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An Extension of Hammett's $\sigma - \varrho$ Relation

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It is proposed that the Hammett $\sigma - \varrho$ relation can be extended to account for the influence of substituents on the rate of reactions in which two groups substituted in a benzene ring react with each other. It is shown experimentally for the reaction of substituted *ortho*nitrophenylazides, in which the azide group reacts with the nitro group, that the more general relation has the form

$$\log_{10} k/k_0 = \sigma_1\varrho_1 + \sigma_2\varrho_2$$

Here σ_1 and σ_2 are the normal substituent coefficients and ϱ_1 and ϱ_2 are partial reaction coefficients. It is argued that they give an indication of the charge distribution in the transition state. The mechanism of the decomposition of *ortho*nitrophenylazide is discussed in terms of the values obtained for ϱ_1 and ϱ_2.

The effect of substituents on the rate of a side chain reaction of benzene derivatives can be described semiquantitatively by means of the Hammett equation [1a]

$$\log_{10} k/k_0 = \sigma\varrho$$

in which k_0 is the rate constant for the reaction of the unsubstituted compound and k is the rate constant for the reaction of a compound which has a substituent *meta* or *para* relative to the reacting group. ϱ is a quantity which depends only on the type of reaction. σ depends only on the substituent one considers and whether it is *meta* or *para* relative to the reacting group.

Since an equilibrium is a balance between two chemical reactions, it is immediately clear that a similar equation will also hold for equilibrium constants of side chain reactions of benzene derivatives.

Clearly the value of a σ-coefficient is only determined relative to some standard reaction for which ϱ is set equal to one. Rather than using a chemical reaction for this, Hammett chose to use the dissociation of benzoic acid. That is, for the equilibrium

$$\varphi^*\mathrm{COOH} \rightleftharpoons \varphi^*\mathrm{COO}^- + \mathrm{H}^+$$

where the star indicates that there is a substituent in the benzene nucleus, one sets arbitrarily

$$\log_{10}K/K_0 = \sigma$$

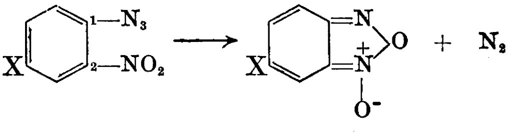
where K and K_0 are now equilibrium constants for the dissociation of the substituted and the unsubstituted acid, respectively.

When the σ-values are determined in this way, the ϱ-value for a reaction or an equilibrium is determined by plotting the logarithm of the rate constants of several differently substituted derivatives *versus* the σ-values. Extensive tables of σ- and ϱ-values have been published [2].

Ever since Hammett discovered that the effect of structure on reactivity could be accounted for by this simple relation, attempts have been made to give it some theoretical justification. $\text{Log}_{10}k/k_0$ is proportional to the difference in standard free energy between the reaction of the substituted molecule and the unsubstituted molecule when an equilibrium is considered. For rate constants it is proportional to a similar difference in standard free energies of activation when the transition state theory is assumed. Therefore, the Hammett equation is often called a "linear free energy relationship". Since for many processes of this kind it has been observed that, within the experimental error, the entropy term is independent of the substituent or a linear function of the activation energy it can, however, be restated as a "linear bonding energy relationship". It is therefore reasonable to assume that the σ-values should be correlated with the change caused by the substituents in electron densities at the reaction site.

Corio and Dailey [3] have shown experimentally that there is such a correlation between σ-values and electron densities determined by nuclear magnetic resonance technique. Van Beek [4] has shown that a relation similar to the Hammett equation also holds for dipole moments. This indicates clearly that the σ-values depend on the change of electron density in the benzene ring, produced by the substituent. Jaffe [5] has succeeded in making this statement at least semiquantitative by correlating the σ-values with electron densities obtained from molecular orbital calculations. In spite of all this one must say, however, that the σ-ϱ relationship itself, as well as the ϱ-values, still must be viewed mainly as an empirical result.

This of course limits the use of the σ-ϱ relationship somewhat, but since one can interpret the σ-and the ϱ-values in terms of electron density, albeit somewhat vaguely, the rule can at least be applied to confirm or reject certain reaction mechanisms which involve a specific charge distribution in the transition state. In order to do this is necessary in some cases, to know whether one can extend the Hammett rule to be valid for reactions in which, for instance, two neighbouring groups in a benzene molecule react with each other. To give a specific example in a reaction such as



which we have studied previously, one would like to know the validity of the relation

$$\log_{10}k/k_0 = \sigma_A\varrho_A + \sigma_N\varrho_N$$

where σ_A and σ_N are the *meta-* and *para-*substituent coefficients for the substituent X, and ϱ_A and ϱ_N are constants. If this relationship is valid, ϱ_A and ϱ_N would naturally be taken as the reaction coefficient for the reaction "at the azide group" and "at the nitro group". Since ϱ is usually negative when a high electron density is favourable for the reaction, this in turn would indicate the charge distribution in the transition state.

To our knowledge a relationship of this kind has never been checked experimentally, although it is a quite obvious extension of Hammett's idea. The purpose of this paper is therefore primarily to verify the extended rule for the reaction mentioned above, and secondly to discuss the values obtained in this case for ϱ_A and ϱ_N in terms of the mechanism which we have previously suggested.

2. The derivatives of *ortho*nitrophenylazide shown in Table 1 were used in this investigation.

In all cases the compounds were prepared from the corresponding derivatives of *ortho*nitroaniline by diazotization and coupling with azide ions. The *ortho*nitroaniline derivatives used were either the purest grade obtainable from Eastman Kodak Organic Chemicals, or compounds prepared at the Laboratories for Organic Chemistry at the University of Copenhagen and at the Technical University of Denmark *. In all cases the melting points of the *ortho*nitroanilines checked with those reported in the literature.

After preparation, the *ortho*nitrophenylazides were stored at 0°C and in most cases the experiments using any compound were completed within two weeks. Under these circumstances only a negligible amount of the azide had reacted in the solid state, except for the case of 2,4-dinitrophenylazide which reacts very fast. In this case, therefore, several preparations were made.

The measurements of the first order rate constant for the decomposition of the azides were measured in an apparatus described previously [6], following the same method. The results obtained are given in Table 1. It is seen that the reproducibility of an experiment is in general better than 2 %. Barring systematic errors, the average of 3—4 experiments may be assumed to be correct to within 1 %. This is probably the best one may hope to obtain by a method of this kind.

Table 2 gives the average values of the rate constants referred to a common temperature. From this table the values of ϱ_A and ϱ_N in the expression

$$\log_{10} k/k_0 = \sigma_A \varrho_A + \sigma_N \varrho_N$$

have been calculated by the method of least squares, using values of σ_A and σ_N taken from the literature. σ_A is the substituent coefficient for the influence of the substituent on the azide group, and σ_N the coefficient for its influence on the nitro group. One obtains

$$\varrho_A = 1.353 \quad \varrho_N = -0.676$$

and Table 2 shows the agreement between measured values of k and the values calculated using the above values of ϱ_A and ϱ_N (and the tabulated values of σ_A and σ_N).

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* We are indebted to Mrs. Else Plejl and Mr. Børge Nygaard for letting us have these chemicals.

Table 1.

Compound	T, °C	$k \times 10^4$, sec^{-1}	Compound	T, °C	$k \times 10^4$, sec^{-1}
$o\text{-NO}_2\varphi\text{N}_3$	76.22	0.867	$4\text{-}\varphi\text{-2NO}_2\varphi\text{N}_3$	80.26	1.599
	76.23	0.893		80.26	1.618
	76.24	0.873		80.44	1.645
	76.27	0.903		80.44	1.671
	81.14	1.492		90.43	4.538
	81.20	1.488		90.44	4.391
	81.22	1.537		90.44	4.478
	81.28	1.488		90.44	4.543
	90.54	3.759		100.11	11.53
	90.54	3.855		100.12	11.75
	90.54	3.717		100.12	12.30
	90.57	3.770		100.15	11.58
	90.57	3.732		100.15	11.07
	90.58	3.843			
	90.63	3.997	$5\text{-CH}_3\text{-2NO}_2\varphi\text{N}_3$	70.76	0.5673
	90.85	3.874		70.76	0.5886
				70.76	0.5866
$4\text{-CH}_3\text{O-2-NO}_2\varphi\text{N}_3$	80.36	0.5000			
	80.36	0.4945		76.25	0.9909
	80.40	0.4970			
				77.18	1.1498
	90.50	1.330		77.18	1.1740
	90.52	1.365			
	90.54	1.324		81.21	1.682
	90.55	1.321		81.24	1.684
	90.56	1.374		81.25	1.707
	90.57	1.343		81.29	1.650
	90.59	1.341			
	90.60	1.374		90.40	3.86
				90.45	4.09
	100.11	3.446		90.46	3.77
	100.12	3.446		90.46	4.06
	100.14	3.521			
	100.15	3.369	$4\text{-Cl-2NO}_2\varphi\text{N}_3$	81.20	1.758
	100.15	3.509		81.22	1.840
	100.30	3.422			
	100.30	3.442	$2,4\text{-(NO}_2)_2\varphi\text{N}_3$	40.32	0.1690
	100.34	3.430		40.32	0.1716
				40.32	0.1662
$4\text{-CH}_3\text{-2NO}_2\varphi\text{N}_3$	70.76	0.3171		40.32	0.1669
	70.76	0.3221		40.32	0.1643
	70.76	0.3224			
				50.38	0.6506
	81.21	0.9274		50.38	0.6486
	81.22	0.9298			
	81.23	0.9298			
	90.48	2.450			
	90.52	2.241			
	90.52	2.232			

The σ-values used are those of Hammett [1,7] except for the phenyl group where later work is more accurate. For m-phenyl a value of 0.06 was used [8]. For the nitro and phenyl groups *para* to the azide group, the corresponding σ-values for reactions of aniline were used [7,9]. Because of the rather large uncertainty and confusion which still exists in regard to σ-values for the phenyl

Table 2. k_{exp} are the experimental values of the rate constant referred to a common temperature 81.20°C and k_{calc} are the rate constants as calculated from the extended Hammett relation. E are the experimental activation energies and $\Delta S^{\ddagger}$ are the activation entropies.

Compound	$k_{\text{exp}} \times 10^4$ sec^{-1}	σ_A[1a]	σ_N[1a]	$k_{\text{calc}} \times 10^4$ sec^{-1}	$E_{\text{kcal/mole}}$	$\Delta S^{\ddagger}$ cal/mole/deg
$o\text{-NO}_2\text{-}\varphi\text{-N}_3$	1.50	—	—	—	25.7	− 5.9
$4\text{Cl-}2\text{NO}_2\varphi\text{-N}_3$	1.80	+0.227	+0.373	1.70	—	—
$4\text{CH}_3\text{O-}2\text{NO}_2\varphi\text{-N}_3$	0.535	−0.268	+0.115	0.544	25.6	− 8.1
$2,4(\text{NO}_2)_2\varphi\text{-N}_3$	25.5	+0.778	+0.710	25.9	27.1	+ 3.9
$4\text{CH}_3\text{-}2\text{NO}_2\varphi\text{-N}_3$	0.927	−0.170	−0.069	0.984	24.8	− 9.3
$5\text{CH}_3\text{-}2\text{NO}_2\varphi\text{-N}_3$	1.67	−0.069	−0.170	1.58	24.2	−10.1
$4\varphi\text{-}2\text{NO}_2\varphi\text{-N}_3$	1.78	+0.009	+0.218	1.92	26.0	− 4.6

group, these data were not used in calculating the ϱ-values. However the rate constant has been calculated and correlates moderately well with the experimental one.

From this we may of course only conclude that this extension of the σ-ϱ rule applies to the reaction in question, but it seems most likely that it should be true in general for substituents which are *meta* or *para* to both the reacting groups.

3. It is of some interest to consider the activation energies and activation entropies of the reactions investigated. Table 2 gives the values of the energies and entropies of activation one obtains.

The plot of $\Delta S^{\ddagger}$ *versus* the experimental activation energy in Fig. 1 shows that the activation entropy increases systematically with the activation energy. When the errors in the determination of E and $\Delta S^{\ddagger}$ are taken into account one may almost take this to be a linear relationship. Such a relationship has been observed previously for other reactions and as mentioned above it is the reason that the Hammett equation may hold even when the activation entropy is not independent of the substituents.

It has been stated for instance by Hammett [1b] that there is no reason to expect a correlation between activation entropy and activation energy. Indeed his whole argument for the existence of the σ-ϱ relation was based on the assumption that $\Delta S^{\ddagger}$ is independent of substituents. Contrary to this point

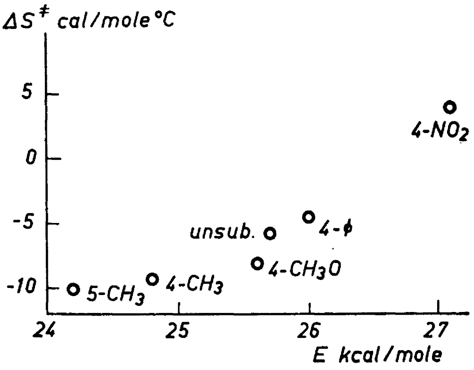
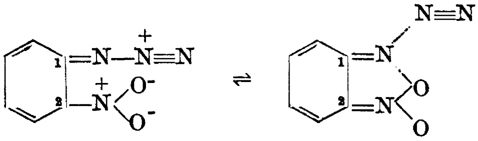


Fig. 1. A plot of $\Delta S^{\ddagger}$ *versus* the experimental activation energy. It shows that the activation entropy increases systematically with the activation energy.

of view, we think that the relation between $\Delta S^{\ddagger}$ and E is perfectly reasonable, at least for unimolecular reactions, and of more general validity than Hammett's assumption. It is clear that if one strengthens the bond which must break by "adding electrons", the molecule must vibrate violently in order to break the bond. This means that the amplitudes of the normal modes in a molecule which is able to break a certain bond when the normal modes get into phase will in general increase as the activation energy increases. This again means that a molecule which can react (*i.e.*, is in the transition state) must have a larger entropy as the activation energy increases. Even though the relationship may not be linear, it will appear almost to be so when used only over a small range of activation energies.

4. We have previously suggested that the reaction of *o*-nitrophenylazides proceeds through the following transition state



in which there is a low electron density around carbon atom No. 1 and a high electron density around carbon atom No. 2. If this mechanism is correct therefore, ϱ_A should be positive and ϱ_N should be negative, since the favourable effect of high electron density implies a negative value of ϱ. The values found experimentally for the two reaction coefficients therefore support the suggested mechanism.

It is seen from this, however, how careful one should be when correlating negative entropies of activation with cyclic transition states and *vice versa* as is often done. In the reaction we have considered here the activation entropy is generally negative and we believe the transition state to be cyclic. For the 2,4-dinitro compound which reacts very fast and has a high activation energy, $\Delta S^{\ddagger}$ is, however, positive and presumably this does not mean that the mechanism of the reaction has changed.

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