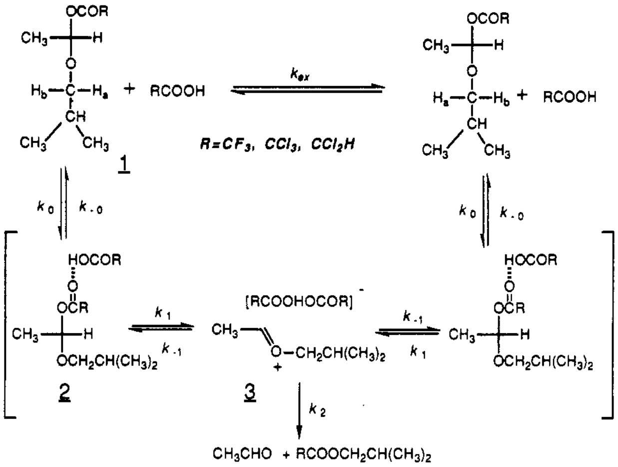
Nucleofugality of Halogenated Acetates for Mechanism Study of Vinyl Ether Polymerization[16]

Living cationic polymerization of electron-rich vinyl monomers has been recognized only recently,[1] and its reaction mechanism is not yet fully understood.[2] A major controversy concerns whether the active species is a carbocation (S_N1) or an activated ester (S_N2). We have recently reported[3] that halogenated acetic acids[4] and their zinc salts in hexane or CH_2Cl_2 give living polymerization of vinyl ethers. The initiating product is known to be an α-alkoxy ester of these relatively nonnucleophilic acetates,[1c,3] which could generate the cationic propagating species readily. Therefore, the leaving group reactivity (nucleofugality) of these groups should be a main focus in the determination of the polymerization mechanism. Even though references to nucleofugality are abundant in the literature,[5] most studies were undertaken in a polar solvent under solvolytic conditions; few studies were done in solvents typical of polymerization. We report our results on the study of leaving group activity of halogenated acetic acids by dynamic ^1H NMR spectroscopy in the attempt to correlate it to a polymerization mechanism.

Isobutyl vinyl ether reacts instantaneously with α-haloacetic acid in hydrocarbon solvents and in halogenated solvents to give 1-(haloacetoxy)-1-[(2-methylpropyl)oxy]ethane (1), which is stable in the presence of excess vinyl ether.[3] The detailed study was undertaken in hydrocarbon solvents, since the α-alkoxy esters were less stable in chlorinated solvents. The methylene resonance in the ^1H NMR spectra shows the expected two doublets, with $^1J = -9$ Hz and $^2J = 7$ Hz. With excess acid, the methylene protons show exchange, evidenced by peak broadening in the spectra, whereas all other peaks are unaffected. Eventually these haloacetates decompose to acetaldehyde and isobutyl acetate.[3] We propose that these findings are consistent with the achiral oxonium ion formation outlined in Scheme I.[6]

The reaction scheme involves two intermediates, the complex between the acid and ester, 2, and the ion pair, 3. The concentration of 2 in these solutions seems to be low. The chemical shift values for any proton of the esters did not change much upon addition of acids in 0.4-4 M excess, thus precluding measurement of the equilibrium constant, K_0, by the NMR method. The forward reaction constant, k_1, reflects the nucleofugality, and k_{-1} and k_2 relate to the nucleophilicity of the anion. In hydrocarbon solvents, most ions exist as contact ion pairs,[7] whereas solvent-separated ion pairs may be possible[8] in the presence of excess acid.

Scheme I



The apparent first-order exchange rates (k) of the two diastereoisomers were estimated from visual comparison of the experimental with simulated ^1H NMR using a three-spin, two-site exchange scheme.[9] Representative experimental and simulated ^1H NMR spectra are shown in Figure 1. The NMR spectra were typically obtained at eight or more temperatures,[10] except in the case of the ester of dichloroacetic acid (DCA). The exchange rate of dichloroacetate was slow, and determination of an accurate reaction rate was difficult. A wide range of spectral changes could be induced by manipulation of concentration and temperature. The two sets of two doublets initially broaden with an increase of temperature or acid concentration and then turn into a single broad peak (Figure 1a). With a large excess of acid, it becomes two sharp peaks due to the coupling to the methine proton of the isobutyl group (Figure 1b). The α-alkoxy esters of DCA and trichloroacetic acid (TCA) were quite stable at room temperature even in the presence of a 10-fold excess of acid. However, with a large excess of trifluoroacetic acid (TFA), the solution became dark brown and a precipitate formed. At higher temperatures, decomposition of the α-alkoxy ester to the isobutyl ester was accelerated, so that a correction for the concentration of acid and ester had to be made in some cases. The exchange rate constants (k_{ex}) were calculated from the following relationships, which are based on the bimolecular reaction model illustrated in Scheme I.

$$-\mathrm{d}[\text{ester}]/\mathrm{d}t = k[\text{ester}]$$
$$= k_{ex}[\text{acid}]^{\alpha}[\text{ester}]$$

Table I summarizes thermodynamic parameters derived from variable-temperature experiments. The activation energy of the exchange declines as the amount of the acid increases.[11] Excess acid must have increased the polarity of the solution. The order of reaction with respect to the acid calculated from the four experiments with TCA was 1.7. This unusual number must be related to the changes in the solvent polarity caused by different amounts of

Table I
Thermodynamic Data of Dissociation at 25 °C[a]

acetic acid	[ester], mM	[acid], mM	solvent	k_{ex}, s^{-1} M^{-1}	$\Delta G^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
CF_3COOH	25	25	hexane	1400	13.1		
CF_3COOH	115	120	methylcyclohexane	480	13.8	8	−21
CCl_3COOH	120	56	cyclohexane	12	15.9		
CCl_3COOH	83	100	cyclohexane	40	15.2	13	−7
CCl_3COOH	42	164	cyclohexane	65	14.9	12	−9
CCl_3COOH	210	1670	cyclohexane	190	14.3	8	−20
CCl_2HCOOH	112	168	methylcyclohexane	0.12[b]	18.6[b]		
CCl_2HCOOH	210	1750	cyclohexane	25	15.5		

[a] Uncertainties are as follows: temperature, ±0.2 °C; k, ±10%; $\Delta G^{\ddagger}$, 0.1 kcal/mol; $\Delta H^{\ddagger}$, 1 kcal/mol; $\Delta S^{\ddagger}$, 2 cal/(deg mol). [b] Extrapolated from higher temperature data.

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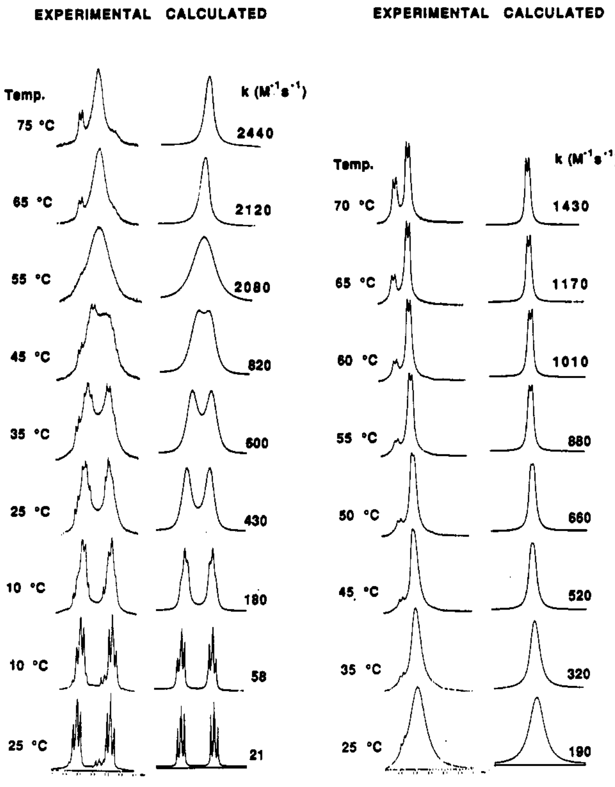

(a) (b)

Figure 1. Experimental and simulated ^{1}H NMR spectra of methylene protons of the isobutyl group in 300 MHz. The peaks at the left shoulder of the major peak(s) are due to the methylene proton of isobutyl haloacetate, which is one of the decomposition products. (a) Trifluoroacetate and trifluoroacetic acid in methylcyclohexane-d_{14}; [ester] = 115 mM, [acid] = 120 mM. (b) Trichloroacetate and trichloroacetic acid in cyclohexane-d_{12}; [ester] = 210 mM, [acid] = 1670 mM.

acid present in this data set. We assumed the order of reaction with respect to the acid is one for the activation energy calculation, since we are dealing with activation energies in constant acid concentrations. Surprisingly, there is a large difference in the exchange rates of TCA and TFA esters, in spite of the fact that the pK_a's[12] of these two acids and the polymerization rates[3] catalyzed by their zinc salts are more or less the same. If the polymerization would proceed via an ideal S_N1 mechanism, the polymerization rate should have a direct correlation with the nucleofugality of the living group. Since the polymerization rate does not correspond with the ionization rate, we propose that the polymerization may not proceed through a fully ionized species as 3 but through activated ester 2 or an intermediate in between 2 and 3, depending on the reaction conditions. Such a compromising mechanism for the nucleophilic substitution reaction is well accepted in the solvolysis reactions.[13] An activated covalent intermediate was also proposed for isobutylene living polymerization systems.[14]

In conclusion, the living cationic polymerization mechanism was considered in view of the classical solvolysis mechanism. We propose that, in the case of vinyl ether polymerization via a halogenated acetic acid ester in hexane, a fully ionic intermediate may not be necessary for the polymerization.[15]

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(8) The energy difference between the contact and solvent-separated ion pair is small (about 8 J mol^{-1} for 2-chloro-2-methylpropane) compared to that between ionic and covalent species: Jorgensen, W. J.; Buckner, J. K.; Huston, S. E.; Rossky, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 1891.

(9) NMRD3 is available from the Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University.

(10) Samples were prepared by mixing a solution of the vinyl ether and the acid of known concentration at room temperature; the reported concentrations of the esters and acids are those of the vinyl ether and excess acids, respectively. Probe temperature was directly measured by inserting a thermocouple immersed in Nujol in a NMR tube. The dependence of the chemical shift to the temperature was estimated from the low-temperature ^{1}H NMR spectra and extrapolated to higher temperature. For stimulation, T_2 was taken as 0.25 s. It is well-known that the estimation of thermodynamic data from the dynamic NMR experiments can be highly erroneous. See for example: Binsch G. *Top. Stereochem.* **1968**, *3*, 97.

(11) Compared to typical solvolysis reactions, such as those discussed in ref 5a, the ΔS^* values are slightly less negative, whereas ΔH^* values are more or less the same as solvolysis reactions.

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(15) Preliminary results indicate that the tacticity of poly(vinyl ethers) prepared in hexane and in CH_2Cl_2 is quite different. Further studies on the understanding of the reaction mechanism in relation to the stereochemistry and reaction kinetics are in progress.

(16) Contribution No. 5592.

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