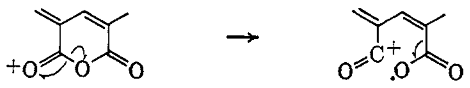

Figure 9.—Loss of CO_2 from lactone.

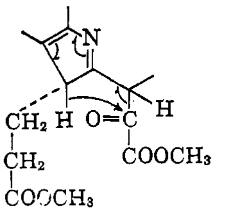

Figure 10.—Loss of $HCOCOOCH_3$.

systems CO is lost only after the loss of another substituent. A possible mechanism for this loss is given in Figure 8. The loss of CO_2 is a somewhat similar reaction (Figure 9), but requires the presence of a group adjacent to the oxygen which can stabilize a positive charge.

Cleavage α to the ring system is observed in the loss of γ-substituents. This is expected in compounds in which the γ-substituent is a simple functional group like CHO or COOR,[7] but it also occurs in these compounds when the γ-substituent is an acetic or propionic acid ester group. In a few unusual cases this type of fragmentation has been shown to occur.[8] However, the loss of a γ-substituent with hydrogen on a carbon near the ring exhibits a novel feature; one or two hydrogens are transferred from the substituent to the tetrapyrrole system. This double hydrogen transfer is even observed when the γ-substituent is an ethyl group. This is obviously a fairly complex reaction and it is not understood at the present time. In the compound XX the loss of $HCOCOOCH_3$ can be explained by the transfer of a hydrogen through a six-membered transition state (Figure 10), producing a porphyrin ion from the chlorin ion, which explains the relatively large peak (35%) for the loss of $HCOCOOCH_3$ plus CH_2COOCH_3. The chlorin ion would be expected to lose $CH_2CH_2COOCH_3$ much more easily than CH_2COOCH_3.

Experimental Section

The compounds used in this study were all either commercial materials or were synthesized by Professor R. B. Woodward and his co-workers.[2,4,5] Many of them are described by Woodward[4,5] and Fischer.[9]

The mass spectra were obtained on an AEI MS9 double-focussing mass spectrometer. The samples were inserted directly into the source by the use of a vacuum-lock probe.[10] Temperatures of 360–480° were needed to evaporate these compounds. The results of accurate mass measurements are reported in the text; heptacosafluorotributylamine[11] was used as a mass standard for the high-resolution work. The ionizing energy was maintained at 70 e.v.

Acknowledgment.—The author would like to thank Professor R. B. Woodward for generously donating the compounds used in this study and for his encouragement and advice, and would also like to thank Dr. M. Barber of AEI Ltd., Manchester, for his many helpful discussions and suggestions. This work was supported by the National Institutes of Health.

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[7] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, pp. 3, 11.

[8] See ref. 7, p. 259.

[9] H. Fischer and H. Orth, "Die Chemie des Pyrrols," II Band, Hälfte 1 and 2, Akademische Verlagsgesellschaft, Leipzig, 1937 and 1939.

[10] M. Barber, R. M. Elliott, and T. O. Merren, International Symposium on Mass Spectrometry, Paris, 1964.

[11] Obtained from Peninsular ChemResearch Inc., Gainesville, Fla.

Solvent Effects. II. The Influence of Aqueous Dimethyl Sulfoxide on Ester Saponification Reactions

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Received April 30, 1965

The rates of alkaline hydrolysis of seven ethyl esters have been determined in aqueous dimethyl sulfoxide (DMSO) solvent mixtures of 0.20 to 0.65 mole fraction of DMSO. The rate constant increase for the branched esters is proportional to the DMSO content over the entire solvent composition range and is attributed to electrostatic effects. The rate constant increase for the straight-chain esters is also sensitive to the DMSO content of the solvent, but exhibits enhanced sensitivity in the solvent composition region of a molar excess of DMSO. The influence of solvent upon the nonbranched ester reaction is attributed to electrostatic effects in the solvent mixtures with a molar excess of water and to a combination of electrostatic and specific solvation effects in solvent mixtures with a molar excess of DMSO.

The dependence of a quantitative structure–reactivity correlation of esters upon solvent was reported in the previous paper of this series.[1] The observed effect on the reaction constants was interpreted in terms of increased importance of steric interference to solvation in aqueous dimethyl sulfoxide relative to aqueous ethanol. The investigation of the alkaline hydrolysis of ethyl acetate[1] and ethyl benzoate[2] in aqueous dimethyl sulfoxide mixtures also revealed a significant solvent effect which was in qualitative agreement with the Hughes–Ingold theory.[3] In addition, the appearance of an activation energy minimum at approximately 0.45 mole fraction of dimethyl sulfoxide was observed with both esters.

In order to gain further insight concerning the observed solvation effects, the importance of various other solvent interaction mechanisms need to be established, particularly anion desolvation[4] and electro-

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[1] D. D. Roberts, *J. Org. Chem.*, **29**, 2714 (1964).

[2] D. D. Roberts, *ibid.*, **29**, 2039 (1964).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345–350.

[4] A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

Table I

Rates of Alkaline Hydrolysis of Ethyl Esters in Aqueous Dimethyl Sulfoxide

Mole fraction of DMSO	Temp., °C.	$k_2 \times 10^4$					Temp., °C.	$k_2 \times 10^4$	
		Acetate[a]	Propionate[b]	*n*-Butyrate[b]	Benzoate[b]	Isobutyrate[b]		β-Phenylisovalerate[c]	2-Ethylbutyrate[b]
0.20	10.0	690		240	57	120	20.0		1.5
	15.0	950		315	84	165	25.0		2.5
	20.0	1250		415	130	230	30.0		3.7
	25.0	1600	1100	540	190	300	35.0		5.4
0.30	10.0	900		275	120	165	20.0		4.1
	15.0	1230		380	180	215	25.0	28	6.2
	20.0	1700		500	250	300	30.0		9.7
	25.0	2230	1400	660	375	400	35.0		14.0
0.40	10.0	1240		365	210	230	20.0		9.0
	15.0	1720		490	320	320	25.0	53	12.5
	20.0	2300		670	470	430	30.0		20.0
	25.0	3130	1800	890	680	580	35.0		28.0
0.45	10.0	1690		460	330	315	20.0		14.0
	15.0	2210		630	450	460	25.0	74	20.0
	20.0	2840		880	630	660	30.0		30.0
	25.0	3800	2100	1150	840	960	35.0		40.0
0.51	10.0	1720		550	375	315	20.0		16.0
	15.0	2200		750	545	460	25.0	100	24.0
	20.0	3100		1010	745	660	30.0		37.0
	25.0	3920	2450	1390	1040	960	35.0		50.0
0.55	10.0	2320		600	500	470	20.0		25.0
	15.0	3000		840	730	670	25.0	130	34.0
	20.0	3940		1150	1040	940	30.0		49.0
	25.0	5290	3400	1600	1455	1270	35.0		60.0
0.60	10.0	3000		810	755	630	20.0		28.0
	15.0	4010		1200	1075	870	25.0	170	43.0
	20.0	5500		1700	1590	1230	30.0		66.0
	25.0		4000	2400	2300	1680	35.0		90.0
0.65	25.0		5300	3200		2200	25.0	260	
0.70							25.0		110.0

[a] All rate uncertainties ±1.0% or less with the exception of the ±2.0% uncertainties exhibited by the data at 0.60 mole fraction DMSO. [b] All rate uncertainties ±2.0% or less. [c] All rate uncertainties ±2.5% or less.

static effects.[5a] Owing to the demonstrated sensitivity to substrate steric effects, the degree of specific solvation should be reduced to a minimum with sterically hindered esters and thus afford a means of measuring the relative importance of the above solvent effects.

As a test of this hypothesis, the present paper reports a study of the solvent interaction mechanism(s) as a function of solvent composition for the saponification of seven ethyl esters in dimethyl sulfoxide–water mixtures. The esters investigated were chosen on the basis of their steric substituent constants[6a] ranging in value from 0.0 (ethyl acetate) to −1.98 (ethyl 2-ethylbutyrate).

The kinetic findings of this work are presented in Table I. Since the subsequent quantitative analysis of solvent effects requires a knowledge of the ability to replicate the rate data,[7] the earlier determinations with ethyl acetate[1] and ethyl benzoate[2] were repeated. Comparison of the paired rate values obtained from the two independent sets of data revealed average differences of ±25 for the ethyl acetate series and ±20 for the ethyl benzoate series.

The sensitivity, *m*, of the substrates to the dimethyl sulfoxide content in the varying solvent compositions is obtained by use of eq. 1. The logarithms of 10^4k_2

$$\log k_2 = mN_{\mathrm{DMSO}} + a \tag{1}$$

are plotted *vs.* the mole fraction of DMSO (N_{DMSO}) in the solvent mixtures in Figures 1 and 2. In all cases the rate constant increases with increasing DMSO content. More importantly, it is noted that, in the critical solvent composition region of N_{DMSO} = about 0.50, the branched esters fail to exhibit the deviation from linearity associated with the nonbranched esters.

For the purposes of this study, it is convenient to divide the data in Figures 1 and 2 into solvent composition regions I and II, based on the two sets of intersecting linear correlations obtained for the straight chain esters. I, $N_{\mathrm{DMSO}} = 0.20$ to 0.50, is a region of a molar excess of water, and II, $N_{\mathrm{DMSO}} = 0.50$ to 0.70, is region of a molar excess of DMSO.

The *m* values obtained by a simple linear regression analysis of log 10^4k_2 *vs.* N_{DMSO} are recorded in Table II. It is readily seen that starting with ethyl propionate the m_{I} values increase with increasing magnitude of E_{S}. Thus, in a solvent composition region of a molar excess of water (50 to 80% vol. DMSO), the solvent effect is dependent upon substrate steric substituent constants. Furthermore, it is noted that the ratio $m_{\mathrm{II}}/m_{\mathrm{I}}$ which represents the enhanced sensitivity of nonbranched esters to increasing DMSO concentration in a region of a molar excess of DMSO is nearly a constant for the three straight-chain esters investigated.

Table III lists the activation parameters for reaction at the various DMSO concentrations. The previously

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[5] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960: (a) p. 535 ff; (b) p. 536.

[6] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956: (a) p. 643; (b) 606; (c) p. 587; (d) p. 643.

[7] The rate data presented in Table I are the average of eight to ten determinations.

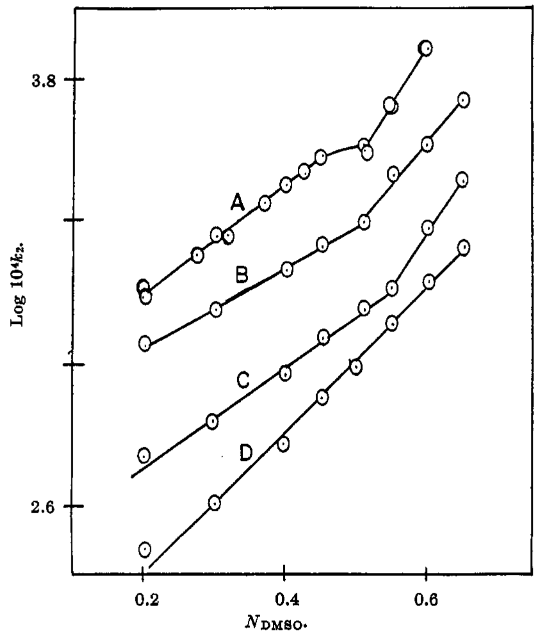

Figure 1.—Effect of the mole fraction of DMSO on reaction rate: A, ethyl acetate; B, ethyl propionate; C, ethyl *n*-butyrate; and D, ethyl isobutyrate.

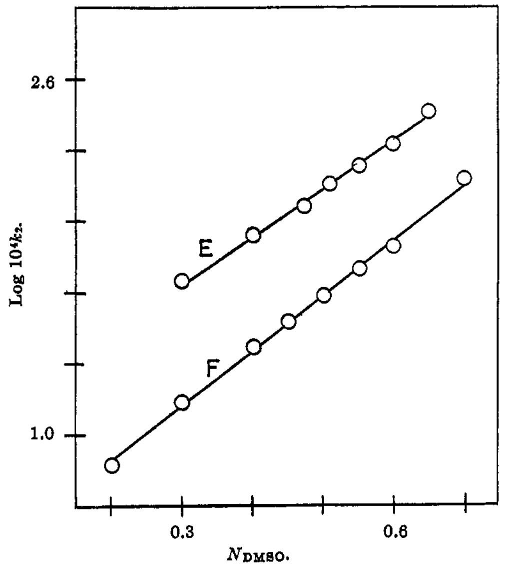

Figure 2.—Effect of the mole fraction of DMSO on reaction rate: E, ethyl β-phenylisovalerate; and F, ethyl 2-ethylbutyrate.

TABLE II

EFFECT OF MOLE FRACTION OF DMSO ON SAPONIFICATION RATE

Ester	m_I[a]	Cor. coeff.	m_{II}[b]	m_{II}/m_I
CH_3CO_2Et	1.51	0.994	2.85	1.9
$CH_3CH_2CO_2Et$	1.11	0.999	2.24	2.0
$CH_3CH_2CH_2CO_2Et$	1.64	0.994	3.10	1.9
$(CH_3)_2CHCO_2Et$	2.09[c]	0.997		
$C_6H_5C(CH_3)_2CH_2CO_2Et$	2.69[c]	0.996		
$(CH_3CH_2)_2CHCO_2Et$	3.24[c]	0.961		

[a] Value of *m* calculated for region I by use of eq. 1. [b] Value of *m* estimated for region II by use of eq. 1. [c] Includes data from entire solvent composition range.

reported[1] activation enthalpy minimum observed for the saponification reaction of ethyl acetate and ethyl benzoate as the DMSO content of the solvent is increased is confirmed and replicated by this work. More importantly, it is noted that the activation energy well and the medium effect discontinuity (see Figure 1) occur at the same solvent composition (N_{DMSO} = 0.45 to 0.50). A modified, but related, correlation is observed for the ethyl butyrate data. Modification results from the substitution of an activation enthalpy discontinuity for the energy well at N_{DMSO} = 0.50. The ethyl isobutyrate and 2-ethylbutyrate data are too irregular to analyze.

TABLE III

THERMODYNAMIC ACTIVATION PARAMETERS FOR ALKALINE HYDROLYSIS OF VARIOUS ETHYL ESTERS IN AQUEOUS DMSO

Mole fraction of DMSO	ΔH^*, cal./mole	ΔS^*, e.u.
	Ethyl Acetate	
0.20	9,100 ± 250[a]	−32 ± 2
0.30	9,500 ± 200	−30 ± 2
0.40	9,600 ± 225	−29 ± 2
0.45	8,400 ± 350	−32 ± 3
0.51	8,800 ± 250	−31 ± 2
0.55	9,700 ± 250	−30 ± 2
0.60	10,900 ± 200	−24 ± 2
	Ethyl *n*-Butyrate	
0.20	8,500 ± 200	−36 ± 2
0.30	9,100 ± 400	−33 ± 3
0.40	9,400 ± 250	−32 ± 2
0.45	9,500 ± 200	−31 ± 2
0.51	9,700 ± 200	−30 ± 2
0.55	10,400 ± 250	−28 ± 2
0.60	11,400 ± 250	−23 ± 2
	Ethyl Isobutyrate	
0.20	9,600 ± 250	−33 ± 2
0.30	9,400 ± 320	−34 ± 3
0.40	9,700 ± 250	−32 ± 2
0.45	10,000 ± 300	−30 ± 2
0.51	11,700 ± 250	−24 ± 2
0.55	10,500 ± 200	−27 ± 2
0.60	10,400 ± 200	−27 ± 2
	Ethyl Benzoate	
0.20	12,400 ± 380	−23 ± 3
0.30	12,000 ± 380	−25 ± 3
0.40	12,200 ± 400	−23 ± 3
0.45	9,800 ± 200	−30 ± 2
0.51	10,600 ± 260	−27 ± 2
0.55	11,400 ± 150	−24 ± 1
0.60	12,300 ± 200	−21 ± 2
	Ethyl 2-Ethylbutyrate	
0.20	15,100 ± 380	−24 ± 3
0.30	14,600 ± 500	−24 ± 4
0.40	13,600 ± 500	−26 ± 4
0.45	12,400 ± 500	−29 ± 4
0.51	13,400 ± 250	−26 ± 2
0.55	10,300 ± 300	−34 ± 3
0.60	13,600 ± 400	−24 ± 3

[a] Two standard deviation units from the mean.

In order to establish continuity of reaction mechanism with variable solvent composition, the rate data obtained at 25° for the ester series, RCO_2Et, were submitted to a statistical treatment employing eq. 2

$$\log k = \log k_0 + \rho^*\sigma^* + \delta E_s \qquad (2)$$

where k_0 is the regression value for the saponification constant of ethyl acetate, ρ^* is the polar reaction constant,[6b] σ^* is the polar substituent constant[6c] for the R group, δ is the steric reaction constant,[6d] and E_s

TABLE IV

CORRELATION OF ALKALINE HYDROLYSIS REACTIONS OF VARIOUS ETHYL ESTERS AT 25° WITH THE TAFT LINEAR FREE-ENERGY RELATIONSHIP

Vol. % DMSO	N_{DMSO}	ρ^*	δ	Constant[a]
85	0.60	1.46	0.95	−0.120
83	0.55	1.44	0.95	−0.243
80	0.51	1.60	0.96	−0.329
77	0.45	1.39	0.98	−0.431
73	0.40	1.67	1.02	−0.480
62.5	0.30	1.70	1.12	−0.579

[a] Regression value for the saponification constant of ethyl acetate.

is the steric substituent constant[1,6a] for the R group. The results of this analysis are recorded in Table IV.

The near invariancy of the steric and polar reaction constants[8] argues against any change of reaction mechanism as the solvent composition changes from a molar excess of water to a molar excess of DMSO. The magnitude of the reaction constants supports the previously proposed[1] looser transition state complex in aqueous DMSO relative to aqueous ethanol. Comparison of the true Y values (experimental rate constants) with the calculated Y values (log k, eq. 2) reveals maximum deviations for the two primary esters (propionate and n-butyrate) at DMSO concentrations greater than 0.50 mole fraction. The branched-chain esters follow a random error distribution.

What are the fundamental causes for the rate increases with increasing DMSO concentration in the solvent mixture? The state of the anion solvation is frequently mentioned[5,9] as a contributing cause. Thus, in aqueous DMSO the activity of the hydroxide ion is dependent upon the following equilibrium

$$[HO^-\cdot nH_2O] + (n - n')DMSO \overset{K}{\rightleftharpoons} [HO^-\cdot n'H_2O] + (n - n')[DMSO\cdot H_2O]$$

where n equals the maximum number of water molecules hydrogen bonded to hydroxide ion. With increasing DMSO content, the equilibrium would be shifted to the right, resulting in a less solvated hydroxide ion.

The effect of anion desolvation as the major contributing cause for the rate constant increases is considered unlikely for the following reasons.

(1) The activity of the hydroxide ion should increase with increasing DMSO[4] resulting in a corresponding increase in reaction rate. This is in accord with the observed rate enhancement; however, this does not explain the dependency of medium effect upon substrate steric substituent constants or the presence of the medium effect discontinuities in Figure 1.

(2) With a small ion, such as hydroxide, it is more realistic[5b] to treat the ion plus the hydrogen-bonded water molecules as a single kinetic unit. If the anion desolvation mechanism were operative, this would imply decreasing size of the nucleophile with increasing DMSO content in the solvent medium. Such a change in the steric bulk of the attacking reagent should be reflected by a variation in the reaction constant parameter, δ. No such response in δ was observed above 0.30 mole fraction of DMSO.

(3) The minimum through which the ethyl acetate activation energies pass as the DMSO concentration is varied is characteristic of a specific solvation mechanism.[10] There is no evidence to associate such an effect with the anion desolvation mechanism.

The quantitative relationship between electrostatic forces and the rate constant is given by eq. 3.[11] In

$$\ln k = Z_A{}^2e^2/2kTD(1/r - 1/r^*) + \ln k_0 \qquad (3)$$

Figures 3 and 4 are plotted the logarithms of the rate constants at 25° against $1/D$. It is again noted that two sets of linear equations, intersecting at the

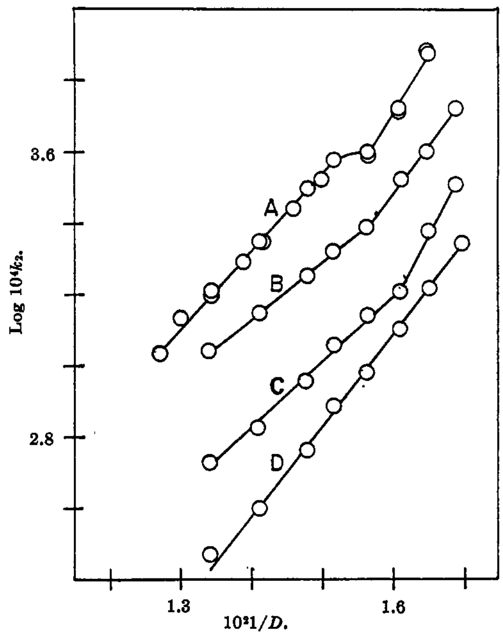

Figure 3.—Effect of solvent dielectric constant on reaction rate: A, ethyl acetate; B, ethyl propionate; C, ethyl n-butyrate; and D, ethyl isobutyrate.

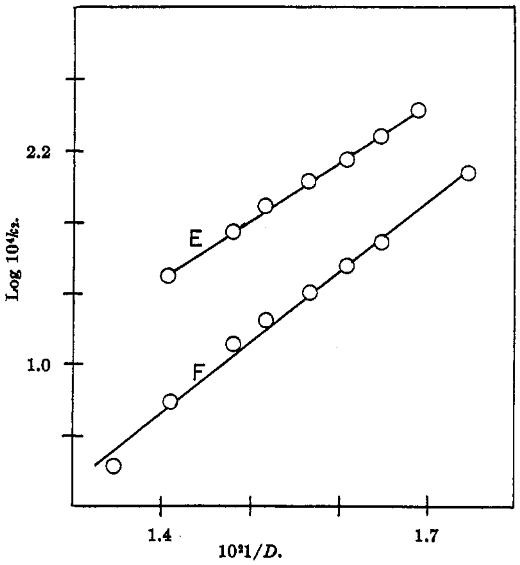

Figure 4.—Effect of solvent dielectric constant on reaction rate: E, ethyl β-phenylisovalerate; and F, ethyl 2-ethylbutyrate.

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[8] The differences between the individual polar reaction constants and their mean is well within one standard deviation unit. The values obtained at N_{DMSO} = 0.3 are considered to be significantly different.

[9] E. Tommila and M. L. Murto, *Acta Chem. Scand.*, **17**, 1947 (1963).

[10] J. B. Hyne, R. Wills, and R. E. Wonkka, *J. Am. Chem. Soc.*, **84**, 2914 (1962).

[11] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 439.

TABLE V

EFFECT OF SOLVENT DIELECTRIC ON SAPONIFICATION RATE

Ester	$\frac{d \log k_2}{d\ 1/D^a}$	Cor. coeff.	$\frac{d \log k_2}{d\ 1/D^b}$
CH_3CO_2Et	2.0	0.996	1.8
$CH_3CH_2CO_2Et$	1.6	0.999	1.4
$CH_3CH_2CH_2CO_2Et$	1.9	0.992	2.0
$(CH_3)_2CHCO_2Et$	2.5	0.997	2.5
$C_6H_5C(CH_3)_2CH_2CO_2Et$	3.3	0.996	3.3
$(CH_3CH_2)_2CHCO_2Et$	3.9	0.993	3.9

[a] Calculated by simple regression of log k_2 vs. $1/D$. [b] Calculated by use of eq. 4; $(d\,N_{DMSO})/(d\,1/D) = 1.20$ with correction coefficient = 0.994 (data obtained from ref. 9).

0.50 mole fraction solvent composition, are necessary for the straight-chain esters, while one set of linear equations satisfactorily correlates the rate data for the branched esters.

If the medium effect on rate is entirely due to dielectric effects, the following relationship should be valid. The values of $(d \ln k)/(d\ 1/D)$ obtained by simple regression analysis and by use of eq. 4 are

$$\frac{d \ln k}{d\ 1/D} = \frac{d\,N_{DMSO}}{d\ 1/D}\,\frac{d \ln k}{d\,N_{DMSO}} \tag{4}$$

recorded in Table V. The agreement between the two sets of values is good and indicates that electrostatic interaction energies are of the correct order of magnitude to account for the observed rate changes over the entire solvent-composition range for the branched esters and over the 0.20 to 0.50 mole fraction of DMSO range for the linear esters.

The rate enhancement in the region of excess DMSO for the straight-chain esters can then be attributed to specific solvation effects, *i.e.*, to short-range nonelectrostatic forces sensitive to steric bulk. Presumedly, this would involve primarily the DMSO molecules which is in accord with the enhanced ability of DMSO to stabilize extended charged structures such as transition states.[5,12]

Experimental Section

All boiling points are uncorrected for stem exposure. Purity of all distilled chemicals was established by gas chromatography.

Ethyl Esters.—Ethyl acetate, b.p. 77°, ethyl propionate, b.p. 99°, ethyl *n*-butyrate, b.p. 122°, and ethyl isobutyrate, b.p. 109–110°, were commercial samples fractionally distilled prior to use. Ethyl β-phenylisovalerate, b.p. 89° (0.4 mm.), was prepared according to published procedure.[1] Ethyl 2-ethylbutyrate was prepared in 85% yield from 2-ethylbutyryl chloride and ethanol, b.p. 149°, lit.[13] b.p. 148.7–150°.

Purification of Solvent.—Dimethyl sulfoxide was purified by distillation from calcium hydride and was stored over 4A Molecular Sieves. Analysis by g.l.p.c. did not reveal the presence of any significant amount of impurity.

Rate Measurements.—The technique and method used were those reported in previous investigations.[1,2]

Treatment of Kinetic Data.—The simple and multiple regression analyses were executed by an IBM 1620 computer.

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(12) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Am. Chem. Soc.*, **83**, 5835 (1961).

(13) F. C. Frostick and C. R. Hauser, *ibid.*, **71**, 1350 (1949).

Solvent Effects in the Oxidation of Sulfur Compounds. The Base-Catalyzed Oxidation of Alkylthiophenes

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Received May 14, 1965

The base-catalyzed oxidation of several alkylthiophenes and toluene with molecular oxygen has been studied in the polar solvent, hexamethylphosphoramide (HMPA). 2-Methyl- and 2,5-dimethylthiophene were converted to thiophene-2-carboxylic acid under the reaction conditions employed. 3-Methylthiophene and toluene were oxidized to thiophene-3-carboxylic acid and benzoic acid, respectively. The initial rates of oxidation of these compounds were measured from the amount of oxygen consumed as a function of time and have been calculated relative to the rate observed for toluene in KO-*t*-Bu–HMPA at 80°. Of particular interest was the fact that 2-methylthiophene oxidized about 50 times faster than the 3 isomer and that $k_{ox}^{KO\text{-}t\text{-}Bu}/k_{ox}^{KOH}$ for 2-methylthiophene at 80° was 25. Explanations for the observed results are presented and discussed. In addition, a brief study on the low-temperature anionic oxidation of thienylaldehyde and 2-thienyl methyl ketone was also carried out. Mechanistically, it would appear that the reaction proceeds by an anion-radical mechanism which leads to unstable hydroperoxide intermediates.

Previous studies on the anionic oxidation of sulfur compounds have shown that polar solvents have a marked effect on the rate of oxidation of mercaptans (thiols)[1-3] and hydrogen sulfide.[4] Similar observations have also been noted in the oxidation of acidic and nonacidic hydrocarbons,[5,6] the isomeric picolines,[7] and ketones.[8] An examination of the literature disclosed that anionic oxidation of weakly acidic sulfur compounds such as the alkylthiophenes has not been previously attempted. In fact, most studies on the oxidation of heterocyclic aromatic sulfur compounds have been concerned with the oxidation of thiophene or benzothiophenes in the presence of strong oxidizing agents

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(1) T. J. Wallace and A. Schriesheim, *Tetrahedron Letters*, **No. 17**, 1131 (1963), and references therein.

(2) T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **29**, 888 (1964).

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(5) (a) Y. Sprinzak, *J. Am. Chem. Soc.*, **80**, 5449 (1958); (b) G. A. Russell, *et al.*, *ibid.*, **84**, 4154 (1962); (c) *ibid.*, **84**, 2652 (1962), and references therein; (d) G. A. Russell, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 107 ff; (e) G. A. Russell, *Chem. Eng. News*, **40**, 49 (April 20, 1964); (f) G. A. Russell and E. G. Janzen, Preprints, Petroleum Division, 148th National Meeting of the American Chemical Society, Detroit, Mich., Sept. 1964, Vol. 9, No. 4, p. D-129.

(6) T. J. Wallace, A. Schriesheim, and N. Jacobson, *J. Org. Chem.*, **29**, 2907 (1964).

(7) W. Bartok, D. D. Rosenfeld, and A. Schiresheim, *ibid.*, **28**, 410 (1963).

(8) W. E. Doering and R. M. Haines, *J. Am. Chem. Soc.*, **76**, 482 (1954).