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Solvent and Steric Effects on the Solvolysis of Polyvinylsulfonic Acid Esters[1]

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The solvolysis of ethanesulfonic acid esters followed closely first-order kinetics, while the case of polyvinylsulfonic acid esters gave strongly-curved first-order plots according to the solvent composition. With a high acetone content, the solvolysis rates of polymeric sulfonic esters decreased gradually with the lapse of time, while in a high water content, the solvolysis was suppressed at the beginning of the reaction but was accelerated remarkably with the reaction time. The former finding indicates the release from the steric congestion which contributed to the initial rate enhancement, while the latter indicates the aggregation of the polymer molecules owing to their strong hydrophobic character. The solvolysis rates, k_p, for polymeric sulfonic esters were much greater than those, k_m, for monomeric analogs in all cases except isopropyl and *n*-butyl esters in 20% aqueous acetone. The relative rate (k_p/k_m) increased with an increase in the acetone content and was apparently greater with the methyl ester than with the other esters, and the value of (k_p/k_m) in relation to the methyl ester in 80% acetone content reached 15. Furthermore, it was found that the proton catalysis by the neighboring sulfonic acid formed on the lapse of reaction time was absent, and also that the salt effect was negligibly small.

In previous papers[2] we have discussed the specific catalytic effects of polymeric sulfonic acids in the hydrolysis of esters in regard to the expansion of the polymer in solutions and to the geometrical distances between the nearest neighboring sulfonic acid groups on the polymer chain. It is the aim of the present paper to study the solvolysis of polyvinylsulfonic acid esters in various compositions of acetone-water mixtures in order to verify the previous assumption. Four kinds of polyvinylsulfonic esters were used: methyl, ethyl, isopropyl and *n*-butyl esters, the respective alkyl ethanesulfonates as the monomeric analog were also employed for the sake of comparison. While there has been no systematic study of the solvolytic reaction of the sulfonic esters comparable to the work on the organic halides, it has generally been accepted that the mechanism of the displacement involves the scission of the C–O bond, except for the special case of the phenyl ester,[3] which is known to be an S_N1-S_N2 borderline mechanism.[4]

Alkyl esters of sulfonic acids are much more reactive than alkyl bromide towards water, as a result of the greater strength of the sulfonic acid group.[5] Changes in the ester alkyl group, the solvent and the nucleophilic reagent alter the conditions, for example, from those favoring an S_N2 mechanism to those favoring the S_N1 mechanism; the substitution of α-alkyl groups increases the ionization tendency, so that in solvents of a high water content, the solvolytic reaction of the isopropyl ester of sulfonic acid is unaffected by hydroxide ions.[6]

The rates of the solvolysis of sulfonic esters as well as of alkyl halides are also dependent on the nature of the leaving group.[7] The case where the leaving group has a polymer chain has, however, hardly ever been studied.[8] A peculiar polymeric effect was found in this solvolytic reaction of polymeric sulfonic esters.

Experimental

Monomers.—A series of alkyl esters of vinylsulfonic acid was prepared by the method of Whitmore and Landau.[9] From 125 g. (1.0 mol.) of sodium sulfite and 285 ml. (3.30 mol.) of ethylene dibromide, there was obtained 275 g. of crude sodium β-bromoethanesulfonate, which, with 150 g. (0.73 mol.) of phosphorus pentachloride, yield 130.3 g. (65%) of β-bromoethanesulfonyl chloride (n_D^{20} 1.5242; b. p. 85°C/3 mmHg).

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[1] Dissertation submitted by Oh-Kil Kim in partial fulfillment of the requirements for the Ph. D. degree in the Graduate School of the University of Tokyo.

[2] S. Yoshikawa and O-K. Kim, a) This Bulletin, **39**, 1515 (1966); b) ibid., **39**, 1729 (1966).

[3] a) J. Fern and A. Lapworth, *J. Chem. Soc.*, **1912**, 273; b) C. A. Bunton and Y. F. Frei, ibid., **1951**, 1872.

[4] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

[5] S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

[6] R. F. Hudson, G. M. Timmis and R. D. Marshall, *Biochem. Pharmacol.*, **1**, 48 (1958).

[7] A. Streitwieser, Jr., "Solvolytic Displacement Reaction," McGraw-Hill Book Co., New York (1962). a) p. 82; b) p. 45.

[8] H. Morawetz and P. E. Zimmering, *J. Am. Chem. Soc.*, **58**, 753 (1954).

[9] W. F. Whitmore and E. F. Landau, ibid., **68**, 1797 (1946).

Methyl, ethyl, isopropyl and *n*-butyl vinylsulfonates were prepared from 0.11 mol. of β-bromoethanesulfonyl chloride and 0.1 mol. of the corresponding alcohol in the presence of pyridine. The sulfonic esters were redistilled immediately before use.

Polymers.—All the polyvinylsulfonic acid esters were prepared by the bulk polymerization of their respective monomers with γ-irradiation: ten grams of the monomer were poured into an ampoule and evacuated to 1 mmHg; the evacuation and pressuring with nitrogen repeated, and then it was sealed. The polymerization was carried out by exposing it to a ^{60}Co source yielding about 2×10^5 r./hr. for 72 hours at 0°C. The degree of polymerization was determined by the saponification of the polymers with sodium hydroxide into the respective poly-(sodium vinylsulfonate), which was precipitated from 70% methanol and dried in vacuo over phosphorus pentoxide; the value of the intrinsic viscosity[10] of respective poly-(sodium vinylsulfonate) in 0.5 N sodium chloride at 20°C was 10.0 ($\overline{M}_n=13000$) for the methyl ester, 8.2 ($\overline{M}_n=9400$) for the ethyl ester, 9.2 ($\overline{M}_n=11000$) for the isopropyl ester and 2.8 ($\overline{M}_n=1800$) for the *n*-butyl ester.

Other Materials.—Four alkyl (methyl, ethyl, isopropyl and *n*-butyl) ethanesulfonates were prepared from ethanesulfonyl chloride,[11] made from sodium ethanesulfonate[12] and phosphorus pentachloride, and the corresponding sodium alkoxide by modifying the method of Carius.[13] The esters so prepared were colorless liquids having the following boiling points: the methyl ester, 70—72°C/7 mmHg; the ethyl ester, 70—72°C/5 mmHg; the isopropyl ester, 71—73°C/5 mmHg; the *n*-butyl ester, 88—91°C/6 mmHg. The purity of the esters were ascertained by the value of saponification.

Solvolysis Procedure.—The concentrations of all the esters of sulfonic acids were initially adjusted to 7.5×10^{-3}, 1.2×10^{-2} and 3.0×10^{-2} mol./l. in acetone. The reaction mixture was prepared from 8 ml. of the adjusted 7.5×10^{-3} mol./l. ester and 2 ml. of water added from a microburette to make up an 80% acetone solution (v/v); from 5 ml. of the 1.2×10^{-2} mol./l. ester and 5 ml. of water to make up a 50% acetone solution, and from 2 ml. of the 3.0×10^{-2} mol./l. ester and 8 ml. of water to make up a 20% acetone solution. Five or six samples were employed in each run, and each sample, made up from 10 ml. of the mixture, was placed in a glass-stoppered tube placed in a thermostat regulated to 45±0.01°C. The reaction was followed by withdrawing samples from the bath at suitable intervals, and by titrating the liberated sulfonic acid with 0.02 N standard sodium hydroxide using a phenolphthalein indicator. The rate constants, k, for hydrolysis were calculated from the simple first-order equation and the individual rate constants in each run were averaged over the range of approximately 40—50% of the reaction.

Results and Discussion

The solvolysis of ethanesulfonic esters followed first-order kinetics closely as is exemplified in Table I, while those of polyvinylsulfonic acid esters obviously deviated from first-order kinetics depending upon the compositions of the acetone-water mixtures, as is illustrated in Figs. 1, 2, 3 and 4. A common tendency is seen in these figures; polyvinylsulfonic acid esters were solvolyzed more slowly with an increase in the acetone content of the mixed solvents as well as in the cases of monomeric sulfonic ester. The effect of adding water to acetone

TABLE I. SOLVOLYSIS RATES OF METHYL ETHANESULFONATE AND METHYL POLYVINYLSULFONATE IN VARIOUS RATIOS OF ACETONE-WATER MIXTURES AT 45°C

Solvent	ESMe			PVSMe		
$\left(\frac{\text{acetone}}{\text{water}}\right)$	Time min.	$\log(a/(a-x))$	$10^3 k$ min^{-1}	Time min.	$\log(a/(a-x))$	$10^3 k$ min^{-1}
20/80 (v/v)	63	0.0610	2.23	30	0.1114	8.58
	138	0.1290	2.15	73	0.2542	8.05
	232	0.2198	2.18	110	0.3440	7.22
	332	0.3167	2.20	225	0.6239	6.44
	446	0.4249	2.20			
50/50 (v/v)	200	0.0666	0.668	22	0.0775	7.12
	338	0.0989	0.675	120	0.2442	5.32
	392	0.1138	0.669	160	0.2964	4.27
	508	0.1477	0.671	220	0.3686	3.86
	632	0.1895	0.692			
80/20 (v/v)	544	0.0336	0.142	60	0.0730	2.79
	949	0.0573	0.139	140	0.1537	2.54
	1330	0.0784	0.136	267	0.2414	2.08
	1740	0.1022	0.138	360	0.2929	1.88

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10) The molecular weight was calculated by K. Dialer and R. Kerber, *Makromol. Chem.*, **17**, 56 (1956).

11) W. Davies and J. H. Dick, *J. Chem. Soc.*, **1932**, 484.

12) H. G. Houlton and H. V. Tartar, *J. Am. Chem. Soc.*, **60**, 544 (1938).

13) L. Carius, *J. Prak. Chem.*, Band **2**, 270 (1870).

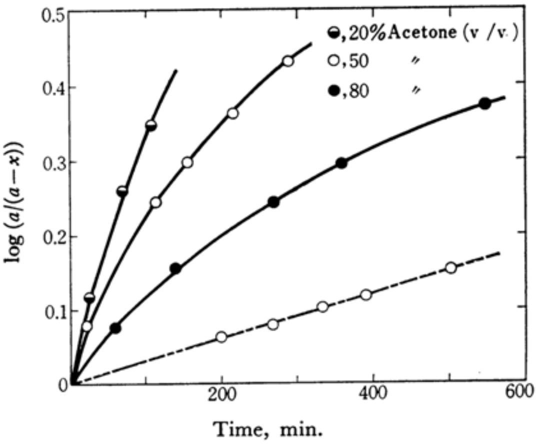

Fig. 1. Solvolysis of methyl polyvinylsulfonate (solid line) and methyl ethanesulfonate (dotted line) at 45°C.

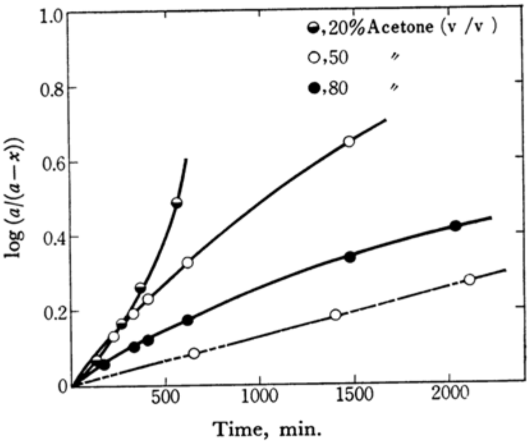

Fig. 2. Solvolysis of ethyl polyvinylsulfonate (solid line) and ethyl ethanesulfonate (dotted line) at 45°C.

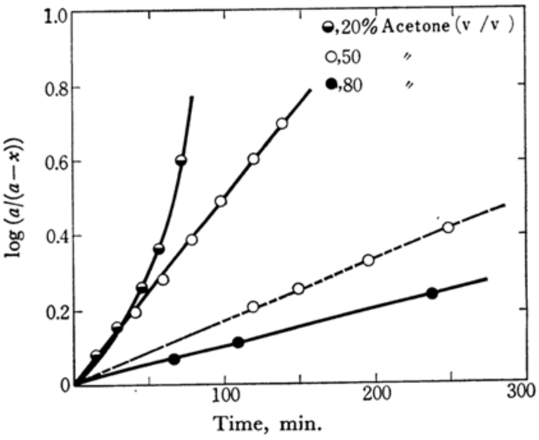

Fig. 3. Solvolysis of isopropyl polyvinylsulfonate (solid line) and isopropyl ethanesulfonate (dotted line) at 45°C.

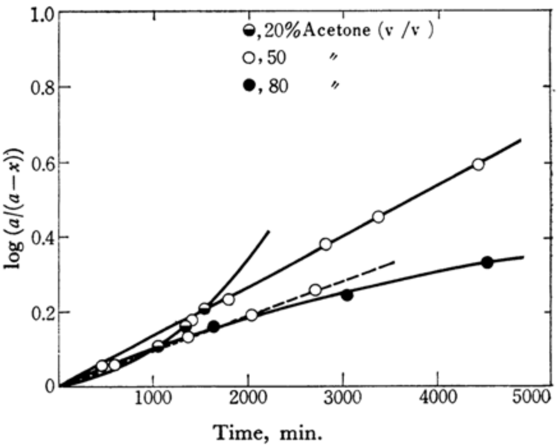

Fig. 4. Solvolysis of *n*-butyl polyvinylsulfonate (solid line) and *n*-butyl ethanesulfonate (dotted line) at 45°C.

is to increase the ionizing ability of the solvent and, thereby, to accelerate the solvolytic reaction, which depends on the stabilization of partial charges in the transition state.

However, in 20% acetone, an unusual phase was found in the solvolysis of polymeric esters. At the beginning of the reaction, the solvolysis rate was suppressed, but it was gradually accelerated remarkably with the lapse of time. Thus different aspects of the solvolytic behavior of polymeric sulfonic esters in a high water content are of interest when discussing the reactivity of the polymer in relation to the expansion in solutions rather than to the change in the reaction mechanism.

The solvolysis rates of polymeric sulfonic esters were much greater than that of the monomeric analog in all cases except those of isopropyl and *n*-butyl esters in 20% aqueous acetone. The relative rate between the polymeric ester and the monomeric analog (k_p/k_m) increased in proportion to an increase in the acetone content. It is also important to note that the ratios of the solvolytic rates between the methyl ester and other esters, $(k_R/k_{Me})_m$ for the monomeric analog and $(k_R/k_{Me})_p$ for the polymeric ester (Table II), decrease with the magnitude of ester alkyl except in the case of the isopropyl ester (because of its well-known high polar causes). The decrease in $(k_R/k_{Me})_m$ may be due mainly to the different polarity on the C–O bond which includes a alkyl group, while the decrease in $(k_R/k_{Me})_p$ may be due mainly to the differences in the polar and hydrophobic characters of the alkyl group on the polymer chain, since the steric factors of ethyl and *n*-butyl groups are considered to be of nearly the same magnitude.

Therefore, the relative value $(k_R/k_{Me})_p/(k_R/k_{Me})_m$ indicates the relative hydrophobic factor of the alkyl group of each polymeric ester in a

TABLE II. SOLVOLYTIC RATE CONSTANTS k (min^{-1}) AND RELATIVE RATES, k_p/k_m RELATED TO AN PECULIAR POLYMERIC EFFECT AND $(k_R/k_{Me})_{p \text{ or } m}$ TO RELATIVE SUBSTITUENT EFFECT IN VARIOUS ACETONE-WATER MIXTURES AT 45°C

Ester	Solvent $\left(\frac{\text{acetone}}{\text{water}}\right)$		Me		Et		*i*-Pr		*n*-Bu	
			10^4k	k_p/k_m	10^4k	k_p/k_m	10^4k	k_p/k_m	10^4k	k_p/k_m
ES	20/80 (v/v)		22.3		13.0		299		8.34	
		$(k_R/k_{Me})_m$	(1.0)		(0.58)		(13.4)		(0.37)	
PVS			75.2	3.4	16.1	1.2	144	0.48	2.92	0.34
		$(k_R/k_{Me})_p$	(1.0)		(0.21)		(1.91)		(0.039)	
ES	50/50 (v/v)		6.68		2.97		40.0		2.08	
		$(k_R/k_{Me})_m$	(1.0)		(0.44)		(5.98)		(0.31)	
PVS			53.0	7.9	12.5	4.2	109	2.7	3.17	1.5
		$(k_R/k_{Me})_p$	(1.0)		(0.24)		(2.05)		(0.060)	
ES	80/20 (v/v)		1.36		0.515		4.69		0.298	
		$(k_R/k_{Me})_m$	(1.0)		(0.38)		(3.45)		(0.22)	
PVS			20.9	15.0	5.08	9.8	23.0	4.9	1.73	6.6
		$(k_R/k_{Me})_p$	(1.0)		(0.24)		(1.15)		(0.083)	

certain solvent composition. The values decrease with the number of alkyl carbon atoms and gradually increase with an increase in the acetone content of mixed solvents. Such changes in the relative values suggest the major importance of the expansion of polymers in solutions. This undoubtedly suggests that, in a solution of a high water content, the random-coiled molecules of the polymeric ester, especially isopropyl and *n*-butyl esters, are greatly aggregated, where the solvent ratio in the immediate neighborhood of the macromolecule may differ considerably from the bulk-average composition of the medium compared to their corresponding differences in other compositions of the solvent; that the conformational movements of the polymer are restricted by their strong hydrophobic character, and that, hence, the reaction probably occurs mainly on the outer layer of the random-coiled molecule.

This interpretation is clearly supported by the illustrations given in Figs. 5, 6, 7 and 8, where the

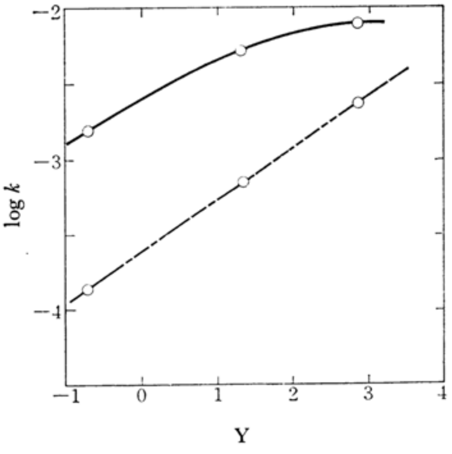

Fig. 5. Solvolysis rates of methyl ethanesulfonate (dotted line) and methyl polyvinylsulfonate (solid line) as a function of ionizing power Y.

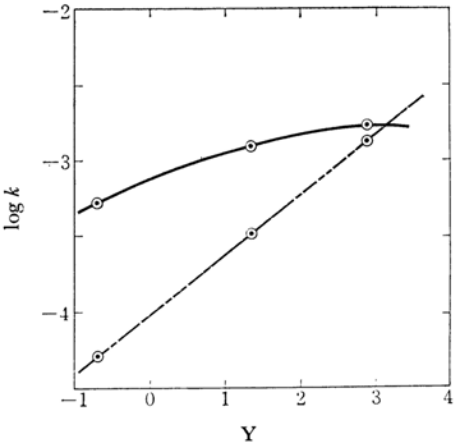

Fig. 6. Solvolysis rates of ethyl ethanesulfonate (dotted line) and ethyl polyvinylsulfonate (solid line) as a function of ionizing power Y.

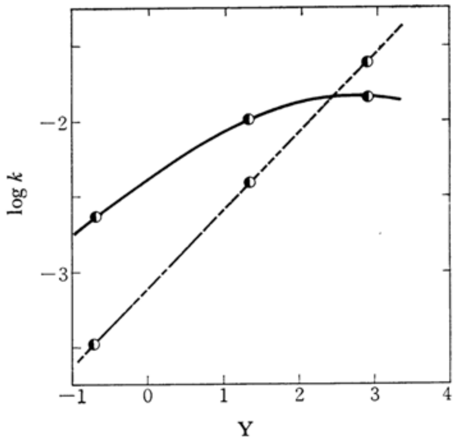

Fig. 7. Solvolysis rates of isopropyl ethanesulfonate (dotted line) and isopropyl polyvinylsulfonate (solid line) as a function of ionizing power Y.

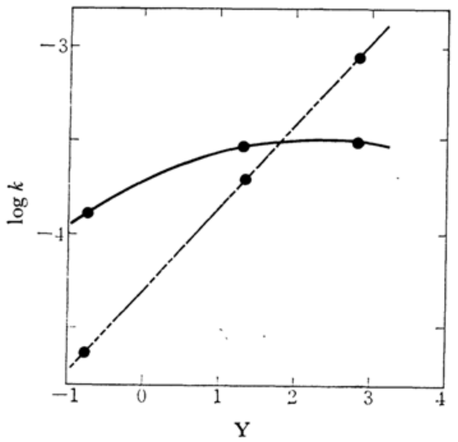

Fig. 8. Solvolysis rates of *n*-butyl ethanesulfonate (dotted line) and *n*-butyl polyvinylsulfonate (solid line) as a function of ionizing power Y.

Grunwald-Winstein correlation[14] is given:

$$\log k = m\mathrm{Y} + \log k_0$$

where Y is the measure of the ionizing power[15] of the solvent; k_0 is the rate of solvolysis in the standard solvent, and the slope m measures the susceptibility of the substrate to the ionizing power of the solvent. While the solvolysis of ethanesulfonic acid esters gives a linear correlation in Y, that of polymeric sulfonic esters deviates from linearity much more remarkably with the number of alkyl carbon atoms. The reaction rates were, however, accelerated by increasing the hydrophilic character of the polymer because of the sulfonic acid groups formed during the lapse of the reaction time.

On the other hand, the initial rate enhancement in the solvolysis of the polymeric ester in solvents of higher acetone contents may account for the major importance of the steric acceleration arising from the steric congestion by hydrophobic solvation on the polymer chain. This interpretation is also supported by the fact that solvolysis rates of polymer in 50% and 80% aqueous acetone (with the exception of 20% aqueous acetone, for the reason mentioned before) gradually became lower as a result of the release from the congestion between the immediate-neighboring alkyl groups with the lapse of reaction time. Steric assistance has been called[16] upon to explain the abnormally fast rate of the solvolysis of highly-branched tertiary alkyl halides. Such a phenomenon was also found in the solvolysis of cycloalkyl tosylate[17]; the solvolysis is accelerated by the steric interference of γ-opposed hydrogen with the tosylate group called non-bonding repulsion.

Furthermore, the ratio of the solvolysis rates between the series of alkyl polyvinylsulfonate and the corresponding ethanesulfonate (k_p/k_m), which indicates a positive polymeric effect, was much greater with the methyl ester than with the other esters and increased upon an increase in the acetone content of the mixed solvents in each run; the value of (k_p/k_m) towards the methyl ester in 80% acetone content attained 15, as is shown in Table II. These observations can be interpreted to suggest that the change in (k_p/k_m), which is dependent upon the alkyl structures of the polymer and the solvent compositions, involves a difference in the affinity of a substrate to a solvent. This may, in turn, cause the difference in the expansion or conformational movements of the polymer molecule.

A supplementary experiment was carried out with a partially-hydrolyzed polymeric ester to assure the absence of proton catalysis by the neighboring sulfonic acid present on the polymer chain. For example, initially 34% hydrolyzed *n*-butyl polyvinylsulfonate was hydrolyzed under the same conditions except that the solvent composition was 45% aqueous acetone; the rate constant was 3.09×10^{-4} (min^{-1}), which demonstrates that there is no intramolecular proton effect. Furthermore, the effect of added common and uncommon ions with both the polymeric ester and the monomeric analog in various systems showed the salt effect to be negligibly small for the noted concentration. The lack of sensitivity in the solvolyzing arylsulfonic esters (even in esters reacting by an apparent $\mathrm{S_N1}$ mechanism) to the salt effect has also been noted by others.[4,18] In addition, solvolytic reactions of vinylsulfonic acid esters were also carried out in order to compare them with those of ethanesulfonic esters. The hydrolysis rates of the former were almost twice as much as the latter; the rate constants of methyl, isopropyl and *n*-butyl vinylsulfonates in 50% aqueous acetone at 45°C were 1.34×10^{-3}, 9.88×10^{-3} and 3.79×10^{-3} respectively. This magnitude in rates can be expected to result from the inductive electron withdrawal of the vinyl group.

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[14] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

[15] The values extracted from the data of Fainberg and Winstein are employed here: A. H. Fainberg and S. Winstein, ibid., **78**, 2770 (1956).

[16] H. C. Brown and R. S. Fletcher, ibid., **71**, 1845 (1945) and ibid., **72**, 1223 (1950).

[17] I. Moritani, S. Nishida and M. Murakami, ibid., **81**, 3420 (1959).

[18] H. R. McCleary and L. P. Hammett, ibid., **63**, 2254 (1941).