

# CHARACTERISTIC FREQUENCY AND CHEMICAL REACTIVITY

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CHEMICAL reactivity as studied in rate measurements often involves only changes in one part of the molecule and the influence of a substituent in another part of the molecule on these changes. The reactions involve the rupture of some bonds and the formation of new ones. In a large majority of cases, these changes require an activation energy which is mostly computed from experimentally determined values of rate constants at different temperatures, using the well-known Arrhenius equation. Systematic changes in the molecule by introduction of substituents at specified parts of a molecule has shown that there is a corresponding variation in the activation energies. From *a priori* considerations, it may be expected that activation energies should be closely related to the bond stretching force constant of the bond primarily affected. Fugassi and Warrick<sup>3</sup> studied an empirical correlation in the case of some unimolecular reactions, while more recently, Flett studied a few reactions to correlate the rate constant with the characteristic frequencies.<sup>2</sup> With the polyatomic systems usually used in these investigations, it is not readily feasible to calculate the force constants; but, for purpose of comparisons, instead of using the frequency as such, the square of the frequency expressed in wave numbers may be expected to give a better picture because of its close relationship with the force constant of the bonds in question. In some cases, results are available only at a single temperature and a comparison of activation energies is clearly ruled out. In such cases, the logarithmic form of the Arrhenius equation suggests the use of the logarithms of rate constant, provided one can assume that the frequency factor remains the same. In the case of substituted benzene derivatives, the difference for a given series is small enough to use this assumption as a first approximation.

In the course of an analysis of the reaction between ethylene derivatives and bromine<sup>1</sup> it was noticed that there was strictly linear relation between the activation energy and the square of the characteristic frequency, provided the mechanism of the reaction was the same. In the present communication, a few other reactions are similarly analysed and the results are presented in Tables I and II and Figs. 1 and 2. The observations of Fugassi and Warrick as well as those of Flett are also considered in the sequel.

TABLE I\*  
*Esterification and Hydrolysis of Esters*

Substituent	Esterification			Acid hydrolysis	Alkaline hydrolysis
	$\log k$	$\bar{\nu}_{C=O}^2 \times 10^{-6}$	$\bar{\nu}_{OH}^2 \times 10^{-7}$	E k. Calories	E k. Calories
<i>p</i> -Nitro ..		2.958	1.254	14.50	12.40
<i>p</i> -Iodo ..				16.70	
<i>p</i> -Bromo ..	1.0899	2.924		16.80	
<i>p</i> -Chloro ..	1.0569	2.934	1.260	16.80	
H- ..	1.2833	2.906	1.260	17.70	14.56
<i>p</i> -Methyl ..	1.2945	2.889	1.264	18.20	15.16
<i>p</i> -Methoxy ..		2.874	1.267	19.65	
<i>p</i> -Amino ..		2.856		20.00	16.70

\* Activation energies from Moelwyn Hughes, *Reaction in Solution* (2nd edn. O. U. P.)

TABLE II  
*Reaction between Primary Amines and Acyl Halides*

Substituent	Substitution in Amine			Substitution in Acyl halide	
	$k_{NH}$	$\bar{\nu}_{NH}^2 \times 10^{-7}$	E	$\bar{\nu}_{C=O}^2 \times 10^{-7}$	E
<i>p</i> -Nitro ..	6.729	1.181	11.80	3.186	5.90
<i>p</i> -Chloro ..	6.623	1.166	7.60	3.165	7.00
H ..	6.591	1.162	7.35	3.161	7.35
<i>p</i> -Methyl ..	6.577	1.159	6.80	3.154	7.80
<i>p</i> -Methoxy ..	6.541			3.150	

TABLE III  
*Reaction between Methyl Halides and Thiosulphate Ion*

Halide	$\bar{\nu}_{C-X}^2 \times 10^{-4}$	E
Methyl Chloride ..	50.41	20.49
Methyl Bromide ..	36.00	19.23
Methyl Iodide ..	28.01	18.78

In every one of the instances chosen, a linear relation between activation energy and  $\bar{\nu}^2$  is observed. Expressing activation energy in calories and the characteristic frequency in wave numbers, the curves obtained can be represented by an equation for a straight line of the form

$$E = a\nu^2 + c,$$

where  $a$  and  $c$  are constants for a particular reaction. It will be observed that distinct differences are noticeable both in the magnitude and the direction of the slope of these lines.

The correlation between the characteristic frequency of the bond and the activation energy of the reaction is thus clear, and in all the cases this factor may be expected to contribute a large part of the observed activation

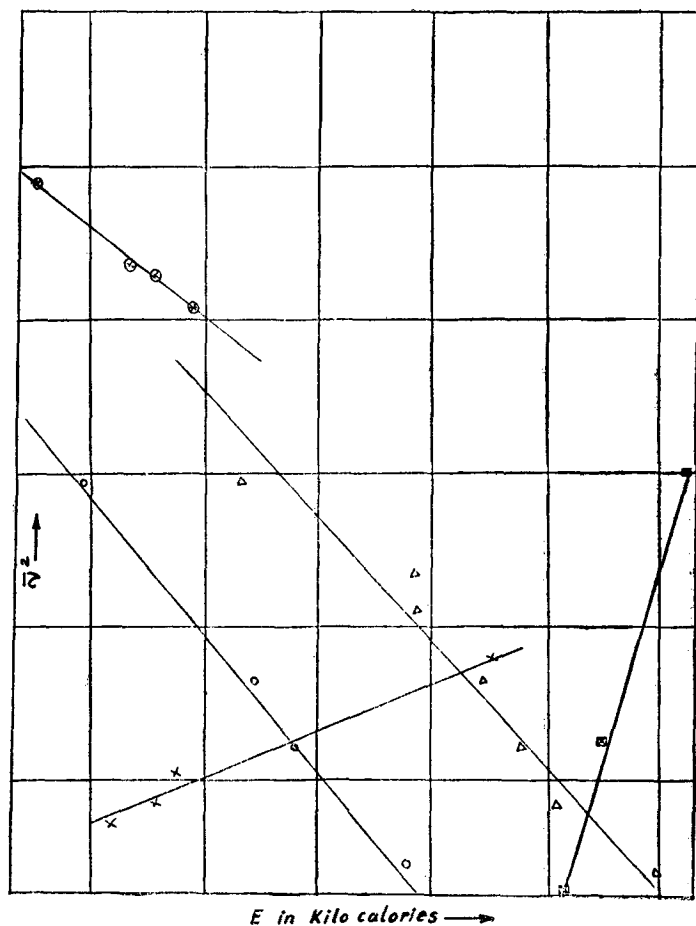


FIG. 1

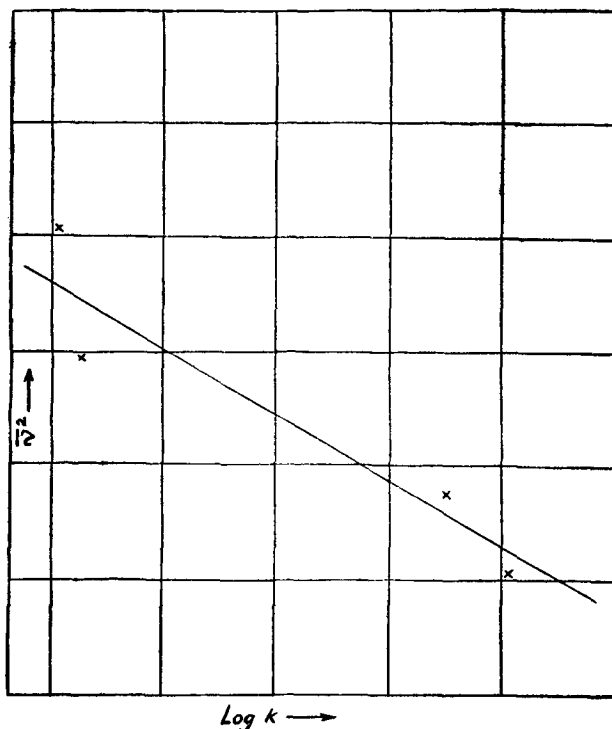


FIG. 2

energies. In the case of hydrolysis of esters, Ingold and co-workers<sup>6</sup> have shown that basic hydrolysis may involve either acyl-oxygen fission or alkyl-oxygen fission while acid hydrolysis is one involving acyl-oxygen fission. For both types of hydrolysis, acyl-oxygen fission involves the formation of a carbonium ion. The ease with which this can take place can be expected to be correlated to the carbonyl frequency which is readily assigned. Though the actual bond ruptured is the C—O bond, it is not feasible at present to distinguish between the two C—O bonds present in the group taking part in the reaction. One can, however, conclude that alkyl-oxygen fission will not show any appreciable correlation with the carbonyl frequency. The present analysis of the data in Table I and Fig. 1 clearly show that in the esters for which both Raman Spectra and reaction kinetics data are available, we are dealing with acyl-oxygen fission for both alkaline and acid hydrolysis

The acylation of amines presents another interesting feature. There is a clear correlation between activation energy and both carbonyl and N—H frequencies. We have chosen for comparison only the symmetric N—H vibration and the linear relationship observed justifies the choice. The

transition state should involve both the N—H and the C—Hal. bonds but in the absence of a clear assignment of the C—Hal. bond in the compounds in question, we are forced to the next best alternative, namely, the carbonyl frequency. As in the case of ester hydrolysis, changes in the polarisability of the adjacent bond may be expected to correspond with changes in the carbonyl frequency with a possible reversal of sign. This expectation is substantiated by the slopes in Fig. 1. A negative slope is obtained when the carbonyl frequency is used for comparison while the N—H frequency gives a positive slope. This is only to be expected since the amino group is directly involved in the transition state.

The reaction between thiosulphate ion and methyl halides brings out another aspect of the problem. While the direction of the change in activation energy is the same as that of the characteristic C—Hal. frequency, the magnitude of change is very much larger in the former. This difference must arise both from the difference in the frequency factor and from differences in the stability of the transition state. The linear relationship indicates none the less the fact that the bond stretching force constant of the bond undergoing change is a major factor to be reckoned with.

In the absence of data at more than one temperature, rate constants alone are available and in such cases, a comparison may be made using the logarithm of the rate constant as has been done by Flett (*loc. cit.*) (Fig. 2). Provided the series of compounds compared have essentially the same frequency factor, deviations from linearity may not be noticed and in the case of substituted benzoic acids, this condition is approximately fulfilled. It can be readily observed that for this reaction, the polarisability of the acyl-oxygen bond is the one factor determining the rate-determining step and that the O—H bond is less significant.

The principal obstacle in extending the analysis or in making any rigorous quantitative generalisations is the relative absence of unequivocal assignments of characteristic frequencies in the case of such of those reactions which are found to be free from complexities in the mechanism in a homologous series or a series of compounds with systematic variations of substituents. Another factor that may have to be reckoned with is the probability of a reaction taking a preferred direction on account of the relatively greater thermodynamic stability of the products. The nitrogen halides are clear examples of this. With all these limitations, however, a certain amount of empirical extrapolations and interpolations are feasible in any one specified reaction of the types considered here. For instance, using the data in the tables and making use of the equation 1, one can predict

the activation energy for the alkaline hydrolysis of the halogeno and methoxy benzoic esters.

Mention was made earlier in this memoir that a close correlation between characteristic frequency and activation energy can be expected provided there is no mechanistic changes. The aliphatic substitution reactions thoroughly investigated by Hughes, Ingold and co-workers may be expected to provide us with a suitable material to test this but the frequency assignments in the case of the several compounds are not sufficiently accurate for proper comparison. One can reasonably expect that the grouping of frequencies will be on the same lines as the grouping of the compounds on a mechanistic basis by these workers.

It is of some interest to consider two instances where Fugassi and Warrick find considerable differences between their calculated values activation energies and the observed ones, the dissociation of nitrogen tetroxide and the decomposition of tertiary butyl alcohol. In the former case it is significant that the use of the experimentally determined value of the heat of the reaction makes the "calculated" value agree closely with the "observed" value. The discrepancy has to be attributed to several causes: the characteristic frequency assumed for the calculation appears to be surprisingly low. Analogy with the bonds involving carbon suggests that this should be in the neighbourhood of  $1000\text{ cm.}^{-1}$  instead of 283 mentioned. The monomer is stabilised by resonance involving structures with a three electron bond. This resonance energy may result in a lowering of the activation energy by its contribution to the transition state. Further, the adjacent charge rule of Pauling<sup>8</sup> which appears to be clearly substantiated in the case of nitrous oxide and the azides<sup>9</sup> suggests that the N—N bond, if present in the  $\text{N}_2\text{O}_4$  molecule, must be extremely weak. The alternative structure of the dimer proposed by Pauling involves a nitrogen oxygen bond and it has to be admitted that there is not enough evidence to rule it out. The other significant discrepancy noticed refers to tertiary butyl alcohol. The causes may be from two sources: the choice of the characteristic frequency and the value of the bond energy used in the calculation. From a study of a number of alcohols, it appears that the characteristic frequency of the C—O bond is in the neighbourhood of  $1050\text{ cm.}^{-1}$ . Accurate values of the bond distance in this compound are not readily available but from single bond covalent radii of the two atoms and the bond distance-bond energy curve of Skinner,<sup>10</sup> the bond energy value for this bond turns out to be nearer 70,000 cal. than the value used. Using these values, the calculated value for the decomposition reaction works up to 66,000 cal. which is quite close to the experimental value of Kistiakowski<sup>7</sup> quoted by Fugassi and Warrick (*loc. cit.*).

Flett (*loc. cit.*) has observed that a close correlation can be noticed between Hammett's  $\sigma$  factor<sup>4</sup> and the characteristic frequency, but it has to be stated that Hammett's empirical equation is subject to certain limitations. The  $\sigma$  and  $\rho$  factors sometimes show variations which may amount to as much as 25% of their values (*e.g.*, *p*-methoxy and *p*-amino and *p*-methyl show variations in the  $\sigma$  factor while bromination of acetophenone show variations in the  $\rho$  factor). The existence of resonance in the structures compared also causes considerable deviations from the generalisations. Any relationship involving characteristic frequencies and activation energies can give values which are nearer but even this is subject to the restriction that comparisons can be made, only if the mechanism of the reaction can be considered to be the same. This has been taken note of in the present analysis, and the relationship found is just an empirical one which may with a fuller data on all the factors influencing the course of the reaction lend itself to theoretical computation.

#### SUMMARY

A linear relationship is observed between the square of the bond frequency and the activation energy in the case of a few reactions in which substituents in the para-position are changed. Earlier work on similar problems is discussed and some discrepancies accounted for.

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