[CONTRIBUTION FROM FURMAN CHEMICAL LABORATORY, VANDERBILT UNIVERSITY]

HAMMETT'S SIGMA CONSTANTS IN CERTAIN ELECTROPHILIC REACTIONS

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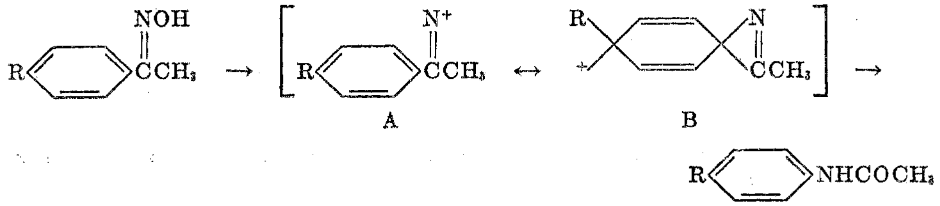
An established aid to the quantitative prediction of organic reaction rates and equilibria and the interpretation of mechanisms is Hammett's rho-sigma equation (1, 2). The values of the sigma constants are derived from weak or strong nucleophilic reactions such as ionization, hydrolysis, or saponification rates (3). It should be interesting to extend such a useful equation to reactions of an electrophilic nature in order to observe changes in the electrical characteristics of substituent groups. The sigma values of certain groups (if not all groups) will probably be more negative (or less positive) than Hammett's values in electrophilic reactions because of the electron-pull on the group by the positive reagent. In fact, if a series of different electrophilic reactions involves a rate-determining, positively charged intermediate of formal charge +1, such as the carbonium ion or the positively charged nitrogen atom, the new sigma values (designated hereafter as sigma$_e$) may be constant within the series.

The Beckmann rearrangement of a series of *para*-substituted acetophenone oximes was selected as a suitable electrophilic reaction for initiating the investigation. An outline of the mechanism of the reaction, as described by Pearson and Ball (4) and modified according to the concept of Cram (5), is probably as follows:



The actual experimental procedure was to dissolve the appropriate acetophenone oxime in concentrated sulfuric acid and to follow the rate of rearrangement by gravimetric determination of the unrearranged ketone as the 2,4-dinitrophenylhydrazone. The results of this procedure are recorded in Table I, and the first order rate constants (at 50.9°) *versus* Hammett sigma constants are plotted in Figure 1.[3] The apparent scatter of points in Figure 1 is by no means an isolated case. Very similar curves are obtained by plotting Hammett sigma values *versus* rates of aromatic substitution, *versus* migratory aptitudes of the pinacol rearrangement, and *versus* solvolysis rates of benzhydryl chlorides. However,

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[1] From Ph.D Thesis, Vanderbilt University, 1952.

[2] From M.S. Thesis, Vanderbilt University, 1952.

[3] The corrected Hammett sigma values for alkyl substituents [Herbst and Jacox (6)] are used throughout this paper.

the interpretation of the typical scatter of points is made difficult by the existence of conflicting theories of mechanism of electrophilic reactions, particularly when alkyl substituents are involved. They are referred to as: (a) the steric hindrance theory, (b) the hyperconjugation theory, and (c) the combined steric hindrance-hyperconjugation theory. It is not possible to state definitely which theory is correct. For every argument in favor of the hyperconjugation theory there is a corresponding argument in favor of steric hindrance (with minor exceptions). However, discussion of the results given in Figure 1 will serve to point out where conflicts exist in the above theories. The discussion is made from the viewpoint of the steric hindrance theory not particularly since the theory appears to be closer to the truth but because it has been neglected in past explanations.

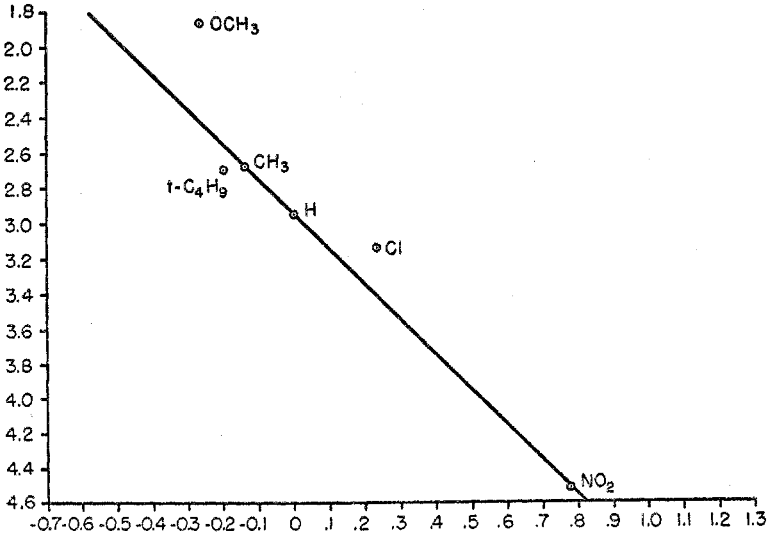

FIGURE 1. BECKMANN REARRANGEMENT OF *para*-SUBSTITUTED ACETOPHENONE OXIMES. —Log rate *versus* Hammett sigma values; rho= −1.95; t = 50.9°

In Figure 1, a straight line is drawn through the sigma values of the *p*-nitro, *p*-methyl, and *p*-hydrogen groups. In other words, it is assumed that these groups have the same sigma$_e$ values as Hammett's values. This assumption implies that the electrical nature of the *p*-methyl and *p*-nitro groups in respect to the hydrogen group is the same no matter if the mechanism of the reaction is electrophilic or nucleophilic and that hyperconjugation in the methyl group is not an important factor in controlling rates of reaction. Corrections must then be applied to the *p*-methoxy, *p*-chloro, and *p*-*tert*-butyl groups so that these points fall on the straight line of Figure 1. As to be expected, the corrected values (sigma$_e$) of the *p*-methoxy group (−0.54) and of the *p*-chloro group (+0.10) are more negative and less positive (respectively) than Hammett's values because of their electromeric properties; *i.e.* these groups have available pairs of electrons which are brought into play by the positive nature of the reagent. On the other hand, the sigma$_e$ value of the *p*-*tert*-butyl group (−0.128) is less negative than

Hammett's value because of steric hindrance. Examination of the intermediate complex, B, given in the equation illustrates how steric hindrance could operate in this reaction even though the *tert*-butyl group is situated in the *para* position.

TABLE I

THE RATE CHARACTERISTICS OF THE REARRANGEMENT OF OXIMES IN SULFURIC ACID

OXIME[a]	t, °C.	$k^b \times 10^3$	$t^c 1/2$	E^d_A	ΔS^e
p-Methylacetophenone	40.90	0.569±.002	1,219	26.38	0.32
	50.90	2.101±.009	329		
	60.90	7.20 ±.03	97		
p-*tert*-Butylacetophenone	40.90	0.547±.003	1,267	26.31	.04
	50.90	2.012±.012	344		
	60.90	6.88 ±.04	101		
Acetophenone	50.90	1.127±.004	615	26.99	.76
	60.90	3.950±.010	175		
p-Chloroacetophenone	50.90	0.714±.003	970	27.41	1.43
	60.90	2.552±.006	271		
Benzophenone	30.90	0.500±.004	1,387	25.31	.92
	40.90	1.934±.009	358		
	50.90	6.63 ±.02	104		
p-Methoxyacetophenone	40.9	5.359±0.098	129	18.65	−17.9[f]
	50.9	13.29 ±0.21	52		
	61.37	32.99 ±0.79	21		
p-Nitroacetophenone	50.9	0.031±0.0007	22,400	29.92	2.9
	61.37	0.129±0.0024	5,360		
	71.0	0.468±0.005	1,480		

[a] Concentration: 0.52 mole/liter in 95.4% sulfuric acid. [b] $k = 2.303/t \log a/a - x$; reciprocal minutes; the precision indices are probable errors (22). [c] $t\ 1/2 = 0.693/k$; minutes. [d] $\log k_2/k_1 = E_A/2.303R \times \frac{T_2 - T_1}{T_2T_1}$; kilo calories. [e] $k = ekT/h\ (e^{-E_A/RT})\ (e^{\Delta S/R})$; Entropy units. [f] The large, relative negative entropy of activation indicates a smaller rate—change with temperature than that of the other oximes. This means that the sigma_e value of the methoxy group would be less negative if a temperature higher than 50.9° had been chosen for comparison and that the value should be used with reservations.

The application of the new sigma_e values to other electrophilic reactions gives better correlation of reaction rates than the use of Hammett's values. However, the correlation is not perfect as mentioned in the examples below.

1. *Beckmann rearrangement of a series of benzophenone oxime picryl ethers.* Chapman and Fidler (7) measured the rates of rearrangement of the *p*-chloro, *p*-methyl, and unsubstituted oxime picryl ethers.[4] The use of sigma_e values pre-

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[4] The rates of rearrangement were adjusted to a common temperature of 85°.

dicts these rates exactly which lends credence to the assumptions made above. The prediction is gratifying since such different conditions were used in this rearrangement.

2. *Pinacol rearrangement.* McEwen and Mehta (8) have plotted the Hammett sigma constants *versus* log of the migratory aptitudes of a series of benzopinacols and obtained a line of positive curvature mainly due to the extraordinary migratory influence of the methoxy group. The use of sigma$_e$ values straightens out this line considerably. However, the migratory aptitude of the *p*-methoxyphenyl group (as predicted from sigma$_e$) is either greater than given (9), or the *p*-methylphenyl migratory aptitude is too great in magnitude. Final conclusions on the pinacol rearrangement should preferably be drawn from actual rate studies.

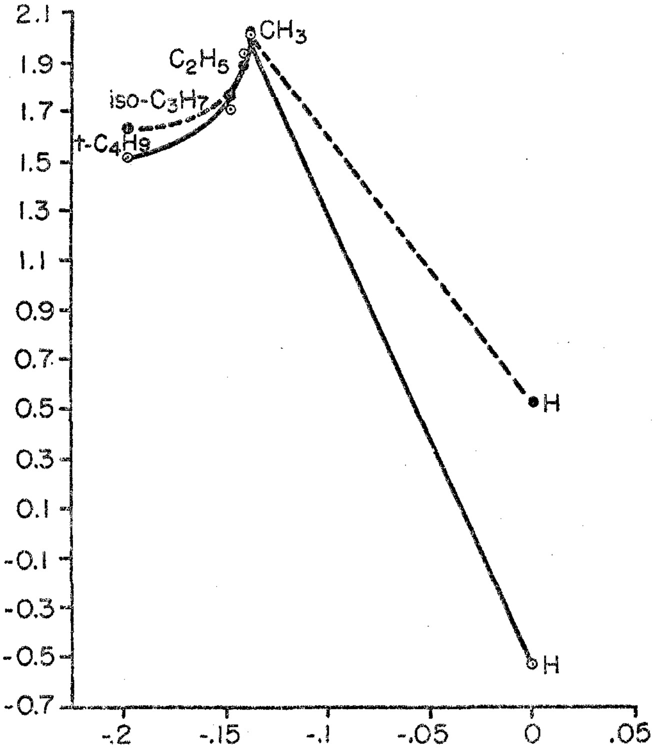

FIGURE 2. SOLID LINE: AROMATIC CHLORINATION (10, 11); log of relative rate *versus* Hammett sigma values; rho= −18. DOTTED LINE: HYDROLYSIS OF BENZHYDRYL CHLORIDES (15); log of relative rates *versus* Hammett sigma values; rho= −10.6.

3. *Aromatic substitution.*[5] In Figure 2 the relative rates of chlorination of a

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[5] The application of Hammett or sigma$_e$ values to prediction of aromatic substitution rates is more subject to error than applications to other electrophilic reactions. Variable *ortho-para* ratios of substitution products make it difficult to assign definite substituent influence to any one position. The accuracy of the application is therefore limited to the extent of variation of *ortho-para* ratios.

series of alkyl benzenes (10, 11) are plotted *versus* Hammett sigma values. This curve is also representative of bromination characteristics (10, 12). The relative rates of chlorination are as follows (C_6H_5R; R=): H, 0.29; CH_3, 100; C_2H_5, 84; iso-C_3H_7, 51; *tert*-C_4H_9, 32. Both De la Mare and Robertson (10) and Berliner and Berliner (12) attribute the falling off of rate in the sequence above to the effects of hyperconjugation. However, the shape of the curved line of Fig. 2 is just as characteristic of a steric effect as of a hyperconjugation effect. Price and Lincoln (13) were the first to suggest this possibility. They attribute steric hindrance to interference with "the solvation stabilization" of the charged transition complex, similar in quinoid structure to the complex, B, in the equation previously given. However, no clear-cut evidence exists to support either the steric hindrance or hyperconjugation theory with the possible exception of the following: De la Mare and Robertson (14) have established the relative rates of chlorination of a series of halogen benzenes (C_6H_5X; X=): H, 100; F, 120; Cl, 11; Br, 7.9. This sequence is in the order to be expected of increasing steric hindrance and in the opposite order of electromeric effect. The question now arises as to whether the sigma$_e$ value of the *tert*-butyl group (−0.128), which corrects for the alleged steric hindrance in the Beckmann rearrangement, will predict the relative rate of chlorination of *tert*-butylbenzene. Unfortunately, it does not. The predicted relative rate from sigma$_e$ is CH_3, 100; *tert*-butyl, 69. Apparently, steric hindrance is of greater influence in chlorination than in the Beckmann rearrangement.

4. *Solvolysis of benzhydryl chlorides.* In Figure 2 (dotted line) the logs of the relative rates of the hydrolysis of benzhydryl chlorides (15) are plotted *versus* Hammett's sigma constants. The curve is very similar to that for aromatic chlorination. The implication is that all remarks concerning substituent influences in aromatic substitution apply to the hydrolysis reaction, including remarks on the bulk effect of the *tert*-butyl group. Arnold and Truett (16a) and Baddeley and Gordon (16b) have previously proposed an intermediate which can exert a steric influence in this reaction and which resembles the quinoid structure of complex B given in the previous equation.[6] Lastly, the data of Altsher, Baltzly, and Blackman (17) on the alcoholysis rates of benzhydryl chlorides are in general agreement with rates predicted from sigma$_e$ values. The *p*-chloro derivative exhibits its electromeric effect, and the *m*-chloro derivative does not since the latter is not in conjugation with the carbon of the carbonium ion.

The general conclusion is that the tentative sigma$_e$ values are sufficiently more accurate than Hammett's values to warrant further applications to electrophilic reactions. Some evidence must be brought to bear on the problem of the behavior of alkyl substituents. They exhibit either a bulk effect with increasing molecular weight and branching or a decreasing hyperconjugative effect in the same order. This problem must be solved before accurate sigma$_e$ values can be obtained which

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[6] These authors (16) have found 3,4-cyclopentenobenzhydryl chloride to hydrolyze faster than the 3,4-dimethyl analog and attribute this fact to steric inhibition of hyperconjugation. The simple bulk theory does not provide an explanation which may be a point in favor of hyperconjugation.

will lead to correct predictions of rates of electrophilic reactions or which will detect deviations from the predictions.

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EXPERIMENTAL[7]

Purification of reagents. The *oximes* were purified according to the procedure of Pearson and Ball (4): acetophenone oxime, m.p. 59.1–59.7°; *p*-chloroacetophenone oxime, m.p. 98.2–98.8°; *p*-methylacetophenone oxime, m.p. 88.0–88.8°; *p*-methoxyacetophenone oxime, m.p. 86.0–88.0°; *p*-nitroacetophenone oxime, m.p. 174.5–175.0°. *p-tert-Butylacetophenone* was made by two procedures: from the Friedel-Crafts reaction (18) (oxime m.p. 111–111.8°, previous softening at 107°, m.p. of resolidified sample 111–111.8°); and from the acetylation (19) of the Grignard reagent of purified *p*-bromo-*tert*-butylbenzene [f.p. 15.3°; reported (20) f.p. 14°] (m.p. of oxime 109–109.5°; m.p. of sample seeded with high-melting form 111–111.6°). Since some low-melting form appeared to be present, *p*-*tert*-butylacetophenone was subjected to purification by fractional freezing. Freezing point of crude ketone was 17.66°, n_D^{25} 1.5191. Freezing point after removal of one-third of partly solidified ketone by centrifuging was 18.01°, n_D^{25} 1.5191. Repetition of this procedure on the purified ketone did not change the freezing point. The oxime from the purified ketone melted at 111–111.5°, pre-

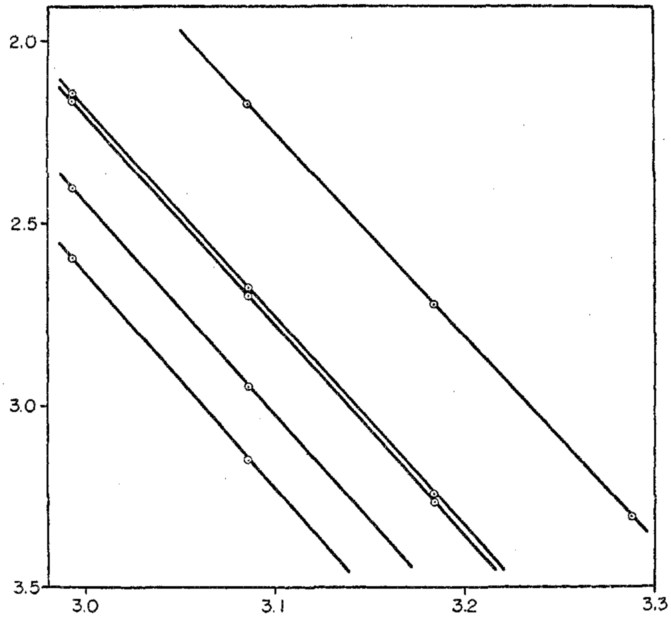

FIGURE 3. REARRANGEMENT OF *p*-SUBSTITUTED ACETOPHENONE OXIMES. —Log rate *versus* reciprocal absolute temperature. From left to right: *p*-chloro, H, *p*-*tert*-butyl, *p*-methyl-acetophenone oximes and benzophenone oxime. The *p*-methoxy and *p*-nitroacetophenone oximes also give a straight line when plotted as above. However, the *p*-methoxy line has a different slope.

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[7] All melting points are corrected, A.S.T.M. specification.

vious softening at 108°, m.p. of resolidified sample 111–112° [reported m.p. (21) 107.8–108.6°]. Apparently, small amounts of a labile, low-melting *syn-anti* isomer were present. However, this oxime and the oximes of lower melting points gave identical results in the rate determinations.

All *rate determinations* were run in Merck C.P. 94.5% sulfuric acid pipetted from a single stock bottle.

Analysis of oximes. The oxidation procedure (4), the 2,4-dinitrophenylhydrazine procedure (4), and a spectrophotometric procedure (1) were thoroughly investigated. The 2,4-dinitrophenylhydrazine procedure (4) gave the most satisfactory results with the following improvements. The samples of 2,4-dinitrophenylhydrazone were filtered using No. 2001 "Selas" porous porcelain crucibles. The precipitates were washed with 300 to 900 ml. of hot water supplied from a continuous feed, siphon washer (1500 ml. capacity). As many as four samples could be washed simultaneously. The precision of analysis for known samples was as follows: *p*-methylacetophenone oxime 99.61 ± 0.08% (correction factor 1.004); *p-tert*-butylacetophenone oxime 99.26 ± 0.16% (correction factor 1.0074); benzophenone oxime 98.58 ± 0.056% (correction factor 1.0144); *p*-chloroacetophenone oxime 98.90 ± 0.20% (correction factor 1.012); acetophenone oxime 99.85 ± 0.15% (correction factor, none); *p*-methoxyacetophenone oxime 100.06 ± 0.21% (correction factor, none); *p*-nitroacetophenone oxime 99.15 ± 0.27% (correction factor 1.009). Reproducible results, in the case of benzophenone oxime, were obtained only after the original dilution was made with 50% by volume methanol-water solution rather than with pure water.

The rate determination. Considerable improvement was made in the technique used previously (4). Individual samples (0.2000 g.) of the oxime were placed in 50-ml., standard-tapered Erlenmeyer flasks. Sufficient sulfuric acid was added to make the concentration 0.52 *molar*. The contents were cooled before the bulk of the oxime was allowed to come in contact with the sulfuric acid. The *well-stoppered* flasks were then swirled to obtain solution and were immersed in a constant temperature bath (zero time taken as one minute after immersion). At regular intervals one flask was removed from the bath and its entire contents were analyzed by the 2,4-dinitrophenylhydrazine method (4) as modified above. Six to eight samples were analyzed for each run. Duplicate runs were also made with a lesser number of samples. The first order rate constants were obtained by applying the Least Squares Principle to the data for the plot of log concentration of the oxime *versus* time in minutes. Precision indices were calculated as probable errors (22). The results are recorded in Table I and illustrated in Figure 3.

SUMMARY

From a study of the rates of rearrangement of a series of *para*-substituted acetophenone oximes, the following sigma$_e$ values (Hammett values corrected for use in electrophilic reactions) were tentatively assigned:

GROUP	SIGMA$_e$	HAMMETT SIGMA
H	0	0
p-CH_3	−0.138	−0.138 (6)
p-OCH_3	−0.54[8]	−0.268
p-*tert*-C_4H_9	−0.128	−0.199 (6)
p-Cl	+0.10	+0.227
p-NO_2	+0.778	+0.778

The sigma$_e$ values are arbitrary since it is not possible to evaluate the relative effects of hyperconjugation and steric hindrance. The sigma$_e$ values are applied

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[8] See Table I, foot-note *f*.

to other examples of electrophilic reactions. They may vary depending upon the electrophilic nature and the steric requirements of the reaction mechanism (2).

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