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butylamine (3.57 m*l*, 15 mmol), dichlorobis (triphenylphosphine) palladium(II) (0.035 g, 0.05 mmol), and cupric chloride (1.34 g, 10 mmol) in acetonitrile (5 m*l*) was stirred under 10 atm of CO at 80°C for 12 hours. The reaction mixture was then diluted with aq. ammonium chloride, extracted with ether, washed several times with distilled water, dried over MgSO$_4$, and evaporated. Chromatography of the residue (0.94 g) on silica gel using hexane/ethyl acetate=3/1 as eluent gave 0.74 g (71%) of (E)-1,3-diphenyl-1-oxo-2-propene: IR (KBr) 1670 cm^{-1}; ^{1}H-NMR(CDCl$_3$) δ7.31-7.82 (m, 10H), 7.92-8.18(m, 2H); mp. 59°C; *m/e*(M$^+$) calcd for C$_{15}$H$_{12}$O 208.2592, found 208.2590.

Satisfactory results were obtained by using PdCl$_2$(PPh$_3$)$_2$ as a catalyst. Triphenylphosphine was found to be a better ligand than others[4] regarding the yields of aryl vinyl ketones (entries 1 and 2). And also, the increase of CO pressure enhanced the yields of the desired aryl vinyl ketones (entries 1 and 3).

The mechanism of the present carbonylative vinylation of arylmercuric chlorides with CO and olefins involves (a) transmetallation of the palladium(II) catalyst with the mercurial moiety to give arylpalladium(II) complex,[5] (b) CO insertion to give the aroylpalladium(II) complex, (c) reaction with olefins according to the Heck's vinylation mechanism to afford aryl vinyl ketones and Pd(O)^{1c}, and (e) reoxidation of Pd(O) to Pd(II) with CaCl$_2$.

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Carrier-Mediated Transport of Some Transition Metal Cations Through Bulk Liquid Membrane Containing Azacrown Ether

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Studies were reported of the variation of cation transport rate through a bulk chloroform membrane containing a neutral macrocyclic carrier with cation (substrate) concentration in the source phase[1,2]. The transport rates (j_s) for potassium salts (KCl, KI, KSCN and KNO$_3$) were found to vary as the square of the cation activity in region of $1 \times 10^{-2} \sim 1$ M using dibenzo-18-crown-6(DBC) as membrane carrier. An associative mechanism, carrier-mediated transport of complexed ion-pair was applied to explain the results[3,4].

To better understand the relationship between carrier properties and transport rates in connection with the above results, extensive numerical simulations were proposed to describe simply and quantitatively various transport mechanisms[3,5]. They are approaches with adaptation and extension of earlier developed kinetic treatments[6,8]. The first model was to depict the carrier-mediated transport of a single substrate species such as aminoacids through the liquid membrane. Depending on the substrate concentration (C_s) and extraction coefficient (k), two kinds of regimes may be observed: at $kC_s \ll 1$, the transport rate is very low and first order with respect to the substrate concentration. At $kC_s \gg 1$, the rate increases up to its maximum and becomes independent of C_s and k. The second model was to describe substrate competition. Although the goal of the most transport experiments through liquid membrane is to achieve the selective removal of a given substrate, experimental results revealed that the selectivity for two substrates is not directly related to the relative transport rates of the two substrates measured in separate experiments[5]. The third one was to describe the facilitated transport of complexed ion-pair. This is the system most widely studied especially in relation to the transport of cation together with anions by neutral ligands like crown ethers and cryptands[1,2,4,9,10]. Due to simultaneous extraction and transport of two species, concentration appears at the second power in the transport rate equation. It is the case described in the opening of this paper.

The principal aim of this paper is to report unusual carrier-mediated transport phenomena of some transition metal cations (Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}, all chlorides) through bulk chloroform membrane containing azacrown ether. One of the azacrowns was 1,12,15-triaza-3,4 : 9,10-dibenzo-5,8-dioxocycloheptadecane (N$_3$O$_2$). The other was 6,9,12-triazabicyclo[15,3,1]-heneicosa-1(21), 17,18-triene-2,6-dione(PAC). The synthetic methods of the carriers and experimental procedures to obtain transport rates were just the same as described elsewhere[1,4,9,11].
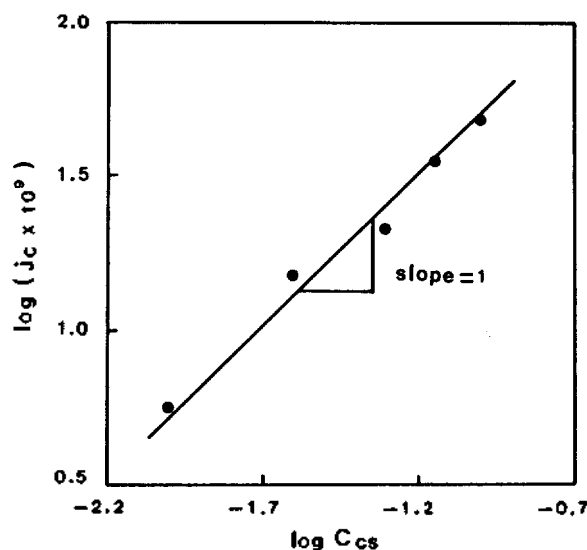

N$_3$O$_2$ PAC
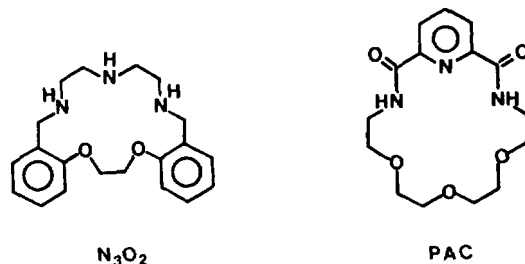
Since the membrane phase was stirred during the experiments, the rate was diffusion-limited and diffusion of the complexes through the membrane phase can not be rate-determining. The k values determined by extraction method[12] were larger than 1×10^2 for all the investigated systems and the first model could be excluded in the discussion. There-

Table 1. Variation of Transport Rate with Salt Concentration in Source Phase on N_3O_2 and PAC

	N_3O_2			PAC	
Salt	C_{cs} (mol/l)	j_c (mol/h×10^9)	Salt	C_{cs} (mol/h)	j_c (mol/h×10^{10})
$NiCl_2$	0.010	0.25	$NiCl_2$	0.10	
	0.025	1.00		0.25	
	0.050	1.23		0.50	nd*
	0.070	2.67		0.70	
	0.100	3.60		1.00	
$CoCl_2$	0.010	3.29	$CoCl_2$	0.10	
	0.025	6.99		0.25	
	0.050	11.76		0.50	nd*
	0.070	26.42		0.70	
	0.100	32.53		1.00	
$CuCl_2$	0.010	4.210	$CuCl_2$	0.10	1.00
	0.025	10.95		0.25	2.45
	0.050	16.91		0.50	3.17
	0.070	27.91		0.70	5.51
	0.100	35.69		1.00	7.67
$ZnCl_2$	0.010	6.01	$ZnCl_2$	0.10	11.48
	0.025	14.65		0.25	34.52
	0.050	21.19		0.50	44.62
	0.070	34.60		0.70	57.80
	0.100	45.50		1.00	116.00

nd*: not detectable

Figure 1. Plot of log j_c vs. log C_{cs} for $ZnCl_2$ on N_3O_2. The other systems also showed similar results except $NiCl_2$ and $CoCl_2$ on PAC. Therefore, the other plots were omitted.

fore, the carrier-mediated transport rate of the transition metal cations was supposed to vary as more than square of the substrate concentration at least. Howerver, as shown in Table 1 and Figure 1 the plot of log j_c vs. log C_{cs} does not have slope of larger than two but one. It is not hard to expect that the slope of one does fit rather dissociative mechanism than associative mechanism[10]. A recent study on

the transport of potassium picrate through the chloroform membrane containing DBC as carrier revealed that the slope was about one[4] in concentration region of less than $1×10^{-3}$ M. It was understood in terms of incomplete ion-pair formation in the membrane phase because of low salt concentration and large size of the anion.

However, incomplete ion-pair formation in our study could not be possible, because the concentration was relatively high. The order of observed rates was $Zn^{2+}>Cu^{2+}>Co^{2+}>Ni^{2+}$ as shown in Table 1. The order could be correlated well neither to the natural order of stability of transition metal complexes nor to the association constants[11] of the metal cations with the two respective carriers determined by extraction method[12] in water-chloroform layers. The results also support that rate-determining step in the investigated systems is rather dissociative process of the complexed ion-pair than associative process. Although kinetic stabilities have been little studied, the dissociation rate ratios for some azacrown complexes of Cu(II) to Ni(II) were reported to be $2\sim10^4:1$ depending on the azacrowns[13]. The rate ratios dramatically demonstrate the manner in which rate-determining dissociative process can be applied to the transport behavior of the transition metal cations through the chloroform membrane. In conclusion, the dissociative process[14] is rather important than associative one in which concentration appears with first power in the rate equation. A more detailed description of this study as well as other physical behaviors of the azacrown ethers will be described in the following paper.

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Studies on the Synthesis and Chemical Properties of 1,2,5-Thiadiazolidine-3-one 1,1-Dioxide Derivatives: Synthesis of N-Alkylsulfamides by Cleavage Reactions of N-(4-Methoxybenzyl)- and N-(3,4-Dimethoxybenzyl)-N'-alkylsulfamides with Trifluoroacetic Acid

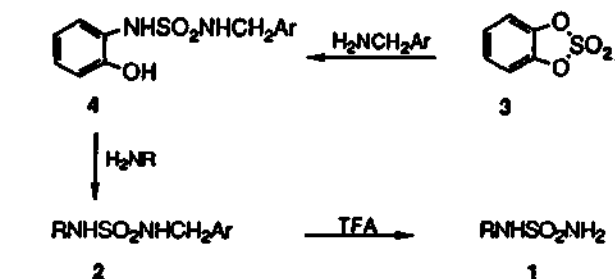Chai-Ho Lee*, Mee Sun Lee, Young-Haeng Lee, and
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We have recently reported the utility of N-alkylsulfamides
1 in the synthesis of heterocycles bearing sulfamide moiety[1].
Two general procedures have been introduced for the preparation of **1**; the monoalkylation of sulfamide itself with alkylamines in water[2] and the successive reactions of chlorosulfonyl isocyanate with formic acid or benzyl alcohol followed
by alkylamines[3]. We now wish to disclose a convenient new
procedure for the synthesis of **1**, which involves the acid
cleavage reaction of N-(4-methoxybenzyl)- and N-(3,4-dimethoxybenzyl)-N'-alkylsulfamides **2**.

Treatment of catechol sulfate **3** with 4-methoxybenzylamine or 3,4-dimethoxybenzylamine in DMF at 0°C for 1
hr in the presence of triethylamine resulted in the formation
of the sulfamate esters **4** in quantitative yields[4]. Reaction
of these sulfamate esters **4** with various alkylamines in boiling dioxane afforded the unsymmetrical sulfamides **2** in 90-

Table 1. Synthesis of Sulfamate Esters **4**, Unsymmetrical Sulfamides **2**, and N-Alkylsulfamides **1**

Compounds	Ar	R	Mp. (°C)	Yield (%)
4a	4-methoxyphenyl		116-115	98
b	3,4-dimethoxyphenyl		79- 80	97
2aA	4-methoxyphenyl	benzyl	115-116	91
aB	4-methoxyphenyl	phenethyl	110-111	90
aC	4-methoxyphenyl	3-phenylpropyl	137-138	92
bA	3,4-dimethoxyphenyl	benzyl	105-106	90
bB	3,4-dimethoxyphenyl	phenethyl	76- 78	91
bC	3,4-dimethoxyphenyl	3-phenylpropyl	89- 90	90
1A		benzyl	107-108	85
B[5]		phenethyl	68- 69	87
C		3-phenylpropyl	65- 66	88

92% yields (see Table 1). Treatment of these sulfamides **2**
with trifluoroacetic acid at rt for 3 hr and recrystallization
of the resulting solid from water then produced N-alkylsulfamides **1** in 85-88% yields (see Table 1).

This cleavage reaction is believed to proceed by protonation at the nitrogen first, from which the stable 4-methoxybenzyl or 3,4-dimethoxybenzyl cation is smoothly removed.

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5. Spectral data of the compound **1B** are as follows: IR (KBr)
3350, 1320, 1120 cm^{-1}; ^{1}H-NMR (MDSO-d$_6$) δ 2.78 (t, 2H,
$J=7.3$ Hz), 3.07-3.14 (m, 2H), 6.56 (s, 2H), 6.95 (t, 1H,
$J=6.6$ Hz), 7.19-7.41 (m, 5H); ^{13}C-NMR (DMSO-d6) δ
35.25, 44.26, 126.15, 128.35, 128.66, 139.37 ppm.

Selectivity Control in Chlorination of Phenol by Changings Surfactant Concentration

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For the last several years, the effect of hydrophobicity