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trum of the p-xylyl radical compared with that obtained using the original Engelking type nozzle. From the survey spectrum, we have found that the collisional vibrational cooling is efficient at the exit of the nozzle throat.

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The Effect of Alkali Metal Ions on Acyl-Transfer Reactions: Unusually High Na+ Ion Selectivity in the Reaction of 8-(5-Nitroquinolyl) Benzoate with Alkali Metal Ethoxides in Ethanol

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The effect of metal ions on acyl-transfer reactions has been extensively studied due to the importance in biological processes.[1-7] However, most studies have been focused on divalent metal ions such as Ni^{2+}, Zn^{2+}, Cu^{2+}, *etc.*[1,2] The study of alkali metal ions has not been much investigated but initiated only recently.[3-7] Buncel and his coworkers have found that alkali metal ions behave as a catalyst in the reaction of alkali metal ethoxides (EtOM) with *p*-nitrophenyl diphenylphosphinate (PNPDPP) in ethanol (EtOH).[3a] The catalytic effect was found to increase with increasing the charge density of alkali metal ions (*e.g.*, $K^+<Na^+<Li^+$).[3a] However, on the contrary, alkali metal ions have been reported to act as an inhibitor in the reaction of PNPDPP with alkali metal aryloxides (ArOM) in EtOH, and the inhibiting effect increases with increasing the charge density of alkali metal ions.[4a] Interestingly, in the reaction of EtOM with p-nitrophenyl benzenesulfonate (PNPBS) in EtOH, Li^+ ion behaved as an inhibitor while K^+ and Na^+ exhibited catalytic effect.[3b,4b] Therefore, it has been understood that alkali metal ions play as a catalyst or inhibitor in the above nucleophilic substitution reactions depending on the type of substrates (phosphorus vs sulfur centered ester) and nucleophiles (EtO⁻ vs. ArO⁻), and the catalytic or inhibiting

ability is in the order $Li^+>Na^+>K^+$ or $K^+>Na^+>Li^+$.[3,4]

Recently, we have reported a similar result for the reaction of EtOM with *p*-nitrophenyl 2-furoate (PNPF)[4d] and 2-thiophenecarboxylate (PNTC)[4e] in EtOH, *i.e.*, alkali metal ions exhibited catalytic effect and the catalytic ability was in the order $K^+>Na^+>Li^+$. For a more systematic study, we have performed the reaction of EtOM with *p*-nitrophenyl benzoate (**1a**) and 8-(5-nitroquinolyl) benzoate (**1b**) in EtOH. We wish to report unusually high Na+ ion selectivity together with the role of alkali metal ions in the present system.
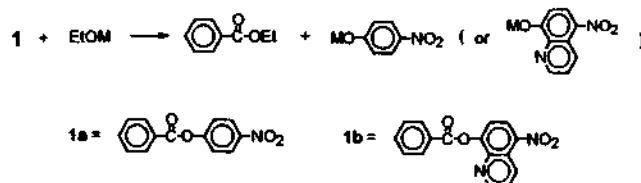
The reactions were followed by monitoring the appearance of the leaving group at 400 nm (**1a**) or 455 nm (**1b**) using a Hitachi U-2000 UV-vis spectrophotometer equipped with a Neslab RTE-110 model constant temperature circulating bath. All the reactions were performed

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under pseudo-first-order conditions in which the concentration of EtOM was in excess of the substrate in EtOH at 25.0 ± 0.1 °C. Pseudo-first-order rate constants (k_{obs}) were obtained from the plots of $\ln(A_\infty - A_t)$ vs. time, which were linear over 4 half-lives. The kinetic data are summarized in Table 1 and demonstrated graphically in Figures 1-3.

As shown in Table 1, **1a** appears to be about 3-6 times more reactive than **1b** toward EtOM. Generally, nucleofugality has been known to increase as the basicity of the leaving group decreases. Since the pK_a values of the leaving group in **1a** and **1b** are 7.1 and 6.0, respectively, **1b** is expected to be more reactive than **1a**. Therefore, the unexpected reactivity order observed in the present system is quite interesting. One might attribute the low reactivity of **1b** to field effect due to the N atom having lone pair electrons in the quinolyl moiety, or to steric effect since the the leaving group in **1b** is bulkier than the one in **1a**. However, deviations have often been observed in the Brönsted-type plots (log k vs. pK_a of leaving groups) for the reactions in which the leaving group departure occurs after the rate determining step (RDS).[8] Therefore, one might argue that the reaction of **1a** and **1b** proceeds in a different manner.[9]

As shown in Figure 1, the plots of k_{obs} vs. [EtOK] in the presence of 18-crown-6 ether (18C6), a complexing agent, are linear for both **1a** and **1b** systems. However, in the absence of such a complexing agent, the corresponding plots show upward curvatures. The curvature appears to be more significant for the reaction of **1b** than **1a**. A careful examination of Figure 1 reveals that EtONa is the most reactive and exhibits the highest deviations from the linearity in Figure 1 for the reaction of **1b**. These results suggest that alkali metal ions act as a catalyst and the catalytic effect is obviously in the order $Na^+ > K^+ > Li^+$ in the present reaction of **1b**. Such an order of catalytic effect (the high Na^+ selec-

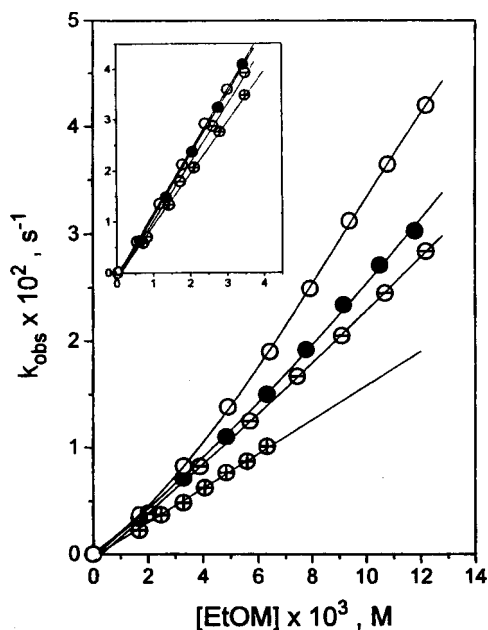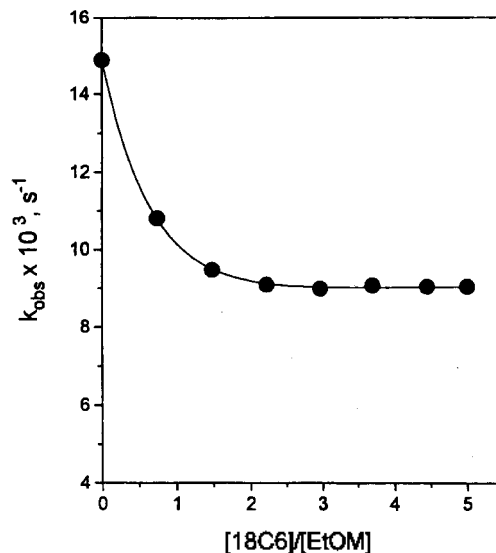**Figure 2.** The effect of added complexing agent (18C6) on the reaction of 8-(5-nitroquinolyl) benzoate (**1b**) with EtONa in absolute ethanol at 25.0 ± 0.1 °C. [EtONa]=5.08×10^{-3} M.
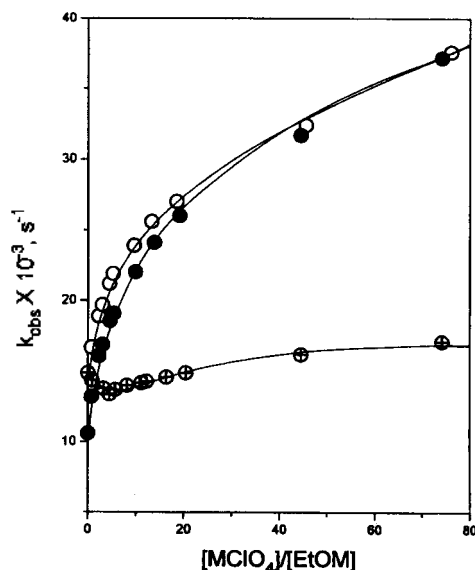

Figure 3. The effect of added $MClO_4$ on the reaction of 8-(5-nitroquinolyl)benzoate (**1b**) with EtOM in absolute ethanol at 25.0 ± 0.1 °C. EtONa+$NaClO_4$ (○), EtOLi+$NaClO_4$ (●), EtONa+$LiClO_4$ (⊕) ([EtOM] : [EtONa]=5.08×10^{-3} M, [EtOLi]=4.93×10^{-3} M).

Figure 1. Kinetic data for the reactions of 8-(5-nitroquinolyl) benzoate (**1b**) with EtOLi (⊖), EtONa (○), EtOK (●), and EtOK-18C6 (⊕) in absolute ethanol at 25.0 ± 0.1 °C. The inlet of the figure represents the corresponding reaction of p-nitrophenyl benzoate (**1a**).

tivity) has never been reported, i.e., the order of catalytic (or inhibiting) effect was found to be $Li^+ > Na^+ > K^+$ or the reverse as mentioned above.[3,4]

In order to confirm that Na^+ ion behaves as a catalyst, the reaction of **1b** with a constant [EtONa] has been performed in the presence of 18C6 of varying concentration. The kinetic results are graphically demonstrated in Figure 2. One can see that k_{obs} value decreases with increasing the ratio of [18C6]/[EtONa] up to near 2, and then remains constant beyond that point. This result clearly suggests that Na^+ ion behaves as a catalyst.

If Na^+ ion exhibits truely the highest catalytic effect in the present system, addition of unreactive Na^+ salt would

Table 1. Experimental conditions and k_{obs} values for the reaction of *p*-nitrophenyl benzoate (**1a**) and 8-(5-nitroquinolyl) benzoate (**1b**) with EtOM in ethanol at $25.0\pm0.1\,°C$

M	[EtOM]$\times 10^3$, M	$k_{obs}\times 10^3$, s^{-1}	
		1a	**1b**
Li	2.01-12.2	20.7-135	3.84-28.4
Na	1.68-12.2	18.5-163	3.69-42.0
K	2.09-12.7	22.3-163	4.50-33.2
K+18C6	1.68-6.34	14.2-61.0	2.24-10.1
[18C6]/[EtOK]=4			

cause the most significant rate enhancement. In order to examine the effect of added salts, the reactions of **1b** with EtOM have been performed in the presence of $MClO_4$ (M= Na and Li). The kinetic results are demonstrated in Figure 3. As shown in the Figure, additions of $NaClO_4$ cause significant increase in rates for the reaction of **1b** with EtONa and EtOLi. Such a rate enhancement upon additions of $NaClO_4$ appears to be more significant for the reaction of **1b** with EtOLi. On the contrary, the rate for the reaction of **1b** with EtONa decreases upon the initial additions of $LiClO_4$ and followed by gradual increase upon further additions of $LiClO_4$. However, the effect added $LiClO_4$ appears to be not significant for the reaction of **1b** with EtONa. These results clearly indicate that Na^+ ion shows the most significant catalytic effect in the present system.
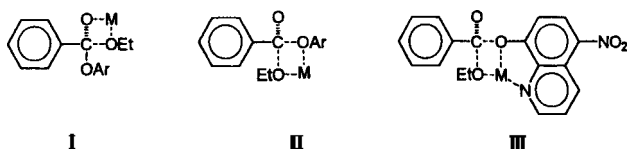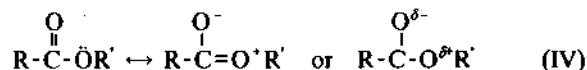

Although EtOH is a protic solvent, its polarity is moderate. In such a moderate polar solvent, metal ions are not as strongly solvated as in high polar solvent (*e.g.*, H_2O). Therefore, metal ions can be stabilized through interactions with their counter anion by forming ion pair or chelation with Lewis bases in the medium.[10] One can consider chelations I and II in the transition state (TS) are possible in EtOH. The chelation I would cause rate enhancement by increasing electrophilicity of the carbonyl carbon atom. Similarly, the chelation II would also increase the reaction rate by increasing nucleofugality of the leaving group. Therefore, one might attribute such chelations to the catalytic effect shown by the alkali metal ions in the present system.

The 4-membered chelations (I and II) are not considered as strong as the 5-membered chelation (III). This argument is consistent with the result that the catalytic effect is much more significant in the reaction of **1b** than **1a**, since chelation III is not possible for the reaction of **1a**. However, one might suggest that the chelation III (or II) would be only effective when the leaving group departure is involved in the RDS whether in a concerted or stepwise mechanism. Because the enhanced nucleofugality by chelation II or III would not cause any rate enhancement, if the leaving group departure occurred after the RDS.

Haake *et al.* have suggested that the ether-like O atom in carbonyl or phosphinyl esters develops a partial positive charge due to π interaction with the carbonyl oxygen as

shown below (IV).[11] Williams *et al.* have calculated the effective charge on the ether-like O atom in various esters, *e. g.*, +0.7 and +0.8 for *p*-nitrophenyl acetate and benzenesulfonate, respectively.[12] Complexation of alkali metal ions with the ether-like O atom in the leaving group (II or III) would reduce the effective charge of the ether-like oxygen atom. Such a change in the effective charge would increase not only the nucleofugality of the leaving group but also the electrophilicity of the carbonyl carbon, resulting in rate enhancements whether the leaving group departure is involved in the RDS or not. This argument explains nicely the present kinetic results.

$$R-\overset{O}{\underset{||}{C}}-\ddot{O}R' \leftrightarrow R-\overset{O^-}{\underset{|}{C}}=O^+R' \quad \text{or} \quad R-\overset{O^\delta-}{\underset{|}{C}}-O^{\delta+}R' \quad (IV)$$

The catalytic effect observed in the present system is quite opposite from the result obtained by Fife *et al.* for hydrolysis of quinolyl esters.[1a] Fife *et al.* have not found any catalytic effect even for strong Lewis acids such as Ni^{2+} and Cu^{2+} in aqueous medium.[1a] It is not so surprising, since H_2O can strongly solvate metal ions and prevent the quinolyl moiety in **1b** from chelating even strong Lewis acids due to its high polarity. However, EtOH is a moderate polar solvent and stabilization of alkali metal ions by forming complexation as III in the transition state would be important, which in consequence results in large rate enhancements (alkali metal ion catalysis) in the present system. More systematic studies are currently underway to understand the high Na^+ ion selectivity observed in the present system.

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Observation of the Vibronic Emission Spectra of Pentafluorobenzyl Radical Generated in a Jet

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Free radicals exist only transiently as reaction intermediates, created in one step and quickly consumed in a subsequent step of a complex chain reactions.[1] For those interested in fundamental issue of chemistry, the structure and characteristics of radicals serve at least to define the nature of chemical reactivity.[2] The benzyl-type radicals are one of the most important species in chemical reaction of aromatic compounds, so they have been subjects of numerous spectroscopic studies by the method of both experiment[3-7] and theory.[8] Lee and coworkers[9-13] have produced many benzyl-type radicals by subtracting a hydrogen atom from the substituted toluene compounds in a corona excited supersonic expansion. Thrush group[3,4] has published interesting papers for the vibronic assignments of the substituted benzyl radicals using laser induced fluorescence technique. Also Cossart and coworkers[14] have determined the symmetry of the excited electronic state from the analysis of rotational contour of vibronic bands observed by emission spectroscopy. The rotational constants of substituted benzyl radicals have been accurately determined from the high resolution rovibronic spectra[15,16] as well as the rotational contour analysis of the spectra.[14,17] Although fluorine substituted benzyl radicals are the most suitable candidates for spectroscopic experiments, only monofluorobenzyl radicals have been so far investigated.

In this study, we have observed for the first time to the best of our knowledge the vibronic emission spectra of pentafluorobenzyl radical in the gas phase with a technique of corona excited supersonic expansion. The provisional vibronic assignments of the radical have been made from the spectra.

The experimental setup employed in this work is similar to those described previously.[18] Briefly, the pentafluorobenzyl radical was generated in a jet with He as a carrier gas in a corona excited supersonic expansion from pentafluorotoluene(Aldrich, reagent grade) and used without further purification. The precursor was vaporized at room temperature inside the vaporizing vessel made of thick Pyrex glass bottle under 2.0 atm of He gas. The concentration of the precursor in the gas mixture was adjusted for the maximum emission intensity and believed to be about 1% in the gas mixture. Since the corona discharge of the precursor compound produces heavy soot deposits clogging the nozzle throat, we have employed a modified Engelking type nozzle of 0.5 mm pinhole diameter developed in this laboratory[19] which substantially reduces the clogging by inducing the excitation after expansion of the molecules. The new nozzle was also effective for improving the quality of the spectra by reducing the arching noise limiting the signal to noise ratio of the spectrum. The typical discharge condition was 5 mA at the 2000 V dc potential through 150 kΩ current limiting ballast resister. The discharge voltage was adjusted for the maximun total fluorescence from the origin band using the narrow band optical interference filter.

The chamber was evacuated by a mechanical vacuum pump of 800 L/min capacity, obtaining the chamber pressure of 1.5 Torr during the expansion with 2.0 atm of backing pressure. With electric discharge of the precursor, the pentafluorobenzyl radical was generated in the downstream of the green jet. The downstream jet area of 4 mm in diameter below the nozzle throat was collected through the quartz lens of 38 mm diameter and 50 mm focal length placed inside the expansion chamber and focussed onto the