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W.R. Gilkerson
University of Kansas, Lawrence

Gordon A. Gallup
UNL, ggallup1@unl.edu

M.M. Jones
University of Kansas, Lawrence

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A Special Case of the Hammett Equation

W. R. GILKERSON*, G. A. GALLUP*, and M. M. JONES†
University of Kansas, Lawrence

Introduction

The Hammett equation was first used for coordinating information on the kinetics of organic reactions by Hammett and Pfluger (1). It was later extended by Hammett (2) (3) (4) and is now extensively used in studies concerned with the effect of changes in structure of an organic compound on the kinetics of various reactions these compounds undergo. The Hammett equation is

$$\log \frac{k}{k_o} = \sigma \rho \qquad \text{(I)}$$

where

k=rate constant for a reaction of a substituted compound
k_o=rate constant for the reaction of the unsubstituted compound
σ=constant specific for the substituent
ρ=constant specific for the reaction

Hammett has shown that it is necessary to restrict the use of this equation to series of reactions in which the entrophy of activation is constant *if the constant σ is to be related to the electrical effects of the substituent on the reaction.* This can easily be shown to require that changes in the kinetic energy must be the same for the series of reactions studied (5).

One of the results of later work on the correlation of the kinetics of the reactions of certain types of organic compounds has been to show that the Hammett equation may be used to relate the rates of substituted and unsubstituted compounds *even when there are marked changes in the entropies of activation in a series* (6) (7) (8) (9) (10) (11). There are at least two explanations for this result which can be shown by a careful consideration of the Hammett equation and its relation to the Absolute Reaction Rate Theory.

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*AEC Fellows

†duPont Fellow

Discussion

The Absolute Reaction Rate Theory shows that the rate of a chemical reaction is of the form

(II)
$$k = K \frac{KT}{h} e^{-\frac{\Delta F^*}{RT}}$$

where

k is the rate constant for the reaction
κ is the transmission coefficient
K is Boltzmann's constant
T is the absolute temperature
h is Planck's constant
ΔF^* is the standard free energy of activation
R is the gas constant

Fram equation II we can easily obtain an expression for the difference in logarithms of any two rates as:

(III)
$$\log \frac{k_1}{k_2} = \frac{\Delta F_2^* - \Delta F_1^*}{RT}$$

where the subscripts refer to the two reactions.

From thermodynamics we may write

(IV)
$$\Delta F^* = \Delta H^* - T\Delta S^*$$

When this is introduced into equation III we get

(V)
$$\log \frac{k_1}{k_2} = \frac{(\Delta H_2^* - T\Delta S_2^*) - (\Delta H_1^* - T\Delta S_1^*)}{RT}$$

(VI)
$$\log \frac{k_1}{k_2} = \frac{\Delta H_2^* - \Delta H_1^*}{RT} - \frac{\Delta S_2^* - \Delta S_1^*}{R}$$

If, for the moment, we ignore the restriction of Hammett's equation to series of reactions where $\Delta S_1^* = \Delta S_2^*$ we may combine equations VI and I and write

(VII)
$$\sigma\rho = \frac{\Delta H_2^* - \Delta H_1^*}{RT} - \frac{\Delta S_2^* - \Delta S_1^*}{R}$$

It should be remembered that this is essentially the implicit assumption in the work which fits Hammett's equation to a series of reactions in which $\Delta S_1^* \ldots \Delta S_2^*$. There are two situations in which the Hammett

equation will fit data on reactions of this type. These two cases will be discussed in turn.

I. Reactions in which

(VIII)
$$\frac{\Delta H_2^* - \Delta H_1^*}{RT} \gg \frac{\Delta S_2^* - \Delta S_1^*}{R}$$

In reactions of this type the differences in the enthalpies of activation are sufficient to mask any effect of the differences in entropies. A numerical example of such a reaction is easily given. The figures given are typical. If the change in the heat of activation is 5000 cals and the entropy change is cal deg mole (Setting T = 300°K)

(IX)
$$\frac{\Delta H_2^* - \Delta H_1^*}{RT} \simeq 8$$

(X)
$$\frac{\Delta S_2^* - \Delta S_1^*}{R} \simeq 0.5$$

Here the change in ΔS^*, while not 0, is too small to effect the value of $\sigma\rho$ within the limits of error, generally in the neighborhood $\pm 10\%$. It is this type of behavior which allows the Hammett equation to be fit to a series of reactions in which ΔS^* is essentially constant. If the restriction of constancy of ΔS^* were absolute very few reactions could be correlated by means of equation (I). Hammett (5) generally allows ΔS^* to vary at least 0.2 e.u. and frequently more if the change in enthalpies of activation is sufficiently large.

II. Reactions in which

(XI)
$$\frac{\Delta S_2^* - \Delta S_1^*}{R} = \text{constant} \times \frac{\Delta H_2^* - \Delta H_1^*}{RT}$$

Such reactions have been reported in the literature (8) (9) (10) (11). The graph of the data of Blomquist and Bernstein Fig. 1 gives a very good straight line plot of ΔS^* vs ΔH^*.

Table I. Data of Blomquist and Bernstein (10) on the thermal decomposition of p-substituted t-butyl perbenzoates in phenyl ether.

Substituent	H* Kcal/mole	S* cal mol^{-1} degree
p-OCH_3	35.8	12.2
p-CH_3	36.1	12.6
Unsubstituted	37.5	15.8
p-Cl	39.3	19.7
p-NO_2	41.3	23.7

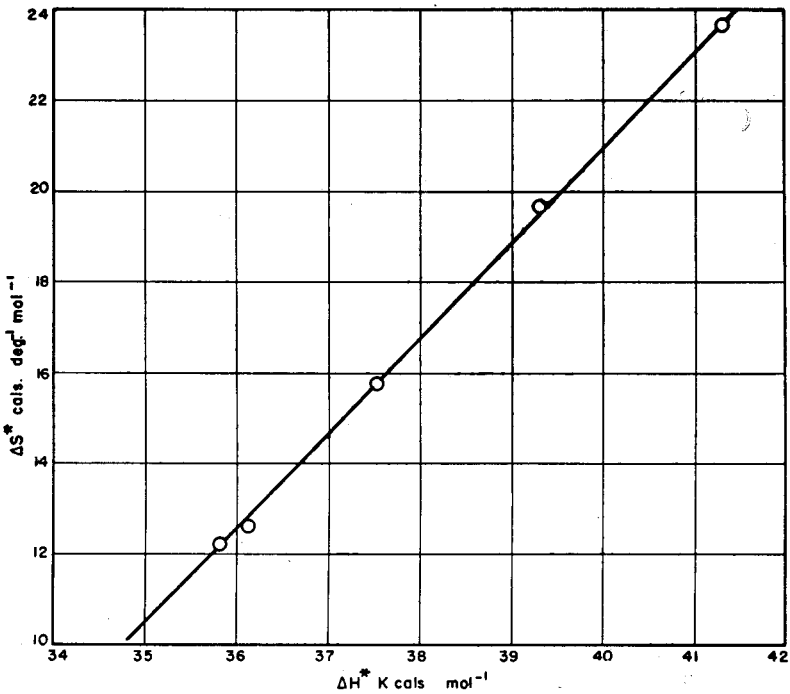

Fig. 1

The data of many other references have been given in terms of collision theory. These data, however, may be used to calculate ΔS* by means of the relation: (12)

(XII)

$$k_{soln} = e \frac{KT}{h} e^{-\frac{E\,exp.}{RT}} e^{\frac{\Delta S^*}{P}}$$

(XIII)

$$\text{also} \quad k_{soln} = Z\, e^{-\frac{E_{exp.}}{RT}}$$

(XIV)

$$\text{so} \quad Z = e \frac{KT}{h} e^{\frac{\Delta S^*}{R}}$$

(XV)

$$\log Z = \log 16.3 \times 10^{12} + \frac{\Delta S^*}{R}$$

(XVI) $$\Delta S^* = 2.3\, R\, (\log Z - 13.222)$$

Table II. Data of Branch and Nixon. The Rates of Alcoholysis of Acyl Chlorides.

Substituent	log Z	log Z-13.22	...S*	...E*
p-NO_2 benzoyl	5.5	-7.7	-35.2	11,100
p-Br benzoyl	6.2	-7.0	-32.0	13,450
p-I benzoyl	6.2	-7.0	-32.0	13,450
p-Cl benzoyl	6.5	-6.7	-30.6	13,850
benzoyl	6.6	-6.6	-30.2	14,400
p-F benzoyl	7.8	-5.4	-24.6	14,650
p-CH_3 benzoyl	7.5	-5.7	-26.0	15,900
p-CH_3O benzoyl	9.4	-3.8	-17.4	18,650

These data are presented graphically in Fig. 2.

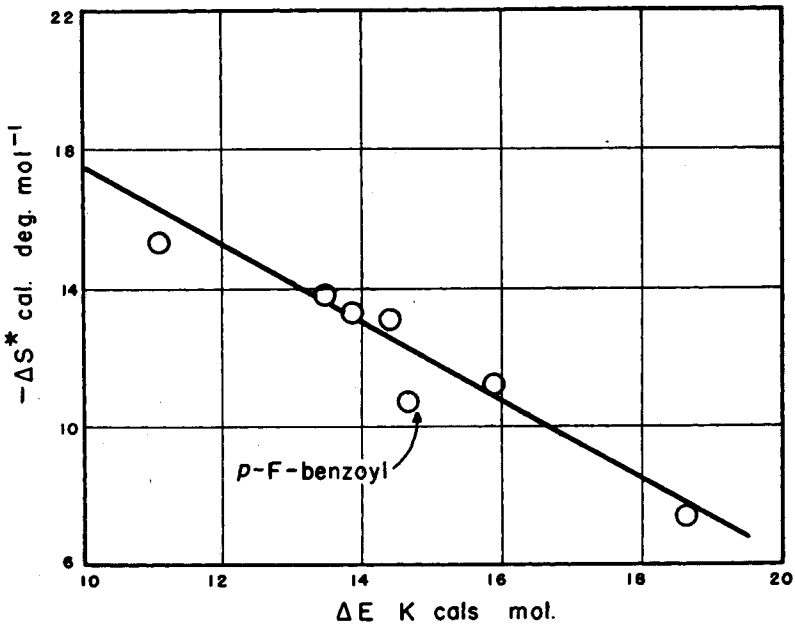

Fig. 2

The data of Timm and Hinshelwood (8) were plotted as log Z vs ΔE^* by the authors of that paper and a linear relationship was found. This behavior is equivalent to a linear relationship between ΔS^* andΔE^*. The data of Davis (9) and of Burkhardt et. al. (6) also show a similar trend of ΔS^* with ΔE^*. The data of Cristol et. al. do not possess the same regularity but their overall deviation is quite large. These facts emphasize the point that the Hammett equation is primarily a linear free energy relationship. If both ΔH^* and ΔS^* are representable as linear functions of some property of the substituents, ΔF^* will also be. This raises the question "Can the σ constants still be given the same interpretation as in reactions where ΔS^* is a constant?" The answer to this question will depend upon the particular reaction studied, but when the

σ constants used are the same as when ΔS^* is constant it seems reasonable to retain their original interpretation. When this is done, however, we should be wary about using such reactions to distinguish between the electrical effects of substituents with nearly equal σ values.

Summary

The usefulness of the Hammett equation in some unexpected instances is explained on the basis of the Absolute Reaction Rate Theory. Caution is recommended in the use of such reactions in theoretical studies of substituent effects.

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