular size of the attacking group and steric shielding on the carbonyl carbon atom are smaller in the case of acetates than those of benzoates. Consequently, the rate of attacking process in the exchange reaction is retarded in the case of benzoate comparing with the case of acetate. In base-catalysed hydrolysis of esters, the magnitude of the steric shielding on the reaction center is almost same as the case of exchange reaction, but the attacking group is smaller in the case of hydrolysis comparing with the case of exchange reaction. Therefore, the steric effect on the rate of base-catalysed hydrolysis of esters is smaller than that of the exchange reaction, and the hydrolysis rates are mainly affected by the electropositivity of the carbonyl carbon atom (Table Ⅳ).

TABLE V. Relative Exchange Rates of Phenyl Esters
C_6H_5-OCOR

C_6H_5	$R=C_6H_5$	$R=CH_3$
	$<10^{-3}$	ca. 10^{-3}
	ca. 10^{-2}	1.15
	〃 10^{-2}	0.51
	〃 10^{-2}	1.00
	3.30	—
	0.57	ca. 240
	3.84	〃 370

Meanwhile, the ratio of the increase of the hydrolysis rate which is caused by the introduction of two nitro groups into benzoic acid largely exceeds the increasing ratio of the exchange rate which is due to the same structural change of acyl group. In the case of phenyl benzoate, the steric shielding on the carbonyl carbon atom is not affected by the structural change of benzoic acid; and the same steric relation is expected in the case of ethyl benzoate. The bulk of the attacking group in the case of exchange reaction is slightly altered by the structural change of benzoic acid, and the steric effect on the exchange rate caused by the structural change of acyl group may act in the same order as the effect on the hydrolysis rate. The electropositivity of the carbonyl carbon atom in the ester is strongly affected by the substituents on benzoic acid, and it results in the remarkable acceleration of the hydrolysis reaction. However, there is not observed the same effect on the exchange rate caused by the same structural change of benzoic acid, and it is indicated that the rate-determining step in the

TABLE VI. Relative Exchange Rates of Phenyl Esters and *pKa* of the Corresponding Phenols

R	Relative exchange rate of R-OCOR′ ($R'=CH_3$ or C_6H_5)	*pKa* of ROH	References
	ca. 10^{-3}	10.02	21)
	1.15	7.21	22)
	0.51	8.40	17)
	1.00	7.14	17)
	ca. 400	4.11	23)
	〃 200	5.22	17)
	〃 500	5.23	24)
	〃 10^{-3}	10.21	22)
	〃 10^{-1}	7.84	25)
	〃 10^{-3}	10.15	18)
	〃 10^{-3}	9.94	26)

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21) E. F. G. Herington, W. Kynaston: Trans. Faraday Soc., **53**, 138 (1957); C. A., **51**, 12607^b (1957).
22) A. I. Biggs: Trans. Faraday Soc., **52**, 35 (1956); C. A., **50**, 12606^e (1956).
23) R. G. Bates, G. Schwarzenbach: Helv. Chim. Acta, **37**, 1069 (1954).
24) S. Kertes: J. Chem. Soc., **1955**, 1386.
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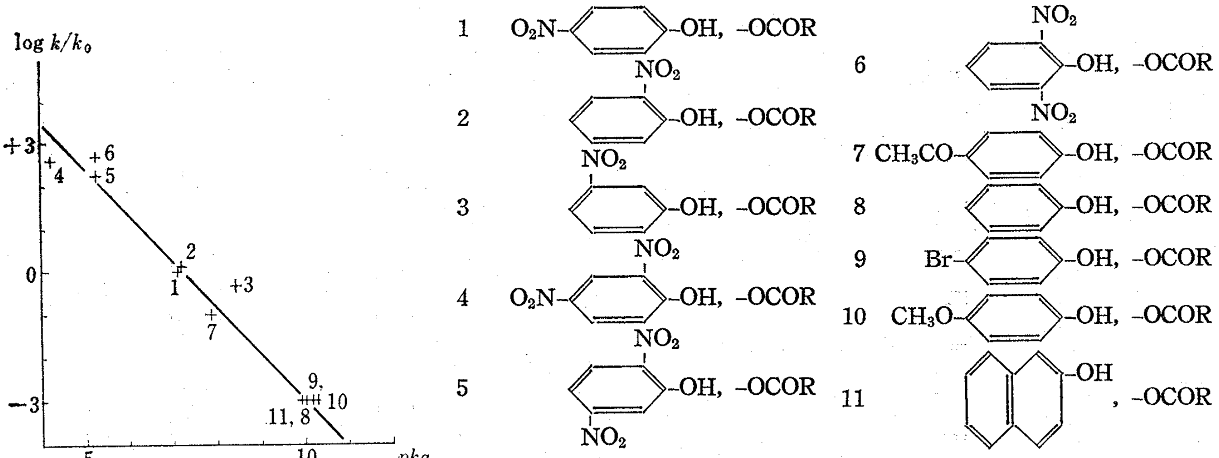
exchange reaction is not the attacking process but the bond migration step which follows the attacking process. Therefore, the exchange rate is mainly affected by the lability of the ester bond, and it can be understood that the exchange rate is mainly due to the polar effect of the substituents existed on the phenol ring. Besides, the effect of *pKa* change of the acid on the preliminary equilibrium may act in the same order as that of the base, and the effect may be smaller than the effect due to the polarity of substituents existed on the phenol ring.

Concerning the effect on the exchange rate due to the substituents on the phenol ring, the series of benzoates show the same feature as the series of acetates, as shown in Table V. This relation means the existence of the same rule which governs the exchange rate of acetates and that of benzoates. Using this relation, the polar effects due to the substituents existed on the phenol ring can be estimated throughout the series, and the relative exchange rates are obtained. The relative exchange rates are compared with the acidities of the corresponding phenols, and their relations are shown in Table VI. When the relative exchange rates are plotted in logarithmic scale against *pKa* values of the corresponding phenols, the linear relationship is obtained as shown in Fig. 4. It may be reasonable to suppose the parallel relation between *pKa* value of the corresponding phenol and lability of the ester bond which combines the phenolic oxygen with the carbonyl carbon atom. Since the bond migration step is the rate-determining step, the exchange rate is determined by the lability of the ester bond. Accordingly, it is expected that the exchange rates are related to *pKa* values of the corresponding phenols. This inference is supported by the linear relation in Fig. 4.



k_0: Exchange rate of *p*-nitrophenyl ester

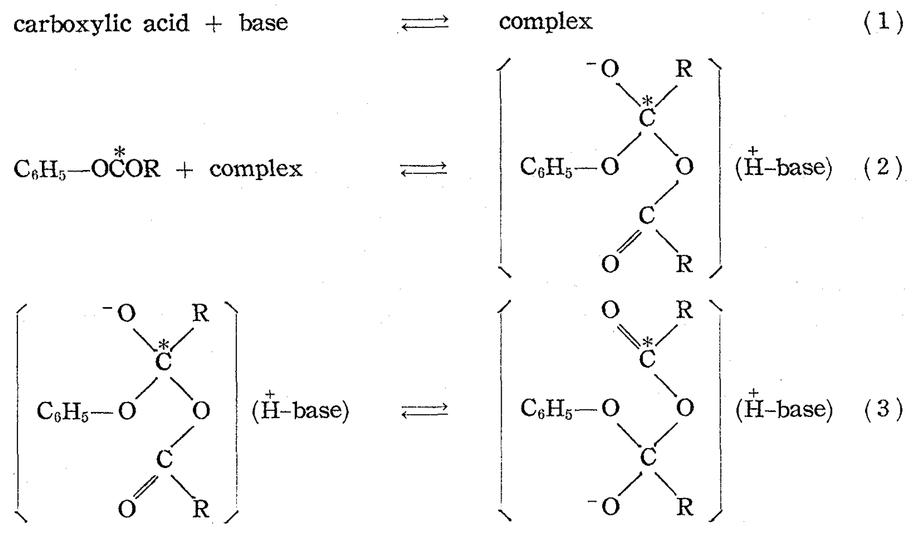
Fig. 4. Relationship between Exchange Rate and Dissociation Constant of the Corresponding Phenol

The reaction mechanism proposed for the exchange reaction can explain all of the experimental evidences, and the general mechanism for the acyl exchange reaction is shown in Scheme 1.

Conclusion

The rates of the exchange reaction between various phenyl esters and the corresponding carboxylic acids in the presence of various bases are expressed by McKay's formula. The exchange rate is affected by structural changes of each component, and the mechanisms are explained as follows.

The structural change of base affects the preliminary equilibrium (1), and the structural change of acyl component affords effects on the recction (2) and partly on



Scheme 1.

the preliminary equilibrium (1). The rate-determining step (3) is affected by the substituents existing on the phenol ring. The reaction (3) is analogous to SNi mechanism[27,28] with respect to the steric course, and this is different from the mechanism of base-catalysed hydrolysis of esters.

The structure of the product formed by the preliminary reaction (1) may be severely influenced by the mole-fraction of each component. In the case of exchange reaction undertaken in pyridine, it is most probable that the preliminary reaction produces the hydrogen-bonding complex which is transformed into the ion-pair complex when the ester approaches to the hydrogen-bonding complex. The resulting complex participates to the true exchange reaction. The rate of the true exchange step (3) is related to lability of the ester bond, and accordingly, the exchange rate shows relation with *pKa* value of the corresponding phenols.

In the case of dinitrophenyl esters, contribution of the Meisenheimer's complex to the exchange reaction can not be excluded, but Scheme 1 is supposed to be most probable even in this case.

The main factor which controls the exchange rate is the polar effect of the substituents existed on the phenol ring. The other factors afford the secondary effects on the exchange rate, and they are weaker than the effect caused by the substituents on the phenol ring.

Accordingly, the exchange rate can be predicted by the reaction conditions, *i.e.*, structure and concentration of each component and temperature.

The exchange rate of phenyl esters may represent the lability of the acyl group, and the high reactivity of *p*-nitrophenyl acetate[29] which has been applied to synthetic works[29,30] can be understood from this viewpoint.

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27) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, A. D. Scott : J. Chem. Soc., **1937**, 1252.
28) D. J. Cram : J. Am. Chem. Soc., **75**, 332 (1953).
29) R. S. Schwyzer, A. Costopanagiotis, P. Sieber : Helv. Chim. Acta, **46**, 870 (1963).
30) R. Gllatthard, M. Matter : *Ibid.*, **46**, 795 (1963).

Summary

The exchange reaction of various phenyl benzoates took place in pyridine, and the kinetic order showed identity with the result of phenyl acetates. The exchange reactions of phenyl benzoates were generally slower than that of the corresponding acetates. Relative rates of the exchange reactions were compared with that of the base-catalysed hydrolysis, and the effect on the exchange rate caused by the structural change of acyl component was attributed to the steric and electronic effects on the reaction of the ester. These effects were smaller than polar effect caused by the substituents on the phenol ring. The rate-determining step was controlled by lability of the ester bond, which was related to *pKa* values of the corresponding phenols.

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