Tetrahedron. Vol. 28, pp. 217 to 225. Pergamon Press 1972. Printed in Great Britain

KINETICS OF THE FRIEDEL–CRAFTS ACYLATION OF BENZENE WITH ALKANOYL CHLORIDES

I. HASHIMOTO,* A. KAWASAKI and Y. OGATA
Department of Applied Chemistry, Faculty of Engineering,
Nagoya University, Chikusa-ku, Nagoya, Japan

(*Received in Japan* 24 *March* 1971; *Received in the UK for publication* 17 *August* 1971)

Abstract—The Friedel–Crafts acylation of benzene with some alkanoyl chlorides has been kinetically studied in ethylene dichloride. At higher initial concentration of the RCOCl–$AlCl_3$ addition complex, simple second-order kinetics are observed, and the relative rates of studied alkanoyl chlorides fit Taft's equation with ρ^* of 3·26 and δ of 0·39. A sequence of reactivities, β-chloropropionyl > phenylacetyl > acetyl > propionyl > *n*-butyryl > isobutyryl > cyclohexanecarbonyl chloride, is observed at 10°. But at lower initial concentration of RCOCl–$AlCl_3$ complex, the second-order rate constant increases with initial concentration of complex. A mechanism involving a pre-equilibrium in the formation of the complex between RCOCl and $AlCl_3$ is presented and discussed.

INTRODUCTION

THERE are countless reports as to the reaction mechanism of Friedel–Crafts acylation,[2] but data on acyl halide reactivity in the acylation are few and are mainly qualitative.[3] Recently, kinetic studies on the relative reactivity of several alkanoyl chlorides in the Friedel–Crafts acylation of mesitylene and benzene have been determined by a competitive method.[4] There is a correlation between the relative rate constant and Taft's polar substituent constant (σ^*) for the alkyl groups in acyl chlorides with ρ^* value of *ca.* 4·0, although this is a rough estimate. For the acylation of toluene with a series of substituted benzoyl chlorides,[5] the available relative rate constant does not give a linear correlation with Hammett's σ, and strangely the rate constant depends on the initial concentration of acyl chloride–$AlCl_3$ complex. Slootmaekers[6] suggested two competitive pathways for the Friedel–Crafts benzoylation, i.e., the reaction of RCOCl–$AlCl_3$ with toluene and with a complex RCOCl–$AlCl_3$–toluene. However, there is some ambiguity in the stability and reactivity of such an intermediate. It is the purpose of the present study to carry out the systematic acylation of benzene with a series of alkanoyl chlorides of known Taft's σ^* values and to elucidate a detailed mechanism through the evaluation of the substituent effect in alkanoyl chlorides as acylating agents.

RESULTS

The kinetics of the homogeneous reaction in ethylene dichloride has been established in acetylation or benzoylation of aromatic hydrocarbons.[7] The rate is second-order, i.e., first-order in aromatic hydrocarbon and first-order in acyl halide–$AlCl_3$ complex (Eq 1). The rate-determining step may be a bimolecular electrophilic attack of the acyl halide–$AlCl_3$ complex on aromatic hydrocarbon (Eq 2).

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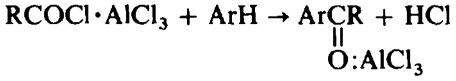
* Present address: Department of Industrial Chemistry, Wakayama Technical College, Gobo, Wakayama.

$$v = k_a[\mathrm{ArH}][\mathrm{RCOCl{\cdot}AlCl_3}] \qquad (1)$$



$$\mathrm{RCOCl{\cdot}AlCl_3} + \mathrm{ArH} \rightarrow \mathrm{Ar}\underset{\underset{\mathrm{O:AlCl_3}}{\|}}{\mathrm{C}}\mathrm{R} + \mathrm{HCl} \qquad (2)$$

The rate of acylation can be followed by measuring the extinction of product alkyl aryl ketone by means of UV spectrophotometry. Second-order rate constants were graphically determined from the plot of $\log(a - x)/(b - x)$ vs. time, in which a and b are the initial concentrations of benzene and acyl chloride–$AlCl_3$ complex, respectively and x is the concentration of product. Rates were followed to *ca.* 55% conversion, where spectrophotometry becomes difficult. The rate data are shown in Table 1.

TABLE 1. RATE CONSTANTS FOR THE $AlCl_3$-CATALYZED ACYLATION OF BENZENE WITH VARIOUS ALKANOYL CHLORIDES (RCOCl) IN ETHYLENE DICHLORIDE

Run	Substituent (R-)	Temp.	Concentration of reactant mole.lit^{-1}			Second-order rate constant $k_a \times 10^3$ lit.mole^{-1}·sec^{-1}
			C_6H_6	$AlCl_3$	RCOCl	
1	$ClCH_2CH_2$	30	0·04	0·01	0·01	—
2		30	0·04	0·015	0·015	—
3		30	0·04	0·02	0·022	3·93
4		30	0·04	0·04	0·044	9·42
5		30	0·04	0·06	0·066	12·6
6		40	0·04	0·04	0·044	21·8
7		10	0·04	0·04	0·044	0·67
8		10	0·20	0·20	0·22	5·83
9	$C_6H_5CH_2$	30	0·07	0·0175	0·0193	4·09
10		30	0·07	0·035	0·0385	4·82
11		30	0·07	0·07	0·077	7·10
12		30	0·07	0·105	0·1155	7·86
13		40	0·07	0·07	0·077	13·3
14		10	0·07	0·07	0·077	1·38
15		10	0·20	0·20	0·22	1·90
16	CH_3	30	0·20	0·025	0·05	1·95
17		30	0·20	0·05	0·05	2·42
18		30	0·20	0·05	0·075	2·66
19		30	0·20	0·05	0·10	2·73
20		30	0·20	0·05	0·15	2·73
21		30	0·20	0·05	0·20	2·75
22		30	0·20	0·10	0·11	3·10
23		30	0·20	0·20	0·22	3·78
24		30	0·20	0·30	0·33	4·09
25		10	0·20	0·20	0·22	0·63
26		45	0·20	0·20	0·22	8·97
27		30	0·20	0·20	0·20	1·58
28		30	0·40	0·20	0·20	1·55
29		30	0·60	0·20	0·20	1·59
30		30	0·20	0·20	0·30	1·65
31		30	0·20	0·20	0·40	1·84

TABLE 1—*continued*

Run	Substituent (R-)	Temp.	Concentration of reactant			Second-order rate constant $k_a \times 10^3$ lit. mole^{-1}. sec^{-1}
			C_6H_6	$AlCl_3$ mole. lit^{-1}	RCOCl	
32	C_2H_5	30	0·20	0·025	0·025	0·55
33		30	0·20	0·05	0·05	0·82
34		30	0·20	0·075	0·075	1·35
35		30	0·20	0·10	0·10	1·43
36		30	0·20	0·30	0·30	1·83
37		30	0·20	0·40	0·40	2·37
38[a]		30	0·20	0·20	0·20	1·74
39		10	0·20	0·20	0·22	0·43
40		45	0·20	0·20	0·22	4·76
41	*n*-C_3H_7	30	0·20	0·05	0·05	0·84
42		30	0·20	0·10	0·11	1·09
43		30	0·20	0·20	0·22	1·48
44		30	0·20	0·30	0·33	1·59
45		10	0·20	0·20	0·22	0·31
46		45	0·20	0·20	0·22	4·17
47	*cyclo*-C_6H_{11}	30	0·20	0·05	0·05	0·292
48		30	0·20	0·10	0·11	0·556
49		30	0·20	0·20	0·22	0·706
50		20	0·20	0·20	0·22	0·225
51		10	0·20	0·20	0·22	0·077
52	*i*-C_3H_7	30	0·20	0·05	0·05	0·310
53		30	0·20	0·10	0·11	0·345
54		30	0·20	0·20	0·22	0·430
55		30	0·20	0·30	0·33	0·499
56		10	0·20	0·20	0·22	0·089
57		45	0·20	0·20	0·22	1·41

[a] Addition of a mixture of $C_6H_5COC_2H_5$ and $AlCl_3$.

In general, the rate constants for the $AlCl_3$-catalyzed acylation of benzene with a series of alkanoyl chlorides obey second-order kinetics, $v = k_a[C_6H_6][RCOCl{\bullet}AlCl_3]$. But the rate constants (k_a) depend on the initial concentration of the $RCOCl–AlCl_3$ complex as shown in Fig 1. Thus, the acylation with β-chloropropionyl chloride deviated from second-order to third-order kinetics at below 0·04M and the reaction is inhibited below 0·01M. The analogous observation has been reported by other workers.[8] The rate constant was independent of the initial concentration of benzene (Runs 27–29) and was affected slightly by alkanoyl chloride concentration, when in slight excess (Runs 17–21, 30, 31).

The rate constants with alkanoyl chlorides relative to acetyl chloride at 0·2M at 10° and activation parameters calculated from the rate data are listed in Table 2.

The order of rate constants is: β-chloropropionyl > phenylacetyl > acetyl > propionyl > *n*-butyryl > *i*-butyryl > cyclohexanecarbonyl chloride.

A plot of the logarithm of the relative apparent rate constants *vs.* Taft's polar substituent constants (σ^*) of the alkyl groups in alkanoyl chlorides gives a poor

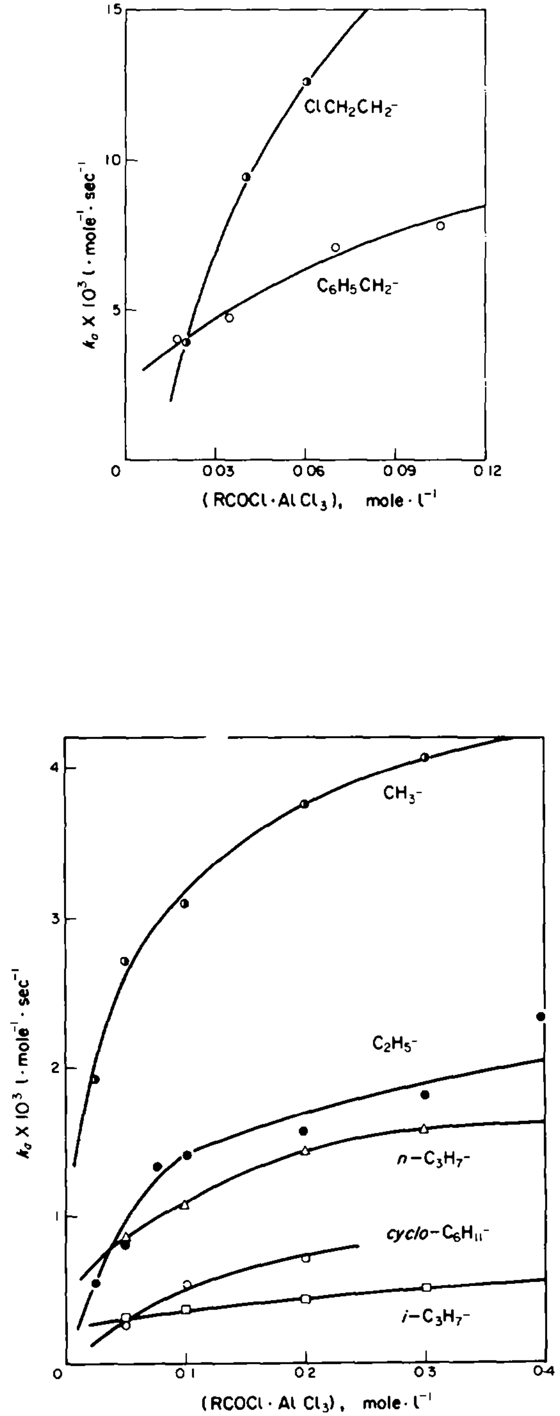


Fig 1. Effect of the initial concentration of RCOCl · AlCl$_3$ complex on the second-order rate constants for the acylation in ethylene dichloride at 30°

TABLE 2. RELATIVE RATE CONSTANTS *vs.* ACETYL CHLORIDE AT 10° AND ACTIVATION PARAMETERS AT 30° FOR THE $AlCl_3$-CATALYZED ACYLATION OF BENZENE WITH VARIOUS ALKANOYL CHLORIDES

Alkanoyl chloride (RCOCl) R—	Relative rate[a] k/k_0	σ^*	E_s	$\Delta H^\ddagger$ kcal/mole	$-\Delta S^\ddagger$ e.u.
$ClCH_2CH_2$	9·25	0·385	−0·90	17·7	10·0
$C_6H_5CH_2$	3·02	0·215	−0·38	13·0	25·7
CH_3	1	0	0	13·2	26·4
C_2H_5	0·68	−0·100	−0·07	11·6	32·8
n-C_3H_7	0·49	−0·115	−0·36	12·8	29·3
cyclo-C_6H_{11}	0·12	−0·15	−0·79	18·8	10·9
i-C_3H_7	0·14	−0·19	−0·47	13·5	29·2

[a] Initial Concns: $[RCOCl\cdot AlCl_3]$ = 0·2 mole/l; $[C_6H_6]$ = 0·2 mole/l.

linear relationship (r = 0·94). However, taking into account the steric substituent constants (E_s), a considerable improvement of correlation coefficient was obtained with a least square treatment (r = 0·983).

$$\log(k_a/k_0) = 3{\cdot}26\,\sigma^* + 0{\cdot}39\,E_s + 0{\cdot}03$$

The ρ^* value obtained here (ρ^* = 3·26) is smaller than reported.[4] Therefore, the acylation must be affected by both polar and steric effects in alkanoyl chlorides. The observed values of enthalpy and entropy of activation for acetyl, propionyl, *n*-butyryl, *i*-bytyryl or phenylacetyl chlorides, which is less sterically hindered, are small than those for β-chloropropionyl or cyclohexanecarbonyl chlorides.

There is a linear relationship between entropy and enthalpy of activation as shown in Fig 3 (r = 0·96).

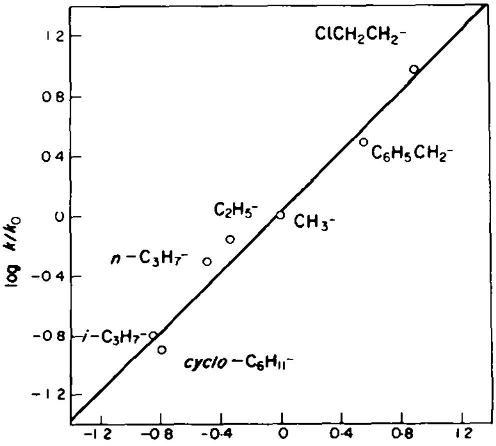


FIG 2. Correlation of the relative rate constants in the $AlCl_3$-catalyzed acylation of benzene with alkanoyl chlorides *vs.* Taft's polar and steric substituent constants in ethylene dichloride at 10°

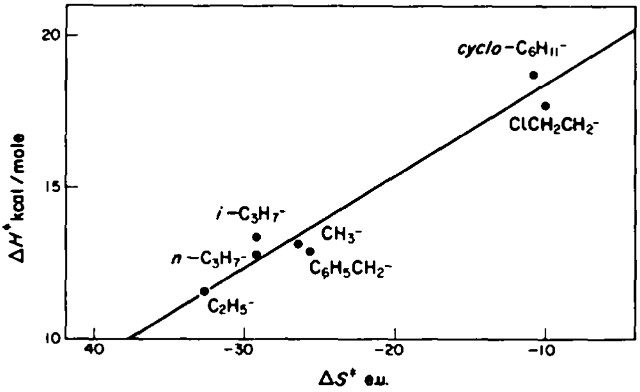


FIG 3. Isokinetic relationship in the $AlCl_3$-catalyzed acylation of benzene in ethylene dichloride at 30°

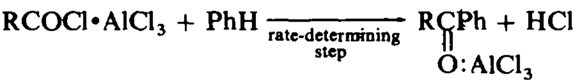
The isokinetic temperature calculated from the slope of a plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ is *ca.* 296°K, which lies close to the midpoint of the experimental temperatures (10–45°). On the other hand, at the temperature of 10°, a plot of the relative rate *vs.* Taft's polar and steric substituent constants gives a good straight line with a rather large ρ^* value. These results are puzzling, since it is generally believed that little substituent effect appears at the isokinetic temperature.[9] However, this may be explained as follows: if two or more interaction mechanisms (i.e., polar and steric) in a reaction exist, in which one predominates, an approximate linear free energy relationship is often observed but the isokinetic temperature obtained is not accurate.[9] This is the case, since the polar substituent effect in the present reaction is ten times as large as the steric effect at 10°.

DISCUSSION

The above results reveal that the rate of the $AlCl_3$-catalyzed acylation of benzene with a series of alkanoyl chlorides at the high initial concentration of $RCOCl$–$AlCl_3$ complex (0·2M) is expressed as:

$$v = k_a[C_6H_6]\,[RCOCl\bullet AlCl_3]$$

The formation of 1 : 1 complex between alkanoyl chloride and $AlCl_3$ is well known.[10] It is also supported by the fact that the presence of alkanoyl chloride over an equivalent amount of $AlCl_3$ has little affect on the acylation rate. High initial concentration of the complex results in a clear-cut substituent effect. Hence, a bimolecular electrophilic attack of the complex on benzene should be rate-determining.



$$RCOCl\bullet AlCl_3 + PhH \xrightarrow[\text{rate-determining step}]{} R\underset{\underset{O:AlCl_3}{\|}}{C}Ph + HCl$$

But our kinetic evidence gives no further speculation on the structure of activated species of acylating agent.

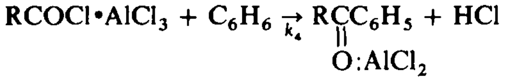
Although the rate constant depends also on the initial concentration of the RCOCl–$AlCl_3$ complex at its lower concentrations, this tendency is large in such acyl chlorides with electron-withdrawing groups as β-chloropropionyl or phenylacetyl chlorides, while it is small in cyclohexanecarbonyl or *i*-butyryl chlorides with electron-releasing groups. This observation suggests: (i) two competitive pathways involving the reactions of RCOCl–$AlCl_3$ with ArH and with RCOCl–$AlCl_3$–ArH; (ii) an increase of rate with increasing polarity of medium due to the complex of product ketone–$AlCl_3$:[11] (iii) a change in reaction mechanism with the variance of acyl chlorides. The explanation (i) is unacceptable because of the independence of the second-order rate constant on the concentration of benzene. The explanation (ii) is also denied by the little change of rate on addition of a mixture of product ketone and $AlCl_3$ to the reaction system, and explanation (iii) may be excluded by the presence of an isokinetic relationship.

This observation is explicable as follows. A dissociative equilibrium of the RCOCl–$AlCl_3$ complex in nitrobenzene is well known, i.e., the RCOCl–$AlCl_3$ complex collapses partly by formation of the $PhNO_2$–$AlCl_3$ complex.[12]

$$RCOCl{\bullet}AlCl_3 + PhNO_2 \rightleftharpoons RCOCl + PhNO_2{\bullet}AlCl_3$$

Similarly, for the present reaction in ethylene dichloride the equilibrium between acyl chloride and $AlCl_3$ forming the complex is expected at the very low concentration, especially with acyl chlorides having electron-withdrawing substituents. The above results suggest the following equations for the acylation,

$$RCOCl + AlCl_3 \overset{K_3}{\rightleftharpoons} RCOCl{\bullet}AlCl_3 \qquad (3)$$



$$RCOCl{\bullet}AlCl_3 + C_6H_6 \xrightarrow[k_4]{} R\underset{\underset{O:AlCl_2}{\|}}{C}C_6H_5 + HCl \qquad (4)$$

where K_3 and k_4 are equilibrium and rate constants of subscripted steps. Therefore, the overall rate is expressed as:

$$v = k_4K_3[C_6H_6]\,[RCOCl]\,[AlCl_3] \qquad (5)$$

where [RCOCl], $[AlCl_3]$ and $[C_6H_6]$ are actual concentrations. Since these values can not be estimated directly, the stoichiometric concentrations, $[RCOCl]_s$ and $[AlCl_3]_s$, must be used to express them.

$$[AlCl_3]_s = [AlCl_3] + [RCOCl{\bullet}AlCl_3] = [AlCl_3]\,\{1 + K_3[RCOCl]\} \qquad (6)$$

$$[RCOCl]_s = [RCOCl] + [RCOCl{\bullet}AlCl_3] = [RCOCl]\,\{1 + K_3[AlCl_3]\} \qquad (7)$$

Since $[AlCl_3]_s$ is nearly equal to $[RCOCl]_s$ in this experiment, $[AlCl_3]$ may be nearly equal to [RCOCl], assuming the formation of the 1:1 complex. Hence,

$$[AlCl_3] = [RCOCl] = \frac{-1 + \sqrt{1 + 4K_3[AlCl_3]_s}}{2K_3} \qquad (8)$$

Thus, the overall rate law approximates to:

$$v = k_4[C_6H_6]\frac{2K_3\{[AlCl_3]_s\}^2}{1 + 2K_3[AlCl_3]_s + \sqrt{1 + 2K_3[AlCl_3]_s}} \qquad (9)$$

On the other hand, the observed rate equation is expressed as:

$$v = k_a[C_6H_6]\,[AlCl_3]_s \tag{10}$$

Combination of Eq 9 with Eq 10, the apparent second-order rate constant is given by:

$$k_a = k_4 \frac{2K_3[AlCl_3]_s}{1 + 2K_3[AlCl_3]_s + \sqrt{1} + +4K_3[AlCl_3]_s} \tag{11}$$

If $2K_3[AlCl_3]_s \gg 1$,

$$k_a = k_4 \tag{12}$$

The second-order rate equation should be observed at high initial concentrations of RCOCl–$AlCl_3$ complex, Eq 4 being rate-determining. Also a positive ρ^* value supports this assumption. The complex formation (Eq 3) is almost complete at 0·2M, hence the observed ρ^* value (3·26) reflects the polar effect on k_4, i.e., the rate of rate-determining step (Eq 4).

If $2K_3[AlCl_3]_s \ll 1$, Eq 11 is transformed to

$$k_a = k_4K_3[AlCl_3]_s \tag{13}$$

Since $[AlCl_3]_s$ is involved in the apparent second-order rate constant (k_a), the reaction should be third-order. A negative ρ^* value may be expected for K_3, since an electrophilic attack of electron deficient $AlCl_3$ on the carbonyl oxygen in acyl chloride is involved in Eq. 3. However, since the polar effect on k_4 is much more important than that on K_3, the overall effect on apparent rate constant (k_a) should give a positive ρ^* value. Hence, the rate tends to be third-order with an increase in electron-withdrawing effect of alkyl substituent in acyl chloride, particularly at the low concentration of the complex.

EXPERIMENTAL

Commercial acetophenone was purified by rectification, b.p. 202°. The other alkyl phenyl ketones were prepared by Friedel–Crafts acylation.[13] Propiophenone, b.p. 215°; *n*-butyrophenone, b.p. 97–98° (7 mm); isobutyrophenone, b.p. 121–122° (32 mm); cyclohexyl phenyl ketone,[14] m.p. 55·5–56°; desoxybenzoin,[15] b.p. 155° (4 mm), m.p. 55–56°; β-chloropropiophenone,[16] m.p. 49°. Benzene was purified by the ordinary method, distilled and stored on Na. Anhydrous $AlCl_3$ was prepared by the reaction of Al metal with dry gaseous HCl and sublimed in a long glass system. Ethylene dichloride was washed with H_2SO_4, water, dried (KOH and P_2O_5) and fractionated, b.p. 83°. Acetyl chloride and *n*-butyryl chloride were of purest grade. Other acyl chlorides were prepared according to the previous procedures.[17] Propionyl chloride,

TABLE 3. ABSORPTION SPECTRA OF ALKYL PHENYL KETONES IN METHANOL

Ketone	λ_{max}, mμ	log ε_{max}
Acetophenone	240	4·1
Propiophenone	240	4·1
n-Butyrophenone	240	4·1
Isobutyrophenone	243	4·1
Cyclohexyl phenyl ketone	243	4·1
Desoxybenzoin	242	4·1
β-Chloropropiophenone	241	4·1

b.p. 77·5–78°; isobutyryl chloride, b.p. 92·2–92·5°; phenylacetyl chloride,[15] b.p. 113° (34 mm); cyclohexanecarbonyl chloride,[18] b.p. 185°; β-chloropropionyl chloride,[19] b.p. 60·5–61° (38 mm).

General acylation. An ethylene dichloride solution of the complex of $AlCl_3$ and acyl chloride was prepared by dissolving two components with stirring at 0° for 1 hr. The solution was added to a solution containing a known amount of benzene in ethylene dichloride and the reaction started at 30° under a flow of N_2. The pressure in the system which is a little higher than the atmospheric pressure, prevented the intrusion of moisture. Aliquots (15 ml) were taken and quenched by ice-water. Organic layers were then separated with ether (15 ml), washed with 10% NaOH aq, water and dried (Na_2SO_4). The solution was diluted with MeOH and analyzed by UV spectrophtometry employing a Hitachi 124 spectrophotometer.

Kinetics and product analysis. The rates were measured by the rate of appearance of alkyl phenyl ketone determined by spectrophotometry. The used wave lengths and extinction coefficients for alkyl phenyl ketones are listed in Table 3. The UV spectra were compared with those of the methanolic solution (10^{-5}M) of authentic samples of the alkyl phenyl ketones to confirm the quantitative acylation.

Second-order rate constants were calculated by the ordinary second-order equation:

$$dx/dt = k_s(a - x)(b - x) \tag{14}$$

where a and b are initial concentration of benzene and $AlCl_3$-RCOCl complex, respectively. The value of x at time t was calculated by means of Eq 15, where ε_K and ε_B are extinction coefficients of alkyl phenyl ketone and benzene, respectively.

$$E = \varepsilon_B(a - x) + \varepsilon_K x \tag{15}$$

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