Table 4. The Powder X-ray Diffraction Data for (BaLa)(MgMo)O_6

h k l	d_o	d_c	I_o	$I_c(I)$	$I_c(II)$	$I_c(III)$	$I_c(IV)$
1 1 1	4.634	4.630	9	0.0	8.4	8.4	0
2 0 0	4.011	4.010	11	11.4	11.4	11.4	11.4
2 2 0	2.835	2.835	100	100	100	100	100
* 3 1 1	2.416	2.418	5	0.0	5.1	5.1	0
2 2 2	2.314	2.315	15	18.0	18.0	18.0	18.0
4 0 0	2.005	2.005	31	34.3	34.3	34.3	34.3
* 3 3 1	1.839	1.840	4	0.0	2.3	2.3	0
4 2 0	1.793	1.793	5	5.4	5.4	5.4	5.4
4 2 2	1.636	1.637	38	40.2	40.2	40.2	40.2
* 3 3 3	1.544	1.543	2	0.0	0.4	0.4	0
* 5 1 1	1.544	1.543		0.0	1.3	1.3	0
4 4 0	1.416	1.418	16	20.5	20.5	20.5	20.5
* 5 3 1	1.356	1.356	1.3	0.0	1.7	1.7	0
4 4 2	1.337	1.337	3	2.3	2.3	2.3	2.3
6 0 0	1.337	1.337		0.6	0.6	0.6	0.6
6 2 0	1.267	1.268	15	17.5	17.5	17.5	17.5
Reliability factor (%)				23.6	5.0	5.0	23.6

All the definitions as the same as in Table 2 except that Ba^{2+} is substituted for Ca^{2+}.

on the assumption that only B-site ions (Mg^{2+} and Mo^{5+}) are ordered. The reliability factor corresponding to $I_c(II)$, 9.8%, has the smallest value. From these facts, we can conclude that in (CaLa)(MgMo)O_6 only the Mg^{2+} and Mo^{5+} ions have a rock-salt arrangement (1:1 ordering) in the B-sites of the perovskite lattice, while Ca^{2+} and La^{3+} ions are randomly distributed in the oxygen-cuboctahedral A-sites. In case of (SrLa)(MgMo)O_6 (Table 3), Only B-site cations are ordered as (CaLa)(MgMo)O_6, comparing the observed intensities with calculated ones. In (BaLa)(MgMo)O_6, however, whether

both A and B-sites ions are ordered or only B-site ions are ordered cannot be distinguished from the intensity calculation (see the column $I_c(II)$ and $I_c(III)$ in Table 4), because the atomic scattering factors of Ba^{2+} and La^{3+} ions are almost the same. However, judging from the result of (CaLa)(MgMo)O_6 and (SrLa)(MgMo)O_6, it would be most probable that Ba^{2+} and La^{3+} ions are also distributed randomly in the oxygen-cuboctahedral A-sites.

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Substituent Effect in the Pyridinolysis of Substituted Phenyl Acetates

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We have previously reported our studies[1] of the pyridinolysis of substituted phenyl acetates in acetonitrile by using ρ_X and ρ_Y. In a through analysis of the mechanism, it reveals that the important thing is to evaluate contribution of the three moieties (substrate, nucleophile, and leaving group) to overall stabilization of the transition state. Knowing the theoretical analysis of the interaction terms, $\rho_{XY}\sigma_X\sigma_Y$, by the Taylor[2] expansion, we first attempted to analyze by experiments.[3-6] In this paper, prior to the study above three moieties, we report the contribution of the two moieties of leaving group and nucleophile.

ρ_X values grow progressibly greater from σ_Y of electron-withdrawing group (EWG) to electron-donating one (EDG) of
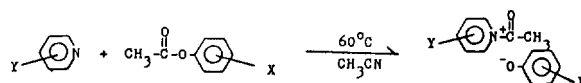
nucleophiles, which indicates that the ρ_X is a function of ρ_Y, but the values are very little and not so large dependence of substituents of nucleophile (Table 2(b)). On the other hand, ρ_Y values are negatively large by change of ρ_X value from EWG to EDG of leaving groups (Table 2(a)). These results suggest that the greater (weaker) necleophilicity of nucleophiles, the more(less) bond-breaking of the C⋯O bond proceeds at the transition state and important fact is that the $|\rho_Y|$ value is larger than the ρ_X value.

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Table 1. Second-Order Rate Constants for the Pyridinolysis of Substituted Phenyl Acetates at 60°C in Acetonitrile (k_{XY}/k_{HH} value)

X Y	4-NO₂	4-Cl	H	3-CH₃	4-CH₃
4-NH₂	2.50	1.77	1.76	1.75	1.71
3,4-(CH₃)₂	1.73	1.39	1.21	1.20	1.20
H	1.39	1.11	1.00*	0.99	0.98
3-COCH₃	0.87	0.71	0.64	0.63	0.63
3-Cl	0.80	0.63	0.59	0.59	0.58

*k_{HH} = 3.40 × 10⁻⁴ l mol⁻¹ sec⁻¹.

Table 2. Reaction Constants (ρ_X, ρ_Y) for Pyridinolysis of Phenyl Acetates

(a) ρ_Y values

σ_X	4-NO₂	4-Cl	H	3-CH₃	4-CH₃
ρ_Y	−0.469	−0.460	−0.447	−0.445	−0.441
	*(r = 0.991)	(0.988)	(0.993)	(0.993)	(0.992)

(b) ρ_X values

σ_Y	4-NH₂	3,4-(CH₃)₂	H	3-COCH₃	3-Cl
ρ_X	0.180	0.175	0.165	0.153	0.148
	*(r = 0.997)	(0.990)	(0.994)	(0.992)	(0.988)

*r: Correlation coefficient.

The plot of $|\rho_Y|$ vs σ_X and ρ_X vs σ_Y are well correlated with $\rho_Y^{(X)}$ = −0.03 σ_X·0.447, (r = 0.965), and $\rho_X^{(Y)}$ = −0.03 σ_Y + 0.165, (r = 0.966), respectively.

Therefore, the rate constants are varied with substituents X and Y and it correlated with $\log k_{XY}$-$\log k_{HH}$ = 0.165 σ_X-0.03 $\sigma_X\sigma_Y$-0.447σ_Y. The most important facts are that the coefficient of the interaction term, $\rho_{XY}\sigma_X\sigma_Y$, is the same small value of −0.03, which is derived from either ρ_X or ρ_Y, and its value indicates that the degree of interactions between nucleophile and leaving group are same but interactions between X and Y are small. ◾

The results are interpreted in terms of concerted mechanism in which involving a metastable tetrahedral intermediate. These are in accord with the mechanism of previously reported our study[1] of the pyridinolysis.

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Chemoselective Reduction of Carboxylic Acid Esters with Potassium Triethylborohydride

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The reduction of carboxylic acid esters to the corresponding alcohols can be achieved readily with various metal hydrides such as lithium aluminum hydride[1] (LiAlH₄), diisobutylaluminum hydride[2] (i-Bu₂AlH), and lithium triethylborohydride[3] (LiEt₃BH), however, little chemoselectivity could be expected from these strong reducing agents. On the other hand, aluminum hydride[4] (AlH₃), borane-dimethyl sulfide[5] (BH₃·SMe₂) (at 65 °C), lithium borohydride (LiBH₄) with 9-methoxy-9-BBN catalyst[6], and LiBH₄-MeOH-Et₂O[7] system have been reported to reduce esters rapidly without attacking nitro and halogen substituents.

Recently we have studied the reducing properties of potassium triethylborohydride[8] (KEt₃BH), and compared with those of lithium derivatives (LiEt₃BH). We found an interesting phenomenon. Thus the reducing power of potassium

derivative to ester is similar to LiEt₃BH which reduces esters in a few minutes, however, it reacts much slowly with other functional groups compared with LiEt₃BH. In this respect the replacement of Li⁺ with K⁺ resulted substantial decrease in reactivity for other functional groups such as epoxides, amides, nitriles etc. We now wish to report such chemoselectivity of KEt₃BH for the selective reduction of esters. Chemoselective reduction of esters with KEt₃BH was studied by competitive reaction. Thus an equimolar mixture of an ethyl ester and other substrate was reacted with 2.2 equivalents of KEt₃BH in THF. The reduction of ethyl caproate in the presence of cyclohexene oxide is representative. To an equimolar mixture of ethyl caproate (1 mmol) and cyclohexene oxide (1 mmol) containing 1 mmol of naphthalene as an internal standard in THF (1 ml) was added to 2.2 mmol of