Heteroaromatic Ring Reactivity. Evaluation of σ^+ Constants in 5-Membered Aromatic Rings Containing Sulfur and Oxygen (1)

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Sir:

σ^+ -Constants have been evaluated in neutral and solvent free systems in the gas phase thermolysis of 1-arylethyl acetates in which the aryl group was 2- and 3-thienyl, 2- and 3-benzothienyl, 2-furyl and 2-benzofuryl.

Aromatic electrophilic reactivity (including reports of linear free energy relationship) of 5-membered heterocyclic ring systems has received considerable attention during the last few years. Studies have been made recently by bromination (2a-2d), chlorination (2a,2c,2d), acetylation (2a), trifluoroacetylation (2e), nitration (2f), protodesilylation (2g), protodetritiation (2h), protodeboronation (2i), protodemercuration (2j), iododeboronation (2k), protodedeuteriation (2l), and by a variety of side chain reactions. For example, solvolysis studies have been made on esters of aryl methyl carbinols (2m). In addition, electrophic aromatic reactivity has also been studied *via* ionization potentials (2n). Somewhat related are the studies of σ and σ^- constants obtained from the evaluation of ionization constants of substituted benzoic acid and phenol using the thiophene nucleus attached to the benenzoid ring reported by Marino, *et al.*, (3). Marino, *et al.*, and Butler have reported σ -constants from ionization constants of various 5-membered ring heterocyclic carboylic acids (4a) and of 5-substituted 2-thiophene carboxylic acid (4b). Homolytic aromatic substitution of thiophene has recently been reported (4c).

With the exception of Linda and Marino's studies of ionization potentials (2m) all of the other studies have been carried out under condensed phase reaction conditions where it is virtually impossible to separate solvent participation on reactivity from the effects of changes in structure of the reacting molecule.

Sometime ago, the advantages of using gas phase thermolysis to determine ring reactivities in a fashion similar to electrophilic aromatic substitution were discussed (5). Here we report the application of this method to a study of the reactivity at the 2- and 3-positions of thiophene, the 2- and 3-position of benzothiophene and the 2-position of furan and benzofuran and compare the results to condensed phase studies.

Heteroaromatic 1-arylethyl acetates were thermolyzed between the temperature of 624° and 657°K to an arylethylene and acetic acid. Under conditions where specially coated reaction walls are used, this decomposition proceeds through a homogeneous, unimolecular first order

$$\text{ArCHCH}_3 \longrightarrow \text{ArCH=CH}_2 + \text{HOAc}$$
$$\underset{\text{OAc}}{|}$$
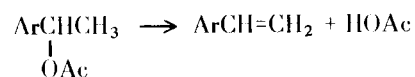
reaction most likely involving a cyclic transition state with a polarized $C^{\delta+}\text{--}O^{\delta-}$ bond. The mechanism of this reaction has been discussed in detail recently (6). It is unlikely that sufficient energy is imparted to the ester during thermolysis to form carbonium ions in the gas phase. The values for log k/k_ϕ in the thermolysis of 1-arylethyl esters correlate (5,7) very well with σ^+ -substituent constants (8). Reactivity as measured by electrophilic aromatic substitution has often been correlated with σ^+ -constants.

Results and Discussion.

The results for the rate constants, log A, E_a, $\Delta S^{\ddagger}$, log k/k_{phenyl} and σ^+ -constants for the thermolysis of these heterocyclic 1-arylethyl acetates are shown in the Table. The σ^+ values obtained from this pyrolysis study are compared to other σ^+ values reported from condensed phase studies, *e.g.* protodesilylation, iododebromination, molecular bromination, protodetritiation, solvolysis of heteroaromatic 1-arylethyl acetates and other data obtained in a similar manner from the pyrolysis of 1-arylethyl acetates (7). When one considers the variation which may result from solvent effects and the marked difference in the methods used to evaluate substituent constants, the similarity in the results is remarkable. The results obtained by electrophilic aromatic substitution in each case are higher than the values obtained from gas phase thermolysis.

Taylor (5a,7) has pointed out the problems and disadvantages of using condensed phase electrophilic substitution reactions which involve high ρ values in determining substituent constants. One of the more obvious

TABLE

Thermolysis of 1-Arylethyl Acetates

Aryl Ring	log A	E_a kcal/mole	$\Delta S^{\ddagger}$ e.u. 645.2°K	$k \, 10^3$ 645.2°K	$k \, 10^3$ 600°K	log k/k φ 600°K	σ^+(a)	σ^+(b)	σ^+(c)	σ^+(d)	σ^+(e)	σ^+(f)	σ^+(g)	σ^+(h)
Phenyl	12.19	42.2±0.3	-4.3±0.5	7.44±2.3%	0.659		0.0							-0.94
2-Furyl	11.71	39.5±0.4	-6.5±0.6	19.8±1.7%	2.06	0.495	-0.75	-0.89		-0.91		-0.97	-0.87	-0.84
2-Thienyl	12.10	40.7±0.3	-4.7±0.5	19.5±1.5%	1.86	0.451	-0.68	-0.79	-0.79	-0.79	-0.84	-0.80	-0.50	-0.47
3-Thienyl	11.99	41.2±0.6	-5.2±1.0	11.1±3.0%	0.950	0.159	-0.24	-0.38	-0.52	-0.60	-0.60			-0.47
2-Benzo[b]furyl							-0.65 (i)							
2-Benzo[b]thienyl	11.16	38.4±1.8	-9.0±2.8	14.4±6.3%	1.470	0.348	-0.53						-0.64	-0.43
3-Benzo[b]thienyl	11.01	38.1±1.2	-9.7±1.9	12.2±3.8%	1.330	0.305	-0.46						-0.65	-0.52

(a) This work. σ^+ constants were calculated using log k_{rel} at 600° and ρ = -0.66 evaluated at 600° (Reference 5a). (b) Pyrolysis, Reference 7. Using Taylor's reported E_a and $\Delta S^{\ddagger}$ values, k_{rel} values were recalculated at 600°K. The σ^+ values were changed down to -0.85, -0.74 and -0.33, respectively. (c) Marino et al., Reference 2a. These values were determined from a plot of log α_f (the log of the partial rate factors) versus the ρ for the reactions. (d) Protodesilylation, Reference 2g. Jaffe and Jones, Reference 2g, reported -0.98 and -0.85 for protodesilylation in MeOH Aq HClO₄ from Eaborn and Sperry, Reference 2g, study. (e) Iododeboronation, Reference 2k. (f) Molecular bromination, Reference 2a. (g) Protodetritiation, Reference 2h. (h) Solvolysis of acetates of arylmethyl carbinols (Hill et al., Reference 2m). (i) This σ^+ value was determined using rate constants at 663.2° for the 1-phenylethyl acetate and 1-(2-benzo[b]furyl)ethyl acetate which were 10.5 x 10⁻³ ± 0.2 and 25.8 x 10⁻³ ± 1.0, respectively. Difficulty was encountered with this compound apparently due to product polymerization which precluded the obtaining of good Arrhenius parameters. A ρ-value of -0.60 was used in calculating σ^+. These data were obtained by Daniel J. Kramer.

advantages of pyrolysis studies in heterocyclic compounds over reactions in polar solvents and acid promoted reactions is that the heteroatom is not solvated or protonated by the acid. Salt formation would cause a marked alteration in ring reactivity. The difference observed could reflect these complications.

The results for the σ^+ values for the 2-furyl and the 2- and 3-thienyl reported in this study are lower than those reported by Taylor (7). Two explanations may account for the difference. The ρ-value is temperature sensitive and was determined to be -0.66 for pyrolysis of benzenoid 1-arylethyl acetate at 600°K (5a). Using Taylor's (6) reported E_a and $\Delta S^{\ddagger}$ values the log k_{rel} values were recalculated at 600°K and σ^+ values were redetermined. These values are within 0.1 of our values (see footnote b in the Table). Secondly, activation of the walls of the reactor may also contributed to the difference. Kineticists consider the slower rates in gas phase reaction to be more accurate for homogeneous reactions as wall reactions are faster. Pyrolysis studies of 1-arylethyl acetate involving heterocyclic ring systems show some signs of being more susceptible to wall reactions than 1-phenylethyl acetate (the standard). Therefore, larger σ^+ values would be obtained in systems where some heterogeneous catalysis takes place.

The σ^+ values for 2-benzofuryl, 2-benzothienyl, and 3-benzothienyl obtained in this study check reasonably well with the only other two reported values, one from solvolysis studies of 1-arylethyl acetates (2m) and protodetritiation (2h).

These results again show the value of this method in determining σ^+-constants and point out the particular virtues in studying the reactivity of heteroaromatic compounds.

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