

PHASE-TRANSFER CATALYSIS OF POLY(OXYETHYLENE) DIMETHYL ETHERS (GLYMES)¹⁾

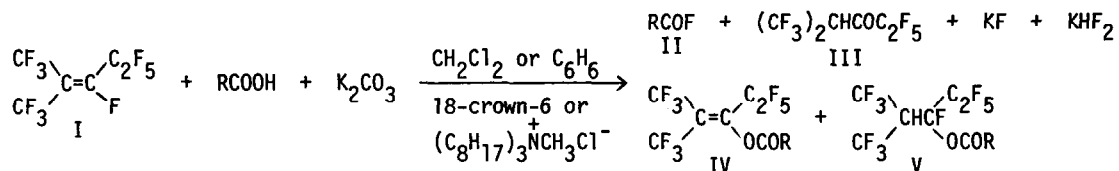
Shozo Yanagida†, Yukihiro Noji, and Mitsuo Okahara

Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Yamadakami, Suita, Osaka 565, Japan

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In the preceding paper²⁾ on metal-ion complexation of noncyclic poly(oxyethylene) derivatives, we demonstrated that linear poly(oxyethylene) derivatives have an extracting power of alkali metal ions comparable to those of the crown ethers. With regard to the catalytic activity of noncyclic poly(oxyethylene) derivatives in synthetic organic chemistry, Menger et al³⁾ first reported that a nonionic surfactant, C₁₂H₂₅(OCH₂CH₂)₂₃OH [Brij 35], catalyzes the hydrolysis of trichloromethylbenzene in heterogeneous system, and explained it as an emulsion or micellar catalysis. Recently, Regen et al³⁾ have introduced the concept of solid phase cosolvent on the catalysis of poly(oxyethylene) monomethyl ethers attached to cross-linked poly(styrene). To our knowledge, however, their phase transfer catalysis on the basis of cation complexation has not fully been exploited, although the compounds armed with a large number of short oxyethylene units have recently been elucidated to have the cation complexing tendency mainly due to topological effect and to be poor to fair phase-transfer catalysts.⁵⁻⁷⁾

In our another preceding paper⁸⁾ we reported that perfluoro-2-methyl-2-pentene undergoes triphase reactions with carboxylic acid in the presence of potassium carbonate and a phase-transfer catalyst (18-crown-6 or trioctylmethylammonium chloride) in dichloromethane or benzene as follows:



We have now found that glymes with more than four oxyethylene units also catalyze the above-mentioned reactions as effectively as 18-crown-6 (Table 1).

These results are quite contrasted with our previous conclusion²⁾ that seven repeating oxyethylene units are at least required to transfer potassium ion effectively from aqueous phase to dichloromethane.

Chaput et al⁹⁾ reported the stability constants of glyme-potassium complexes in methanol. The stability constant of tetraglyme is less than one-tenthousandth of that of 18-crown-6,¹⁰⁾ and even that of heptaglyme less than one-

Table 1. Phase-transfer Reactions of Perfluoro-2-methyl-2-pentene With Potassium Benzoate

Glymes or 18-crown-6	Reaction ^{a)}		Yield(%) ^{b)}			
	(g)	mol% ^{a)}	Time(hr)	II	IV & V	Total
CH ₃ O(C ₂ H ₄ O) ₂ CH ₃	0.45	47	3.5	4	10	14
CH ₃ O(C ₂ H ₄ O) ₃ CH ₃	"	36	"	20	25	45
CH ₃ O(C ₂ H ₄ O) ₄ CH ₃	"	20	"	36	35	71
CH ₃ O(C ₂ H ₄ O) ₆ CH ₃	"	15	"	35	49	84
CH ₃ O(C ₂ H ₄ O) ₈ CH ₃	0.55	14	"	40	57	97
"	"	"	8.0	45	52	97
"	1.00	25	3.5	47	51	98
18-crown-6 ^{c)}	0.45	17	8.0	57	35	92
"	"	"	47	56	36	92
"	1.00	38	24	81	13	94

a). The pentene(I) (0.01 mole), C₆H₅COOH (0.01 mole) and K₂CO₃ (0.005 mole) were stirred under reflux in 30 ml of CH₂Cl₂ with glymes or 18-crown-6.

b). Determined by glpc of the distillate. c). See ref. 8.

thousandth. Smid et al,¹¹⁾ however, observed that the complexation constants of the glymes with fluorenyl alkali salts in THF dramatically increase up to tri-glyme or tetraglyme, depending on the radius of the cation. Further, Martsh et al¹²⁾ noted the strong potassium ion solvation of hepta and octa(oxyethylene) monomethyl ethers in toluene. Considering our result and these earlier findings, the striking catalysis of the glymes may be attributed to the effective complexation with potassium ion due to the lack of the competitive complexation with protic solvent.

It should be noted that, in contrast to 18-crown-6, the yield of benzoyl fluoride(II) did not increase even when the amount of octaglyme was doubled.

Further investigation is now in progress.

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