Molecular Chlorination of Monosubstituted Benzenes and 2-Substituted Thiophens in Acetic Acid at 25°

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Summary The same ρ^+ value is found for a corrected data set for chlorination of 2-X-thiophens in acetic acid at 25° as for *meta*- and *para*-chlorination of monosubstituted benzenes under the same conditions.

RECENTLY, Johnson[1,2] and Schofield[2] criticized 'the generally accepted significance of ρ values' in implying earliness or lateness of rate determining transition state structures. One of the specific examples cited was the molecular chlorination of monosubstituted benzenes[3] and 2-substituted thiophens[4] in acetic acid, where quite different ρ^+ values (-10 and $-6{\cdot}5$) were reported. From the extended selectivity relationship for other electrophilic substitutions on benzenes and thiophens[5] it appeared that the ρ's for these two reactions should be very similar. This inconsistency was resolved when Dr. Butler informed us that the published rates for chlorination of 2-X-thiophens in acetic acid at 25°[4] were in error. The correct entries are in Table 1.

TABLE 1

X	k/l mol^{-1} min^{-1}	k_{rel}[a]
H	1740	1·0
Cl	312	0·35
Br	414	0·47
CO_2H	$9{\cdot}6 \times 10^{-2}$	$1{\cdot}1 \times 10^{-4}$
CO_2Et	$1{\cdot}2 \times 10^{-1}$	$1{\cdot}4 \times 10^{-4}$

[a] Corrected for statistical factor of 2 in X = H.

Yukawa, Tsuno, and Sawada[6] reported that treatment of data from the chlorination of monosubstituted benzenes[3] with their (YTS) correlation gave $\rho = -7{\cdot}95$, $r = 1{\cdot}22$. However, this involved the partial rate factors for the halogenobenzenes which were determined in 60% acetic acid. Since this substantial solvent change may have a major effect on ρ, we have carried out multiple regression analyses of these data sets using the YTS and Brown–Okamoto σ^{+7} correlations where good σ^{08} and σ^{+7} constants were available and the results are listed in the first entries in Table 2.

The ρ from the YTS correlations[6] should be determined from all *meta*- and strongly electron-withdrawing *para*-substituents. Thus it is not surprising that ρ^+ and ρ^{YTS} are considerably different in the X-C_6H_5 data set. In the 2-X-thiophen data set, the value of r in the YTS correlation should likewise be inaccurate since no electron-donating substituents were examined. However, σ^+ effects a reasonable correlation for both data sets.

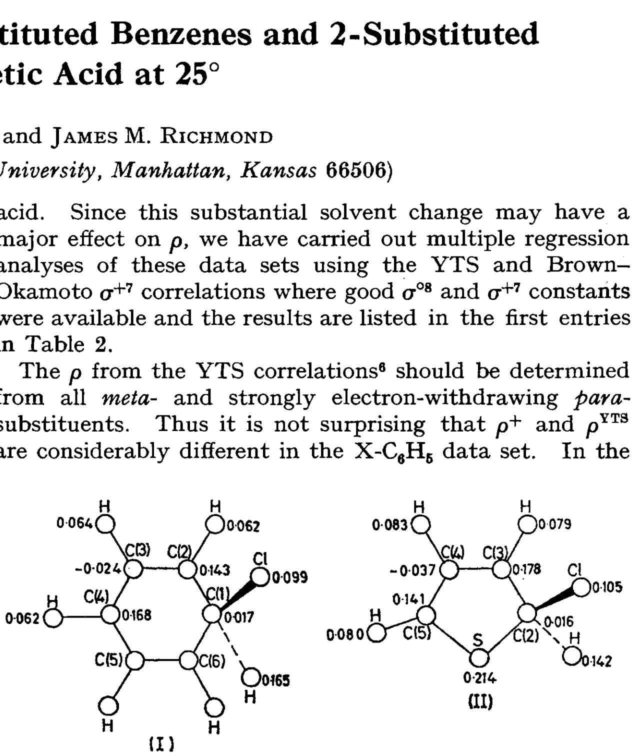

FIGURE. Δq's for ArH → $ArHCl^+$ reactions of benzene and thiophen.

Combining the two relative rate constant data sets and treating with both correlations leads to the third entry in Table 2. As is required from the extended selectivity relationship applied to these two aromatic systems, good correlation is achieved with the $\rho^+ = -9{\cdot}2$. It is interesting that Illuminati[9] has reported $\rho^+ = -6{\cdot}6$ for the chlorination of several deactivated monosubstituted benzenes in 80% acetic acid which appears to demonstrate a pronounced solvent effect on this reaction or may involve a change in the nature of the electrophile.

We have used CNDO/2 calculations[10] to examine these results in light of several recent proposals made concerning substituent effects. The processes were modelled as ArH $\rightarrow$ $ArHCl^+$.[11,12] The thiophen structure used was that determined from electron diffraction data[13] and benzene C–C and C–H bond lengths were 1·390 and 1·084 Å, respectively. In the cations, no alteration of the skeleton was allowed except for an H–C–Cl angle of 109·47° with a C–Cl length of 1·767 Å at the chlorination site. The changes in the charge densities, Δq per atom for this model are given in the Figure.

Forsyth and Noyce[11b] suggested the ρ's in related reactions were proportional to the calculated regional charge densities, Δq_r,[14] at conjugating positions. The Δq_r's at C(4) of (I) and C(5) of (II) are 0·230 and 0·221, respectively, which suggests that quite similar ρ's are expected if this proportionality is valid.

Table 2. Results of multiple regression analyses of relative rate data using YTS and σ^+ correlations.

Data set treated	LFER	p	r	CC[c]	F test	No. of points
$X\text{-}C_6H_5$ (*m* and *p*)[a]	YTS	$-6·61 \pm 0·27$	1·56	0·994	581	9
	σ^+	$-9·56 \pm 0·55$	—	0·989	304	9
2-X-thiophens[b]	YTS	$-8·31 \pm 0·71$	1·56	0·989	137	5
	σ^+	$-9·39 \pm 1·31$	—	0·972	51	5
$X\text{-}C_6H_5$ (*m* and *p*)[a] + 2-X-thiophens[b]	YTS	$-8·26 \pm 0·26$	1·28	0·995	1011	13
	σ^+	$-9·17 \pm 0·35$	—	0·992	697	13
$X\text{-}C_6H_5$ (*p*)[a] + 2-X-thiophens[b] ..	SUMCHIN1[d]	$-9·03 \pm 0·31$	—	0·995	827	11
	SUMCHIN2[d]	$-8·56 \pm 0·30$	—	0·994	809	11

[a] X = *p*-OMe, *p*-Ph, *p*-Me, *m*-Me, *p*-Et, *p*-$CHMe_2$, *p*-CMe_3, *m*-CMe_3, H. [b] X = H, Cl, Br, CO_2H, CO_2Et. [c] Correlation coefficient. [d] Ref. 12.

The question of whether or not the same substituent constants should correlate both of these reactions can also be examined with these calculations. Using the field effect transmission coefficient approximation put forward by Forsyth in his SUMCHIN1 model,[12] we find nearly identical results for (I) and (II). Use of certain other variations on this approximation [*e.g.*, $\Sigma(\Delta q_{\mathrm{nj}} \cos \theta_{\mathrm{in}}/r_{\mathrm{sn}})$, $\Sigma[(\Delta q_{\mathrm{r}})_{\mathrm{nj}} \cos \theta_{\mathrm{in}}/r_{\mathrm{sn}}^2]$, and $\Sigma(\Delta q_{\mathrm{nj}}/r_{\mathrm{sn}})^{12}$] gave similar results. The results of correlation of the benzene and thiophen chlorination data using the SUMCHIN1 and SUMCHIN2 correlations are given in the last two entries in Table 2 which show good agreement with the σ^+ results.

We conclude that with the available data, substituent effects in the molecular chlorination of monosubstituted benzene (*meta*- and *para*-chlorination) and 2-X-thiophens (5-chlorination) in acetic acid at 25° are the same and not anomalous, and that the methods of data treatment and calculations cited above lead to satisfactory agreement.

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