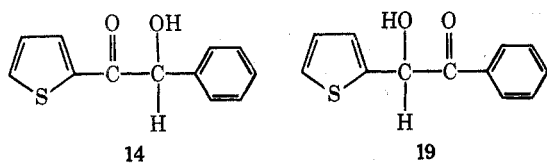thienylmagnesium iodide, to give 14 which was oxidized[20] to 6 as in Scheme I.

(20) The mass spectrum of **14** deserves further comment. It would appear that of the two possibilities for the condensation product between benzaldehyde and 2-thenaldehyde, namely, **14** and **19**, it should be possible

14   19

to distinguish between them on the basis of their mass spectra if cleavage occurred between the acyl and carbinol halves of the molecule. It appears, however, that the initial process upon electron impact is oxidation of the thenil, thus
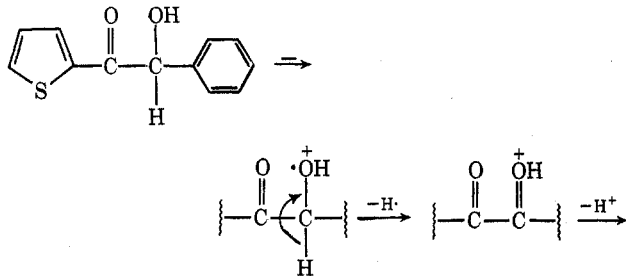
General Procedure for the Thenil–Thenilic Acid Rearrangement.—A 0.010-mol quantity of the thenil was suspended in 25 ml of water containing 2 g of potassium hydroxide. The solution was stirred and heated to reflux under N_2 until solution was effected. If solution was not complete in 1 hr, 10 ml of dioxane was added, and heating was continued an additional 2 hr. The cooled solution was acidified to congo red with concentrated HCl and immediately extracted with ether (two 25-ml portions). The combined dried (Na_2SO_4) extracts were treated with an excess of ethereal diazomethane. After stirring 1 hr at room temperature, the solvent was removed under reduced pressure, and the residue was recrystallized from 60–90° petroleum ether.

with peaks observed at m/e 216 (P − 2, 5%), 111 (2-thenoyl, 55%), 105 (benzoyl, 100%), and 77 (phenyl, 36%). A literature search failed to uncover any reports concerning the mass spectra of benzoins. A mass spectrum of benzoin taken in these laboratories reveals the same behavior, that is, no apparent peak but only signals at m/e 210 (P − 2, 3%), 105 (benzoyl, 100%), and 77 (phenyl, 47%).

Chemistry of Dithienyl Diketones. II. Kinetic Investigations

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The kinetics and thermodynamic parameters of the thenilic acid rearrangement have been followed as a function of substituent effect in the temperature range of 15–80°. A reevaluation of the ionization constants of nine thenoic acids has been made in water at 49.5°. Improved Hammett type correlations are obtained basing a new set of σ values on these ionization constants. The deviation in the Hammett plot caused by the halo substituents is discussed in terms of the mechanism of the rearrangement.

Some years ago Smith[2] and Clark[3] proposed a mechanism for the benzilic acid rearrangement in which attack by hydroxide, 1,2 migration of the aryl group, and proton transfer all occurred simultaneously. This was in contrast to the earlier concept by Ingold[4] that a complex[5] between the diketone and hydroxide preceded rearrangement to the benzilate skeleton with the temporal location of the proton transfer being unspecified. It appeared to be of interest to investigate the existence of a linear free-energy relationship and whatever bearing this might have on the reaction mechanism.

In our preceding article[6] we have described the synthesis of a number of dithienyl diketones (thenils). It was shown that, with the exception of the alkoxy thenils and 3,3′-benzo[b]thenil, these compounds undergo the benzilic acid rearrangement to give the corresponding thenilic acids in good to excellent yields. Thusly, we were able to make a quantitative study of

this rearrangement and, in addition, to further elucidate the electromeric nature of the thiophene ring.

Results

The potassium hydroxide induced rearrangement of the nine thenils in Table I was studied in the temperature range of 15–80°. Corrections were made for thenil consumed prior to t_0 and for the nonideality of the solvent, 2:1 (v/v) dioxane–water. The titrimetrically determined loss in hydroxide was used as basis to compute the observed second-order rate constants by the usual equation.[7a] In all cases, a plot of log [thenil/OH⁻] vs. time was linear to at least 3 half-lives of the thenil, the minor component.[8]

Thermodynamic parameters for each reaction were calculated in the usual manner from the Arrhenius equation and the Eyring equation[9] and are presented in Table II. The entropy of activation, $\Delta S^{\ddagger}_{323°K}$, was

(1) Abstracted, in part, from the Ph.D. dissertation of G. P. N.

(2) D. G. Ott and G. G. Smith, *J. Amer. Chem. Soc.*, **77**, 2325 (1955).

(3) M. T. Clark, E. G. Hendley, and O. K. Neville, *ibid.*, **77**, 3280 (1955).

(4) C. K. Ingold, *Annu. Rep., Chem. Soc. (London)*, 124 (1928).

(5) A claim is made for the isolation of this intermediate complex which, depending on reaction conditions, can give benzilic acid or can be decomposed back to benzil and hydroxide: G. Scheuing, *Chem. Ber.*, **56**, 252 (1923).

(6) R. D. Schuetz and G. P. Nilles, *J. Org. Chem.*, **36**, 2486 (1971).

(7) (a) F. H. Westheimer, *J. Amer. Chem. Soc.*, **58**, 2209 (1936), has shown that the rearrangement is first order in base and first order in diketone. Thus, we employed the usual second-order equation as in S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, p 18; (b) p 91.

(8) It became quite tedious with compounds such as 5,5,-dimethyl-2,2′-thenil to perform rate studies beyond 2 half-lives, since this would have required individual runs lasting longer than 3 days.

(9) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 71.

TABLE I
SECOND-ORDER RATE CONSTANTS FOR THE THENILIC ACID REARRANGEMENT AT VARIOUS TEMPERATURES

Compd[a]	Registry no.	15°	30°	40°	50°
2,2'-Thenil	7533-07-5	6.07×10^{-5}	2.35×10^{-4}	$5.35 \pm 0.14 \times 10^{-4}$	$1.22 \pm 0.04 \times 10^{-3}$
5,5'-Dimethyl-2,2'-thenil	30135-04-7	1.22×10^{-5}	4.50×10^{-5}	$9.85 \pm 0.73 \times 10^{-5}$	$1.96 \pm 0.30 \times 10^{-4}$
5-Methyl-2,2'-thenil	30135-05-8	3.84×10^{-5}	1.28×10^{-4}	$2.74 \pm 0.13 \times 10^{-4}$	$5.20 \pm 0.31 \times 10^{-4}$
5,5'-Dichloro-2,2'-thenil	30135-23-0	$1.29 \pm 0.04 \times 10^{-2}$	$4.50 \pm 0.33 \times 10^{-2}$	$9.18 \pm 0.14 \times 10^{-2}$	1.86×10^{-1}
5,5'-Difluoro-2,2'-thenil	30135-26-3	$5.11 \pm 0.14 \times 10^{-3}$	$1.81 \pm 0.07 \times 10^{-2}$	3.90×10^{-2}	$8.07 \pm 0.35 \times 10^{-2}$
5,5'-Di(2''-thenyl)-2,2'-thenil	30288-11-0	1.24×10^{-4}	4.88×10^{-4}	1.12×10^{-3}	$2.57 \pm 0.12 \times 10^{-3}$
2,2'-Benzo[b]thenil	30135-06-9	8.53×10^{-4}	3.84×10^{-3}	$9.77 \pm 1.23 \times 10^{-3}$	$2.36 \pm 0.07 \times 10^{-2}$
2-Thienylphenyl diketone	30135-07-0	1.99×10^{-5}	3.11×10^{-5}	$1.82 \pm 0.14 \times 10^{-4}$	$3.68 \pm 0.12 \times 10^{-4}$
3,3'-Thenil	30135-08-1	3.61×10^{-5}	7.92×10^{-5}	$1.31 \pm 0.07 \times 10^{-4}$	$1.87 \pm 0.15 \times 10^{-4}$

Compd[a]	60°	70°	80°	r[b]
2,2'-Thenil	$2.46 \pm 0.08 \times 10^{-3}$	$4.96 \pm 0.11 \times 10^{-3}$	$9.36 \pm 0.11 \times 10^{-3}$	0.999+
5,5'-Dimethyl-2,2'-thenil	$3.84 \pm 0.31 \times 10^{-4}$	$7.54 \pm 0.45 \times 10^{-4}$	$1.57 \pm 0.15 \times 10^{-3}$	0.999
5-Methyl-2,2'-thenil	$1.00 \pm 0.02 \times 10^{-3}$	$1.93 \pm 0.07 \times 10^{-3}$	$3.40 \pm 0.07 \times 10^{-3}$	0.999
5,5'-Dichloro-2,2'-thenil	3.60×10^{-1}	6.70×10^{-1}	1.20	0.999+
5,5'-Difluoro-2,2'-thenil	1.60×10^{-1}	3.03×10^{-1}	5.55×10^{-1}	0.999+
5,5'-Di(2''-thienyl)-2,2'-thenil	$5.11 \pm 0.38 \times 10^{-3}$	$1.14 \pm 0.07 \times 10^{-2}$	$2.01 \pm 0.34 \times 10^{-2}$	0.998
2,2'-Benzo[b]thenil	$5.46 \pm 0.23 \times 10^{-2}$	$1.12 \pm 0.08 \times 10^{-1}$	2.33×10^{-1}	0.999+
2-Thienylphenyl diketone	$8.79 \pm 0.62 \times 10^{-4}$	$1.48 \pm 0.07 \times 10^{-3}$	$3.65 \pm 0.25 \times 10^{-3}$	0.996
3,3'-Thenil	$3.07 \pm 0.11 \times 10^{-4}$	$4.60 \pm 0.24 \times 10^{-4}$	6.85×10^{-4}	0.997

[a] Rate constants shown without standard deviations are those extrapolated from the Arrhenius plot. [b] Correlation coefficient for the Arrhenius plot.

TABLE II
THERMODYNAMIC CONSTANTS FOR THE THENILIC ACID REARRANGEMENT

Compd[a,b]	$\Delta H^{\ddagger}_{323K}$	$\Delta S^{\ddagger}_{323K}$	$\Delta F^{\ddagger}_{323K}$	Log A[c]
2,2'-Thenil	15.0 ± 0.3	-25.6 ± 1.3	23.3 ± 0.7	7.676
5,5'-Dimethyl-2,2'-thenil	14.5 ± 1.0	-30.8 ± 5.5	24.4 ± 2.8	6.522
5-Methyl-2,2'-thenil	13.3 ± 0.4	-32.5 ± 2.4	23.8 ± 1.2	6.162
5,5'-Dichloro-2,2'-thenil	13.5 ± 0.6	-20.3 ± 1.6	20.0 ± 1.1	8.820
5,5'-Difluoro-2,2'-thenil	14.6 ± 0.4	-20.5 ± 1.5	20.6 ± 0.9	8.773
3,3'-Benzo[b]thenil	16.8 ± 1.0	-14.2 ± 1.8	21.4 ± 1.6	10.155
5,5'-Di(2''-thienyl)-2,2'-thenil	15.2 ± 1.3	-23.6 ± 4.0	22.8 ± 2.6	8.104
2-Thienylphenyl diketone	15.6 ± 0.6	-26.1 ± 3.0	24.0 ± 1.6	7.569
3,3'-Thenil	8.40 ± 0.8	-49.5 ± 5.4	24.4 ± 2.5	2.447

[a] $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ are in units of kcal/mol; $\Delta S^{\ddagger}$ is in cal/(°K mol). [b] A plot of $\Delta S^{\ddagger}$ vs. $\Delta H^{\ddagger}$, omitting the values for the halothenils, gives an isokinetic temperature of 242 ± 24°K. [c] A is the preexponential factor from the Arrhenius equation.

calculated[10] by eq 1. The uncertainties in the energy of activation and, consequently, the enthalpy of activa-

$$\Delta S^{\ddagger}_{323} = 4.576 \log A - 60.689 \qquad (1)$$

tion were calculated by Benson's method[7b] with the errors due to temperature being assumed negligible. Errors in the entropy of activation were estimated from Wiberg's expression.[11]

Previous efforts at correlating physical parameters in thiophene compounds with Hammett's σ values based on the ionizations of benzoic acids have been only partially successful.[12]

Accordingly, potentiometric determinations of the ionization constants of nine thenoic acids in Table III were made in water at 49.5°. From these, the corresponding "σ_θ" values were calculated as the log of the

(10) A simple combination of the Eyring equation with the Arrhenius equation together with the relationship that $\Delta H^{\ddagger} = E_a - RT$ gives eq 1 which is valid at 323°K, although in the range 293-353°K the maximum error within 30°K of this temperature is only 0.4%.

(11) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 379.

(12) For example, see H. H. Jaffe and H. L. Jones, *Advan. Heterocycl. Chem.,* **3**, 240 (1964); R. D. Schuetz and D. M. Teller, *J. Org. Chem.,* **37**, 410 (1962); P. A. TenThije and M. J. Janssen, *Recl. Trav. Chem. Pays-Bas,* **84**, 1169 (1965).

ratio of the ionization constants of the unsubstituted vs. the substituted acids.

Discussion

The entropies of activation are in agreement with those expected for a reaction involving considerable restricted geometry in the transition state. The entropy of activation of -14.2 eu for the rearrangement of 2,2'-benzo[b]thenil indicates that a lesser degree of ordering may be necessary in going from the ground state to the transition state for the reaction. This may be due to steric interactions in the ground state which invoke a specific conformation of the benzo[b]thienyl rings. Coincidentally, this geometry may be similar to that required by the transition state and hence shows up as a less negative entropy of activation, relative to the other thenils.

In a similar manner, the high value of $\Delta S^{\ddagger}$ of -49.5 eu for the 3,3'-thenil rearrangement could indicate that the geometry of the transition state bears little resemblance to the geometry of the ground state. It must be kept in mind, however, that according to the Ingold mechanism for the rearrangement the observed thermodynamic data would be a function of either the

TABLE III

IONIZATION CONSTANTS AND σ VALUES FOR NINE THENOIC ACIDS

Compd	Registry no.	$pK_a{}^{a,b}$	σ_θ	σ^c
2-Thenoic acid	527-72-0	3.617 ± 0.016	0.000^d	
5-Methyl-2-thenoic acid	1918-79-2	3.784 ± 0.019	-0.167 ± 0.035	-0.170 ± 0.02
5-Chloro-2-thenoic acid	24065-33-6	3.341 ± 0.014	0.276 ± 0.030	0.227 ± 0.02
5-Nitro-2-thenoic acid	6317-37-9	2.620 ± 0.018	0.997 ± 0.034	0.778 ± 0.02
5-Fluoro-2-thenoic acid	4377-58-6	3.430 ± 0.014	0.187 ± 0.030	0.062 ± 0.02
5-Methoxy-2-thenoic acid	29212-22-4	3.842 ± 0.014	-0.225 ± 0.030	-0.268 ± 0.02
3-Thenoic acid	88-13-1	4.157 ± 0.014		
3-Benzo[b]thenoic acid	5381-25-9	4.032 ± 0.036	0.125 ± 0.050^e	0.042 ± 0.02
2-Benzo[b]thenoic acid	6314-28-9	3.336 ± 0.012	0.251 ± 0.028	0.042 ± 0.02

[a] At 49.5°; ranges are the average of the standard deviations of three runs of nine determinations each. [b] Corrections to thermodynamic pK values may be made from the extended Debye-Hückel equation with the ion size parameter $= 9$ Å, and the ionic strength ~ 0.001. This will raise the pK values given by 0.015, but this value cancels in calculating σ_θ. [c] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958). [d] By definition. [e] Based on the pK_a of 3-thenoic acid.
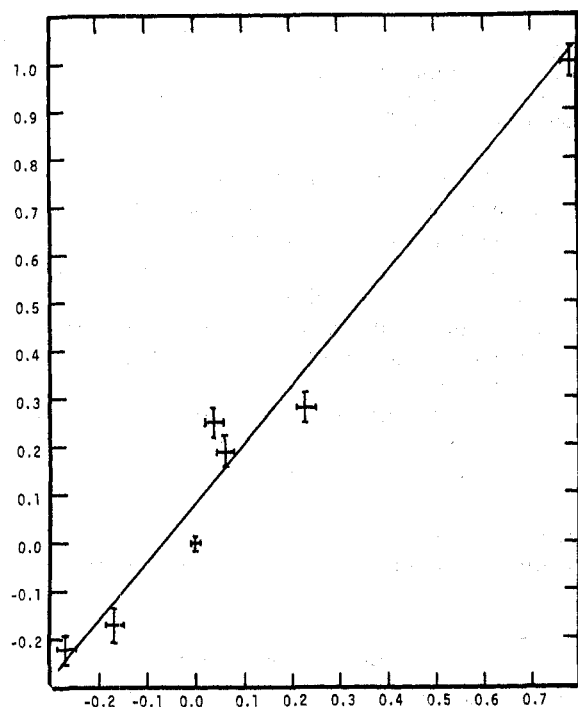
Figure 1.—Plot of σ vs. σ_θ based on the data in Table III.

equilibrium reaction between the thenil and hydroxide or the rearrangement of that intermediate to the thenilate anion, depending on the relative free energies of activation for each step.

Other factors, such as differences in solvation between the ground state and the transition state, will also affect the entropy of activation, but such effects should be small relative to steric effects.

The rearrangement of 2,2'-thenil is faster [k = 1.22×10^{-3} l./(mol sec)] than benzil [k = 1.00×10^4 l./(mol sec[13])] at 50° in 2:1 dioxane–water. This is a rather clear manifestation of the electron-withdrawing nature of the 2-thienyl group which parallels the acidity of benzoic acid (pK_a = 4.229 at 49.5°) vs. 2-thenoic acid (pK_a = 3.617 at 49.5°). One is tempted to postulate stabilization of the incipient negative charge at the migration origin via d-orbital interaction, although at this point there is nothing to substantiate this. It can be noted, though, that 3,3'-thenil in which the sulfur is one more carbon removed

from the active site of the diketone rearranges at a rate much closer to that of benzil.

From Table III, it is evident that while electron-donating substituents have roughly the same magnitude electron-withdrawing substituent effects are enhanced in thiophene compounds compared to the corresponding benzene compounds. Thus, it appears that there cannot be an accurate, simple relationship between substituent effects in benzene vis-à-vis substituent effects in 5-substituted 2-thiophenes, especially those with electron-withdrawing groups. This is further exemplified by a plot of σ vs. σ_θ from Table III. This plot (Figure 1), shows only a "fair"[14] correlation, r = 0.943. Considerable improvement in correlating reactivities in thiophenes might be expected by using σ_θ instead of σ.

Returning to the benzilic acid rearrangement, in either the concerted (Smith–Clark) or the two-step (Ingold) mechanism, the rate of rearrangement should be dependent on the electrophilicity of the carbonyl carbons (plural) and to some extent on the stabilization of the developing negative character at the migration origin.

Ingold mechanism
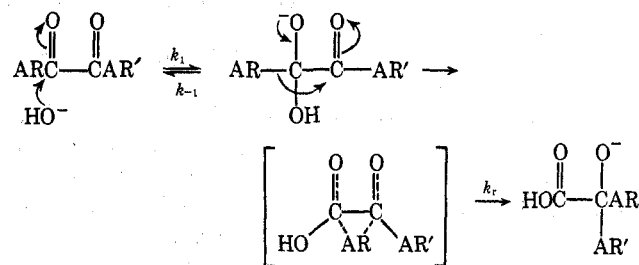
Smith–Clark mechanism
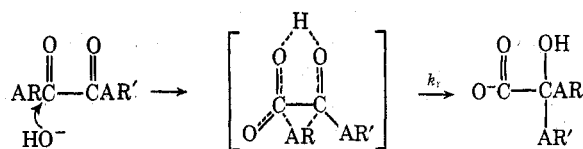
Evidence of this is shown in the Hammett plot (Figure 2) for which a linear relationship is given when using the sum of the substituent constants for 2,2'-thenil, 5-methyl-2,2'-thenil, and 5,5'-dimethyl-2,2'-

(13) J. Hine and H. W. Haworth, *J. Amer. Chem. Soc.*, **80**, 2274 (1958).
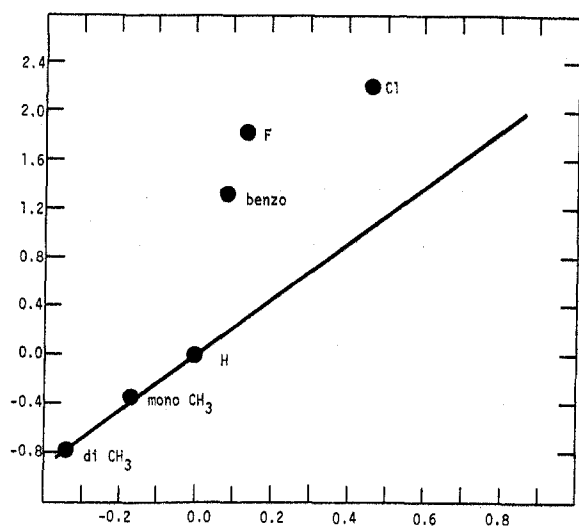
(14) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

Figure 2.—Hammett plot at 50° based on σ for the first six compounds in Table II ($r = 0.923$). The line through the first three points has been extended to show the deviation from linearity as a result of the electron-withdrawing substituents.
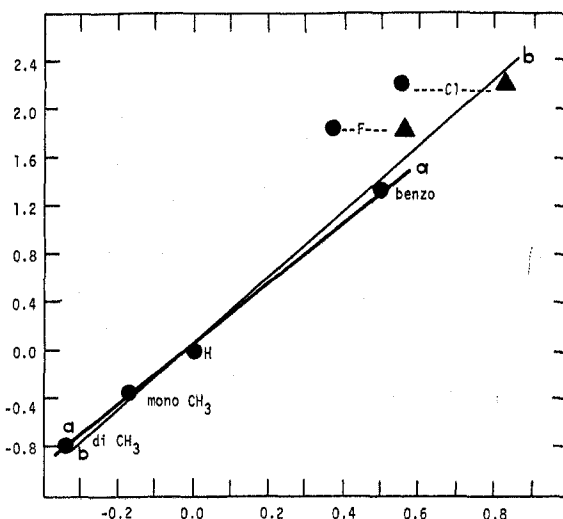

Figure 3.—Hammett plot at 50° based on σ_θ for the first six compounds in Table II: a, plotted by $2\sigma_\theta$ ($r = 0.964$); b, same as a but with the chloro and fluoro σ_θ values multiplied by 3 rather than 2 ($r = 0.994$).

thenil.[15] Thus, in all of the Hammett plots the substituent constants were summed.

The correlation coefficient for the plot in Figure 2 is only fair, $r = 0.923$. The main deviation is caused by the electron-withdrawing groups. If the plot is made using σ_θ (Figure 3) instead of σ, the correlation is much improved, $r = 0.964$, although still less than desirable. It can be noted that the benzo group now falls in line, but the halo substituents are still considerably displaced from linearity.[16] If the sum of the σ_θ's for chloro and fluoro are multiplied by 1.5, the fit to the Hammett plot in Figure 3 becomes excellent, $r = 0.994$.

It is tempting to conclude that this rate enhancement due to the halo substituents, above that predicted on the basis of their σ_θ values, would be evidence for the equilibrium step in accord with the Ingold mechanism. However, the observed kinetic data can give information concerning only the overall energy of activation encountered in going from reactants to products.

If the $\Delta F^{\ddagger}$ for the formation of the complex is much less than the $\Delta F^{\ddagger}$ for the rearrangement of the complex, we would observe kinetically only substituent effects on the latter. Such results would be indistinguishable from the case with no prior equilibrium, i.e., the Smith-Clark mechanism. A break in the Hammett plot could be ascribed to other mechanistic perturbations. However, it may be noted that the effect of the substituents may be disproportionate in regard to the magnitude of the free energies of activation for each step especially in going from electron-donating to electron-withdrawing groups. This would also cause a break in the Hammett plot.[17]

The slope of the regression line (ρ) for the plot in Figure 3 was virtually temperature independent,

2.624-2.667 in the range of 15-80°. The magnitude of ρ again emphasizes the enhancement of the reaction rate by electron-withdrawing groups.

Evidence has shown[18] that the 2-thienyl group can function as a resonant electron donor or an inductive electron-withdrawing group. While 5-(2'-thienyl)-2-thenoic acid was too insoluble to permit potentiometric pK_a determinations, a secondary value for σ_θ could be determined. Using a value of 2.66 for ρ, the Hammett plot yields a value of $+0.04$ for σ_θ of 2-thienyl. While this figure is agreeably comparable to the σ value for phenyl (-0.01 ± 0.05), it is probably more evident that the substituent constant for 2-thienyl will be reaction dependent and no one value can be properly assigned.

Experimental Section

The thenoic acids, whose pK_a's were determined, were prepared by silver oxide oxidation of the corresponding aldehydes.[19] They were purified by three crystallizations from water followed by drying in a pistol at 56° (1 Torr) and then stored over phosphorus pentoxide for 1 week. The ionization constants were determined in water according to the method of Albert and Serjeant,[20] using a Beckman Model 1019 research pH meter equipped with Corning No. 476002 reference electrode and a Beckman No. 40498 glass electrode. The cell in which the pK_a determinations were made was thermostated at 49.5°. Care was taken to ensure temperature equilibrium of the entire system including the electrodes before measurements were made. The titrant, CO_2-free potassium hydroxide, was prepared from 0.1 N "Acculutes" (Anachemia Chemical Co., Champlain, N. Y.). Only distilled freshly boiled water was used in all dilutions. Reagent grade dioxane was further purified by stirring over lithium aluminum hydride for 24 hr, followed by a 6-hr reflux and then distillation. It was stored over 5A molecular sieves. After 3 days, any unused dioxane was repurified. Temperatures were determined using a Will Scientific No. 26846, -5 to $+101°$ thermometer stated to comply with NBS Circular No. 8. The temperatures were further checked by a calibrated

(15) The rate constants for the rearrangement are also related by $k = (k_0k')^{1/2}$ where k is for the hybrid compound and k_0 and k, are the rate constants for the symmetrical thenils. The same relationship holds (within experimental error) for 2,2'-thenil, 2-thienylphenyl diketone (the "hybrid"), and benzil.

(16) A plot of $\Delta F^{\ddagger}$ for the rearrangement of these thenils vs. σ_θ also exhibits a break for the halo substituents.

(17) J. O. Schreck, *J. Chem. Educ.*, **48**, 103 (1971).

(18) S. Gronowitz, *Advan. Heterocycl. Chem.*, **1**, 89 (1963); E. A. Hill, M. L. Gross, M. Stasiewics, and M. Manion, *J. Amer. Chem. Soc.*, **91**, 7381 (1969); D. S. Noyce, C. A. Lipinski, and G. M. Loudon, *J. Org. Chem.*, **35**, 1718 (1970).

(19) See part I of this series and ref 9 for the preparation of the aldehydes. The oxidation procedure was essentially that of E. Campaigne and W. M. LeSuer, *Org. Syn.*, **33**, 94 (1953).

(20) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Wiley, New York, N. Y., 1962, Chapter 2.

Hewlett-Packard No. 2801A quartz digital thermometer. Temperatures are believed accurate to +0.04°.

Kinetic measurements for all of the thenils, with the exception of 3,3'-benzo[b]thenil, 2,2'-benzo[b]thenil, and 5,5'-di(2''-thienyl)-2,2'-thenil, were carried out in the same manner. A sample of the thenil, in the range of 2.5–3.0 mmol, was weighed to 0.1 mg and placed in a 250-ml Teflon screw cap bottle, along with a magnetic stirring bar. The thenil was dissolved in 100.0 ml of equilibrated dioxane with stirring. The solution was continuously stirred during the kinetic run by means of a submersible magnetic stirrer mounted directly beneath the reaction vessel. A 50.00-ml quantity of 0.1 N temperature equilibrated potassium hydroxide solution was pipetted into the thenil solution with vigorous stirring. The vessel was sealed with a screw cap arrangement that permitted the insertion and withdrawal of a pipette. A 10.00-ml aliquot of the thenil solution was immediately withdrawn. The aliquot was quenched in a 10-ml sample of ice cold acetone and the clock was started.

The sample was titrated to either a phenolphthalein (pH 8.3) or thymol blue (pH 8.0) end point with 0.01 N hydrochloric acid. At various intervals, depending on the rate of potassium hydroxide disappearance, 10-ml aliquots were withdrawn and titrated in the same manner. Simultaneously with the kinetic runs, a blank sample was determined under the same conditions described above, except that the thenil was omitted. In this manner it was possible to correct for any acidic impurity present in the thenil and also for any reaction of the base with the solvent. During the 80° runs and to a lesser extent at 70°, a small correction (by never more than 3%) was found to be necessary. At other temperature, the correction was too small to be measured.

Samples of 3,3'-benzo[b]thenil, 2,2'-benzo[b]thenil, and 5,5'-di(2''-thienyl)-2,2'-thenil were too insoluble to be determined at the concentrations used above for the other thenils. Accordingly, samples in the range 0.3–0.8 mmol, but never less than 0.1000 g, were used in the kinetic determinations. The amount of dioxane used was 100 ml, but the 50 ml of potassium hydroxide was replaced by 15 ml of potassium hydroxide and 35 ml of water. All other conditions were the same.

Since a mixture of dioxane and water does not constitute an ideal solution in the thermodynamic sense, the following equation was used to calculate the actual volume of the reaction mixture at the start of a given kinetic run

$$V_{mix} = \frac{v_1(\rho_1) + v_2(\rho_2)}{\rho_{mix}}$$

where v_1 and v_2 are the volumes of dioxane and water measured out, ρ_1 and ρ_2 are the densities of dioxane and water at a given temperature,[21] and ρ_{mix} is the density of the mixture at the same temperature.[22] In these calculations, the thenils and potassium hydroxide are assumed to behave ideally. All linear plots were refined by least-squares analysis. All calculations were preformed on a Wang 320 electronic calculator.

(21) F. Horvaka, R. A. Schaefer, and D. Dreisbach, *J. Amer. Chem. Soc.*, **58**, 2264 (1936).

(22) H. Hartmann, *Z. Phys. Chem. (Leipzig)*, **191**, 197 (1942).

Metal-Catalyzed Hydroperoxide Reactions. II.[1]
Molybdenum-Catalyzed Epoxidations of Styrene and Some Substituted Styrenes

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Received January 11, 1971

A kinetic study has been carried out on the epoxidation of styrene and some substituted styrenes by *tert*-butyl hydroperoxide in the presence of molybdenum naphthenate. In benzene solution the reaction is first order in peroxide (in the range 0.1–0.3 M), in alkene (0.2–0.4 M), and in catalyst (0.0–4.58 × 10⁻⁴ g-atom of Mo kg⁻¹). The rates for the substituted styrenes show considerable scatter for attempted correlations with various free-energy relationships; however, a $\rho\sigma$ plot gives $\rho = -1.4 \pm 0.6$ (95% confidence levels). Thus, the rate-determining step presumably involves electrophilic attack upon the alkene. With styrene as solvent the reaction is first order in hydroperoxide but displays no simple dependence on molybdenum concentration. The apparent order in catalyst decreases as its concentration is increased in a manner which, though not fully understood, suggests either some form of special complexing or lack of true solubility in the medium.

Alkenes are readily epoxidized by organic hydroperoxides in the presence of catalytic amounts of molybdenum and vanadium compounds.[2–7] The kinetics of the epoxidation have been reported for 1- and 2-octene in the presence of molybdenum hexacarbonyl[4,5] and for cyclohexene with vanadium acetylacetonate.[7] The former reaction is first order in catalyst and alkene,[4] and apparently first order in peroxide, but the first-order rate constants obtained vary with initial peroxide concentration.[5] The vanadium-catalyzed cyclohexene epoxidation is also first order in catalyst and alkene, but the rate dependence on peroxide has been shown to be analogous to the Michaelis–Menten equation for enzyme catalysis.[7] Two noticeable features of this latter reaction are the marked inhibition by small quantities of *tert*-butyl alcohol, a reaction product, and rapid catalyst deactivation, effects apparently absent in the molybdenum-catalyzed octene epoxidation.[4,5] The proposed mechanism[4–7] involves rapid reversible complex formation between peroxide and catalyst preceding a rate-determining heterolysis of the complex O–O bond.

This paper describes a kinetic investigation of the molybdenum catalyzed epoxidation of styrene and some substituted styrenes, in order to clarify the position with regard to the kinetics and mechanism of the molybdenum-catalyzed epoxidation and also as part of a general study of substituent effects in aromatic systems.

Results and Discussion

Epoxidations were carried out using *tert*-butyl hydroperoxide (subsequently referred to simply as "peroxide") and followed by iodometric titrations of re-

(1) (a) The research described in this paper has been carried out under support by the National Research Council of Canada, Grant No. 34-02-01. (b) Part I: G. R. Howe and R. R. Hiatt, *J. Org. Chem.*, **35**, 4007 (1970).

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