555. *The Kinetics of the Decomposition of the Addition Compounds formed by Sodium Bisulphite and a Series of Aldehydes and Ketones. Part II.* General Discussion of Energy–Entropy Relations.*

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In connexion with the experimental study in the preceding paper a general survey, classification, and interpretation of energy–entropy correlations in reaction kinetics is attempted.

Certain of the results given in Part I exhibit a relation between the parameters of the Arrhenius equation. The change in rate over a series of related reactions is lessened by a change in frequency factor tending to offset, in some measure, the effect of a change in activation energy. Effects of this kind are very common but usually left unexplained and their nature is here further discussed in more general terms.

The possibility that certain manifestations of the compensation effect are apparent and not real was discussed in Part I. With the bisulphite addition compounds the compensation associated with the so-called *ortho*-effect is of a regular type indicating the continuous operation of some dominant factor, whereas for other substituents the compensation is characterised by a scatter of experimental points and a less obvious pattern. In general a scatter of results in a kinetic study is attributable either to experimental error or to the interplay of two or more structure-sensitive factors rather nicely balanced with respect to one another. When the same investigation yields results both of marked regularity on the one hand and of considerable scatter on the other, the second explanation for the scatter seems the more likely.

The existence of a rather general compensation effect has long been in evidence.[1] A comprehensive survey of the literature on the subject would be beyond the scope of the present paper but enough examples will be quoted to illustrate the possible types of behaviour. Certain general conclusions can be drawn and the fact emerges that the effect is fundamental and operates according to the same principles in unimolecular or dissociative reactions and in bimolecular or associative reactions.

Much of interest in chemical kinetics comes from the study of related reactions forming a series. It is convenient to consider the simplest molecule capable of undergoing the reaction concerned and to think of modifications of this molecule as causing " substituent effects." These are often resolved into electronic and steric components but the nature of the latter is often obscure. Another convenient parameter variation can be made by considering change of medium. The bond stretching, compressing, and polarisation brought about by substituents in the reacting molecule can equally well be caused by the presence of solvent molecules. In solution there is always an interplay of " substituent " and " solvent " effects whereas in the gas phase substituent effects can be studied in their pure form. Where possible it is convenient to indicate the magnitude of any compensation effect by quoting the slope of the line obtained when $\log A$ is plotted against E (in kcal.).

Some Typical Examples.—The decomposition of bisulphite addition compounds described in Part I provides an example of an elimination reaction taking place in solution and there are also some interesting results on the elimination of sulphur dioxide from simple cyclic molecules,[2] the pure molten material being used as solvent medium. At pH 3 and at pH 5, respectively, the results for the bisulphite compounds of *ortho*-substituted benzaldehydes give good lines of slopes 0·61 and 0·64, and indeed the whole of the benzaldehyde sub-group provides evidence for an approximately linear relation between $\log A$ and E.

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* Part I, preceding paper.

[1] Syrkin, *Z. anorg. Chem.*, 1931, **199**, 28; Schwab, *Z. phys. Chem.*, 1929, *B*, **5**, 406; Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1334; Christiansen, *Acta Chem. Scand.*, 1948, **3**, 61; Leffler, *J. Org. Chem.*, 1955, **20**, 1202.

[2] Drake, Stowe, and Partansky, *J. Amer. Chem. Soc.*, 1946, **68**, 2521.

As reported in Part I, however, the complete group of compounds shows an irregular and less marked compensation. The results for the three sulphur dioxide eliminations cover a wide range of activation energies (15 kcal.) and give an excellent line of slope 0·51.

Two interesting unimolecular reactions which have been studied in a series of solvents are the *cis-trans*-isomerisation of azobenzene and of *p*-chlorophenyl diazocyanide.[3] These give slopes of 0·68 and 0·58, respectively, and cover an activation energy range of 5 kcal. The results show some scatter but the variety of solvents used makes the very existence of a compensation effect unusually striking. In the case of *cis*-azobenzene a wide range of solvent media including acetic acid, *cyclo*hexane, and the pure material was covered. Thus " solvent effects " whatever their nature, may sometimes produce correlated shifts in E and $\log A$ of very much the same order of magnitude as those produced by structural modifications of a reactant in a constant solvent. In other cases, however, such as the thermal decomposition of *o*-nitrophenyl azide,[4] E and $\log A$ are much the same for reaction in a number of solvents and even in the pure liquid medium.

Many bimolecular reactions in solution have been studied but, unlike the unimolecular reactions mentioned above, any given reaction in a series of unrelated solvents usually yields rather irregular results. The benzoylation of *N*-nitroaniline and the reaction between methyl iodide and pyridine,[5] both in a series of solvents, provide examples of highly complex solvent effects.

When modification of a solvent is achieved by varying the relative amounts of two components in a solvent pair rather than by substituting one pure solvent for another definite energy–entropy relations may be observed. The reaction of pyridine and methyl iodide [6] in benzene–ethanol gives a linear plot of $\log A$ against E of slope 0·67. This reaction yields quite different results in other solvent pairs such as benzene and nitrobenzene or *iso*propyl ether and nitrobenzene. The energy of activation is here relatively constant over the range of solvent media while $\log A$ varies by an amount comparable with that observed in cases where there is correlation and where E varies over a range of about 5 kcal. The scatter of results about a line of constant activation energy is suggestive of the interplay of two effects, and the same type of behaviour is shown by three other reactions involving the formation of quaternary ammonium salts in benzene–nitrobenzene.[7] The alkaline hydrolysis of ethyl benzoate [8] yields a line of slope 0·53, the data including results obtained in pure water and in water–ethanol, water–acetone, or water–dioxan. When water–methanol [9] mixtures are used the same slope is at first found, but at high alcohol content the compensation begins to fail.

The influence of both structure and solvent composition on a bimolecular reaction is well shown by the study of the alkaline hydrolysis of γ-lactones.[10] Two reactions involving rather different ring compounds were studied in water and in three water–ethanol mixtures. The eight experimental points fall on one good line of slope 0·55 and the two sets of four points are in the same order although somewhat displaced relatively to one another. This provides a striking example where both solvent effects and structural effects cause compensations of the same order of magnitude.

Reactions which involve the solvent chemically, not necessarily in the rate-determining stage, form a special group. Tommila and his co-workers have greatly added to data on ester hydrolyses of this type since they have used wide ranges of solvent compositions. They have shown the existence of solvation effects which lead to the appearance of minima when either $\log A$ or E is plotted against solvent composition.[11] The results indicate

[3] Hartley, *J.*, 1938, 633; Le Fèvre and Northcott, *J.*, 1949, 944; 1953, 867.

[4] Fagley, Sutter, and Oglukian, *J. Amer. Chem. Soc.*, 1956, **78**, 5567.

[5] Pickles and Hinshelwood, *J.*, 1936, 1353.

[6] Fairclough and Hinshelwood, *J.*, 1937, 1573.

[7] Raine and Hinshelwood, *J.*, 1939, 1382.

[8] Fairclough and Hinshelwood, *J.*, 1937, 541.

[9] Tommila and Ketonen, *Suomen Chem.*, 1945, **18**, *B*, 24.

[10] Hegan and Wolfenden, *J.*, 1939, 508.

[11] Tommila and Hella, *Ann. Acad. Sci. Fenn.*, 1954, *A*, *II*, **53**, 3.

that even when E varies in a quite complicated manner over a range of solvent compositions the regularity of the compensation may remain unimpaired.

When the solvent is kept constant and a series of related bimolecular reactions is studied even a serious scatter of experimental results may be insufficient to conceal the presence of compensation, as in the reduction of substituted nitrobenzenes by titanous chloride.[12] Some series of solvolytic [13] or replacement [14] reactions show no general energy–entropy correlation even when the data are suitable both in quantity and quality, although there does seem to be a rather general tendency in such cases for the rate changes to follow the changes in activation energy. In many cases, however, the plot of log A against E is regular, and activation energy ranges of up to 10 kcal. are frequently covered. The amine-catalysed decomposition of urethanes in benzyl alcohol [15] is a good example. Substituents in the *meta*- and *para*-positions give points on a line of slope 0·44 and *ortho*-substituents fall on the same line, but in a region of appreciably lower activation energies. The slope for the rearrangement of a series of substituted hydrazobenzenes [16] is 0·64 and a range of 10 kcal. is covered.

Frequently the effects of solvent change and reactant modification are difficultly separable. Energy–entropy correlations of different types may be obtained when stoicheiometrically similar reactions are compared, and evidence for mechanistic dissimilarity may thus be obtained. In aqueous ethanol the base-catalysed hydrolysis of some aromatic amides [17] gives results falling close to a line of slope 0·30 whereas for acid hydrolysis the form of the log A–E relation is a curve concave downwards. Sometimes the results for a series of related solvolytic reactions appear as two or more distinct groups for obvious reasons. In the hydrolysis of some tertiary aliphatic halides,[18] for example, the iodides fall on a good line of slope 0·44 while the chlorides form a group some distance away from it. In other cases, however, it is far from obvious why some of the results should fall on a good line while others lie so far away from it that experimental error offers no explanation. The results for the hydrolysis of the anhydrides of some substituted benzoic acids [19] give a line of slope 0·29 but with a number of points significantly below it. Highly specific solvent effects are presumably operating in these cases. An early paper [20] showed that rather complex behaviour might be expected on varying the structure of an ester in an ester hydrolysis since the nature of the solvent is obviously of great importance, but a good deal of regularity has actually appeared. Sometimes, as in the alkaline hydrolysis of a series of esters of α-hydroxypropionic acid [21] in water or the acid hydrolysis of certain acetates [22] in aqueous acetone, the activation energy ranges are rather narrow, though the slopes of about 0·57 and 0·74, respectively, may be quite genuine. The results for the acid hydrolysis of a series of acetates and benzoates in aqueous ethanol [23] give two lines of slopes 0·76 and 0·51. The same benzoates in aqueous acetone give points very close together and it is interesting to note that in both media the only *ortho*-substituted ester appears to be unlike all the others. In aqueous acetone the alkaline hydrolysis of ethyl esters of substituted benzoic acids, *Bz*-substituted phenyl acetates, or *Bz*-substituted benzyl acetates show a different type of behaviour.[22] For each of the three groups the frequency factor is sensibly constant compared with the changes in activation energy, although as in the case of relatively constant activation energy discussed

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[12] Newton, Stubbs, and Hinshelwood, *J.*, 1953, 3384.

[13] Brown, Okamoto, and Ham, *J. Amer. Chem. Soc.*, 1957, **79**, 1906; Brown, Brady, Grayson, and Bonner, *ibid.*, p. 1897.

[14] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.

[15] Mukaiyama and Iwanami, *J. Amer. Chem. Soc.*, 1957, **79**, 73.

[16] Croce and Gettler, *ibid.*, 1953, **75**, 874.

[17] Meloche and Laidler, *ibid.*, 1951, **73**, 1712.

[18] Shorter and Hinshelwood, *J.*, 1949, 2412.

[19] Berliner and Altschul, *J. Amer. Chem. Soc.*, 1952, **74**, 4110.

[20] Newling and Hinshelwood, *J.*, 1936, 1357.

[21] Salmi and Leino, *Suomen Chem.*, 1944, **17**, *B*, 19.

[22] Tommila and Hinshelwood, *J.*, 1938, 1801.

[23] Timm and Hinshelwood, *J.*, 1938, 862.

earlier the results are characterised by a marked scatter. The study of ester hydrolyses has thus further emphasised the general similarity of structural effects and solvent effects with respect to energy–entropy correlations.

Activation Mechanism, Degrees of Freedom, and Ranges of Transition States.—The experimental data for series of reactions in the gas phase are scarce and generally rather imprecise but for reactions in solution they fall into three distinct classes. A relatively rare but important case is that of constant frequency factor. Most common is that associated with marked compensation. The slopes of the log A–E curves do not show a distribution over all possible values but tend to fall in a fairly narrow range. Finally there is the class showing approximately constant activation energy, invariably characterised by a considerable scatter of results, indicative of the interplay of two factors. The simultaneous operation of one factor tending to increase both activation energy and frequency factor, and another tending only to decrease the activation energy, will produce experimental data of the third type.

The operation of such factors can be shown to follow in a very general way from the nature of chemical reactions. Emphasis has sometimes been placed on solvent participation in the transition state [24] but this appears to be only one aspect, though an important one, of a more general phenomenon. Indeed there is a close parallel between phenomena occurring in solution and those in the gas phase. Although suitably documented series of gas reactions are not yet available there are many reactions with apparently abnormally large frequency factors, and this fact itself, as will be shown, is closely connected with the energy–entropy correlation.

In considering variations of rate in a series of reactions the simplest effect to visualise is the electronic influence of a substituent which weakens or strengthens a bond (or bonds) and consequently alters the activation energy. This alteration in E may be progressive and unaccompanied by any change in the entropy of activation.

Solvation may very well modify or even imitate the electronic effect of substituents. Solvent molecules can have a specific action in modifying the influence of individual substituents. If, for example, a substituent of well-marked electrochemical character becomes co-ordinated with a solvent molecule the result may be a considerable modification of its electron-attracting or electron-repelling character, and a corresponding change in reactivity will be manifested by a change in activation energy. This again may be unaccompanied by a change in the entropy of activation. Thus a solvent may exercise an influence in a given reactant molecule kinetically indistinguishable from the classical electronic effect of a substituent. This, however, is far from being the only possible solvent effect, and indeed it would rarely be observed in the absence of other more complex effects. A substituent so far removed from the reaction centre that it is capable of exerting an electronic effect only may yet exert indirect structural effects by a disturbance of the solvent pattern which, as will appear, involves correlated changes in the energy and entropy terms.

In order to see in the most general way how the correlated changes of activation energy and entropy arise it is convenient to start from a well-known fact about unimolecular reactions. Here in the simplest case the entropy term A in the equation $k = A \exp(-E/\boldsymbol{R}T)$ is of the order of magnitude of a bond vibration frequency, the condition for this being that the activation energy is concentrated in one bond in the transition state. That is, there is one critical vibrational degree of freedom in the transition state. But the term A often assumes a value several powers of ten greater than the vibration frequency, the interpretation being that the activation energy is not strictly localised but can be distributed in any way between S degrees of freedom. In these conditions the probability of a transition state is increased by a combinatory factor in which the major term is $(E/\boldsymbol{R}T)^{S-1}/(S-1)!$. There is now a whole range of equivalent transition states and the entropy of activation is increased. If there are many states

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[24] Wynne-Jones and Eyring, *J. Chem. Phys.*, 1935, **3**, 492.

of equivalent energy there must lie, somewhere between them in the appropriate configuration space, a minimum of lower energy. This minimum will presumably correspond to reaction through one transition state only, that in which the activation energy is concentrated in one bond. In a series of reactions there may be varying displacements from the path of minimum activation energy and this circumstance will therefore result, by the operation of the combinatory factor, in corresponding changes in the entropy of activation. This seems to be the essence of an energy–entropy correlation in so far as it may occur in a unimolecular gas-phase reaction.

At first sight the problem of bimolecular reactions appears to be different. Closer consideration, however, shows it to be governed by basically similar principles. According to a commonly applied theorem the energy of activation in a three-centre reaction $A + BC \longrightarrow AB + C$ is a minimum when the transition state is linear, that is when A approaches along the axis of BC which may be taken as the x-axis. A must possess a component of velocity u_x in this direction corresponding to a kinetic energy E' which constitutes part of the activation energy E. Consider next the possibility of an oblique approach along an axis making an angle α with the x-axis. The component in the direction x will not be less than u_x and there must now be an additional component at right angles to x of not less than $u_x \tan \alpha$, say r. It does not matter what the components of r in the directions y and z are so long as $u_y^2 + u_z^2 = r^2$. Thus some at least of the additional activation energy is not contained in one degree of freedom but distributed in any proportion between two degrees of freedom. If an amount E'' is involved then the probability of its presence is not $\exp(-E''/\boldsymbol{R}T)$ but $(E''/\boldsymbol{R}T)\exp(-E''/\boldsymbol{R}T)$. If then the reaction forsakes the path of minimum activation energy, then from the very nature of a minimum, displacement towards a whole range of states of equal energy occurs, all of which are equally likely to lead to reaction. The result is an increase in the entropy factor which works against the effect of the increased activation energy. At first sight the most obvious circumstance imposing the oblique reaction path would be blocking of the path of minimum energy by a steric effect. There is, however, a more general possibility. The measured activation energy represents the most frequently followed reaction path. This may not be that of minimum energy, if for some other set of paths, removed from it, the product of the exponential energy factor and of the entropy factor is greater. The entropy increase appears in the appropriate form of rate equation as a combinatory factor representing the increased probability of a given total energy when shared between multiple degrees of freedom. Much more complex conditions than those schematised in the three-centre problem occur in many bimolecular reactions. The absolute minimum activation energy may be a minimum in a space of many dimensions. Displacements from it can occur in many ways and it is surrounded by a very complex range of states of equal higher energy. This range is in turn surrounded by another more extensive range of states of even higher energy. In a series of reactions structural changes will alter the shape of the energy surfaces, and the reaction path followed will be the accessible one giving the greatest product of the exponential term and the combinatory factor. Rises in the activation energy due to departure from the minimum will then generally be compensated to some extent.

The participation of a solvent may lead to a further multiplication of the number of equivalent transition states. Reactants and products are often unequally solvated and the activated complex may be more or less solvated than the reactant: the result will be a correlated change in the energy and entropy factors. As exemplified in a discussion by Tommila,[11] if the activated complex is more heavily solvated than the reactant, then the spontaneous process of solvation, tending to reduce the potential energy, will cause a lowering of the activation energy. This type of solvent participation must, however, lower the entropy of activation since more molecules are now involved in the definition of the transition state. If, on the other hand, the attainment of the transition state involves a release of solvent molecules initially bound to the reactant, energy must be supplied for the purpose and E will be increased. The provision of energy for the break up of a more or less elaborate solvent pattern may, however, be achieved in many different ways and there is likely to be considerable latitude in the manner in which this energy is shared between what are virtually new degrees of freedom. The above-mentioned combinatory factor thus enters into the expression for the energy distribution and the pre-exponential factor of the Arrhenius equation therefore increases, because the new transition states, although of higher energy, are more numerous.

CLASSIFICATION OF ENERGY–ENTROPY CORRELATIONS

The various kinds of energy–entropy relations may now be conveniently classified. Both " substituent effects " and " solvent effects " fall naturally into line with one another under the different headings, and indeed cannot be separated from one another when both operate together.

I. *Substituent Effects.*—(i) Bond strengths are altered but the form of the transition state is unchanged since the number of degrees of freedom involved in the activation process remains the same. This corresponds to the classical electronic effect and only the activation energy is altered.

(ii) For steric reasons the structural change modifies the contour lines surrounding the activation energy minimum. The number of degrees of freedom involved is increased and thus there is a correlated increase in the energy and entropy terms.

(iii) The structural change imposes a new solvation pattern on the system so that the modified reactant is virtually in a modified solvent. Correlated changes in the energy and entropy terms may appear.

II. *Solvent Effects.*—(i) The solvation pattern changes when the solvent is varied and correlated changes in the energy and entropy terms are caused.

(ii) The specificity of solvent–solute interactions is such that changes from one solvent to another may produce effects equivalent to those produced by changing a substituent in the reactant, an individual substituent group being itself more or less profoundly modified by the solvent. Any of the energy–entropy relations may result here.

In addition to the general classificaton given above there are of course energy–entropy variations due to changes in frequency, mass, and moment of inertia terms which appear in the partition functions describing the transition state. The influence of these effects, however, will be largely outweighed when for one or more of the reasons discussed above there is a significant modification of the relation between activation energy and the number of equivalent transition states. A more detailed knowledge of the operation of the large-scale effects is the primary requirement at present.

DISSOCIATION OF BISULPHITE COMPOUNDS

The broad general classification of energy–entropy relations covers all the cases discussed. In particular, it allows for the operation of both aspects of the correlation postulated in Part I. In the first place substitution of formaldehyde causes a decrease in activation energy with a moderate and irregular compensating decrease in the entropy of activation. In the second place substitution of benzaldehyde brings about similar energy and entropy changes which are rather irregular but nevertheless marked, except in the case of *ortho*-substituents where the compensation is both marked and regular. The increase in activation energy caused by *ortho*-substituents is more or less proportional to the size of the group concerned, in contrast to the effect of substitution on formaldehyde.

In the first case the effect is steric in the sense that it is unrelated to the polarity of the substituent. If the group R or R′ is bulky, entry of the bisulphite group into the ketone R·CO·R′ will be more difficult than into formaldehyde, and the strain in the compound correspondingly greater, with the result that there will be a pressure tending to expel the group and so lower the activation energy of the decomposition. The chief consequence will therefore be the change in E. The irregular entropy compensation seems here most likely to be due to varying combinations of the factors which have been discussed, the influence of the activation energy on the whole remaining dominant.

In the second case the substituents in the benzene ring presumably disrupt the solvent pattern besides exerting electronic effects with consequences which have already been considered. The *ortho*-substituted molecules represent a rather special sub-group, for the progressive stabilisation of the addition compound by increasingly bulky groups would seem to demand an explanation in terms of an interaction between the substituent and the bisulphite group itself. This could hardly occur without a considerable effect on the solvation pattern in the neighbourhood of the reaction centre, and a strong energy-entropy correlation could thus be caused.

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