888. *Border-line Mechanisms in Nucleophilic Displacement Reactions.*

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The description of nucleophilic substitution reactions in the "borderline" region between pure S_N1 and S_N2 mechanisms is discussed. Some of the experimental evidence which has been held to require the postulation of intermediate mechanisms is shown to be compatible with the alternative view that such reactions are made up of concurrent unimolecular and bimolecular processes. Certain theoretical difficulties of the concept of intermediate mechanisms are pointed out.

It is now generally accepted that two distinct mechanisms of nucleophilic substitution (unimolecular or S_N1, and bimolecular or S_N2) may be recognised. The kinetics and other characteristics of these mechanisms have been extensively studied and discussed by Hughes and Ingold, and conditions for the operation of each of the mechanisms to the exclusion of the other have been realised. There is less agreement about the description of reactions which occur under intermediate conditions, *i.e.*, at the border-line between the extreme S_N1 and S_N2 mechanisms. Such reactions are either considered to be made up of concurrent bimolecular and unimolecular processes or to possess intermediate mechanisms.[1–4]

The most direct evidence which is admissible in a discussion of the molecularity of a reaction is a kinetic examination of reaction orders. However, most of the investigated border-line reactions are solvolyses for which the establishment of reaction orders with respect to the solvent is not a straightforward matter and, consequently, unequivocal measurements of an accuracy sufficient to settle the problem do not appear to exist. We have previously shown,[5] in the case of reactions of benzoyl chloride in aqueous acetone, that an analysis of the reaction velocities in terms of concurrent unimolecular and bimolecular processes is adequate—without thereby proving that a different analysis was impossible—and have briefly indicated that the notion of intermediate molecularities could not easily be reconciled with the currently accepted theory of reaction kinetics.

The support of the view that a border-line reaction must be expressible as a sum of unimolecular (S_N1) and bimolecular (S_N2) processes (or, more generally, molecular processes of integral molecularity) has recently been described [4] as " completely indefensible." This extreme opinion is, in part, due to a use of the terms S_N1 and S_N2 in a sense which is at variance with definitions and established practice and ignores the significance [6] of the numerals 1 and 2 in the designation of the mechanisms.

The objects of the present paper are (i) to examine some of the evidence which has been thought to require the concept of reactions of intermediate molecularity, and (ii) to point out some of the general implications of the idea of intermediate molecularity.

Evidence for Intermediate Mechanisms.—(a) *Systematic study of solvent effect.* Winstein, Grunwald, and Jones [1] suggested that it was possible to arrange solvents on scales of reactivity for extreme S_N2 and S_N1 solvolyses and to give a quantitative index to the reactivity of each solvent for each of the two mechanisms. They then showed that the rate of a reaction expected to be a border-line case did not accord with the rate predicted from these solvent reactivities if the reaction were the sum of concurrent S_N1 and S_N2 processes. Their detailed procedure has been criticised by Bird, Hughes, and Ingold.[3] However, even if we accept that procedure and the results, it is not necessary to assume that the border-line reaction is anything but the sum of unimolecular and bimolecular processes.

It is common ground that in a reaction of the type

$$\mathrm{Y^- + R{-}X \longrightarrow \underset{\text{Transition state}}{\overset{-}{\overbrace{\underset{\longleftarrow y \longrightarrow}{Y\cdots R}\cdots X}}} \longrightarrow Y{-}R + X^-} \qquad . \; . \; . \quad (1)$$

the role played by the nucleophilic substituting reagent Y^- diminishes in importance as we go from conditions typical for an exclusive S_N1 process towards the border-line conditions. In this progression the heterolysis of the severed bond (R–X) gradually assumes greater importance, and the formation of the new bond (R–Y) less importance, in contributing to the free-energy change on forming the transition state of the reaction from the reactants. We could also say that the distance (y) between Y and R in the transition state increases, or that Y becomes less firmly attached to R in the transition state, as we pass from the extreme S_N2 conditions to the border-line conditions. It is important to note that any transition state in which there is interaction between Y and R is a bimolecular transition state and, notwithstanding the weakness of the $Y\cdots R$ bond in the

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[1] Winstein, Grunwald, and Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700.
[2] Swain and Langsdorf, *ibid.*, p. 2813.
[3] Bird, Hughes, and Ingold, *J.*, 1954, 634.
[4] Kornblum, Smiley, Blackwood, and Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.
[5] Gold, Hilton, and Jefferson, *J.*, 1954, 2756.
[6] Ingold, " Structure and Mechanism in Organic Chemistry," Bell & Sons Ltd., London, 1953, pp. 310—315.

transition state, the reaction described is bimolecular (S_N2) over the whole range of this progression.

Since, in the border-line region, the interaction between Y and R is of secondary importance in the energetics of the formation of the transition state, it seems plausible to attribute comparable importance to several reaction paths which differ in the distance y of the transition state. The contribution (dv_y) to the specific rate from paths involving bimolecular transition states characterised by the length interval y to $y + dy$ would then be

$$dv_y/[RX] = k_y[Y]F_y \, . \, dy$$

where F_y is a distribution function describing the concentration of Y as a function of the distance y, *i.e.*, a measure of the *a priori* probability of the transition state, k_y is the appropriate rate coefficient, and [Y] the bulk concentration of Y^-. Hence the total specific rate $v/[RX]$ is given by

$$v/[RX] = [Y] \int_{y=a}^{\infty} k_y F_y \, . \, dy \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the integration beginning at the distance of closest approach. It is impossible to specify in detail the course of the function k_yF_y. For the extreme S_N2 mechanism small values of y are expected to make the only important contribution to the integral, whereas in the border-line region k_yF_y may be significant up to larger values of y. The course of k_yF_y will therefore be expected to depend both on the nature of RX and on that of Y. In any case, the factor [Y] outside the integral indicates that the reaction is kinetically of the second order and bimolecular.

In setting up a scale of nucleophilic reactivities of different solvents for typical S_N2 reactions Winstein, Grunwald, and Jones [1] effectively chose as typical S_N2 rate constants the values of $\int k_yF_y \, . \, dy$ which apply when only small values of y need be considered. In using this scale for calculating the rates of border-line reactions—for which larger values of y still make significant contributions to the integral—they accordingly underestimate the bimolecular rate of the border-line reaction and hence observe the discrepancy on which their argument is based. Although this discrepancy indicates a gradual change in the character of the S_N2 reaction, it is no evidence—as has been claimed—against the view that there is a strictly bimolecular contribution to the total rate.

In addition to the gradual change in the bimolecular reaction on moving from the conditions for extreme S_N2 character to the border-line region, there is a gradual increase in the contribution from the reaction which does not involve Y in the transition state at all,[5] *i.e.*, the S_N1 mechanism. Hence the reaction may be described as a sum of bimolecular and unimolecular processes.

The view outlined takes into account all the phenomena on which the thesis of Winstein, Grunwald, and Jones [1] is founded. At the same time it retains the idea that there is an abrupt difference between S_N1 and S_N2 mechanisms as far as the molecularity is concerned. Such an abrupt change is a consequence of the quantisation of matter, inasmuch as there is no gradual transition between *no* molecule and *one* molecule, and it must arise in any development of reaction kinetics based on either collision or transition-state theory.

(b) *Effect of structural changes in* RX. Because of the gradual change of importance of the bond-breaking and bond-forming aspects of S_N2 reactions, the effect of a structural change in RX will in this case be less clear-cut than for S_N1 reactions where, in all cases, bond-breaking is the only phase which needs consideration. A certain substituent group may under certain conditions accelerate and under other conditions retard bimolecular reactions, since the electronic requirements of the bond-breaking and bond-forming processes are opposed. An S_N2 reaction in the border-line region for which bond-breaking is more important energetically than bond-forming will therefore show substituent effects similar to those of S_N1 reactions. Again, on going from the typical S_N2 conditions towards the border-line range and on to S_N1 conditions, we shall accordingly expect to find a gradual change in the effect of substituent groups, as was indeed observed by Swain and

Langsdorf.[2] However, these observations do not require the concept of intermediate molecularity.

Another example of structural effects in an S_N2-like reaction which follow the same order as for S_N1 reactions was recently studied in detail by Kornblum and his co-workers,[4] who found that certain heterogeneous reactions between silver nitrite and alkyl halides were accompanied by a Walden inversion but that structural changes in the alkyl halide affected the rate in the same direction as for S_N1 reactions of these halides. The evidence appears to be compatible with the hypothesis that these reactions are examples of what Ingold has termed [7] a " metal-catalysed S_N2-like substitution." Again, the conclusion that the observations required a mechanism of intermediate molecularity is not necessary.

The above views on the effect of substituents on S_N2 reactions are not novel. In particular, Baker [8] has discussed the effect of *para*-substitution in benzyl bromides [9] in the region of border-line kinetics on similar lines. The idea that the directions of substituent effects for S_N1 and S_N2 reactions must be opposite [4] in all cases is an incorrect generalisation which appears to have grown out of the studies on the effect of alkyl substituents on solvolytic reactions of methyl and ethyl halides where this difference has indeed always been observed.

General Implications of the Concept of Intermediate Molecularity.—Bird, Hughes, and Ingold [3] have reported experimental evidence of a different kind in support of the idea that mechanisms merge into each other. Their observations are those of reaction orders and, if the reactions have the general mechanism considered, are strictly relevant to the problem. It is not proposed to discuss the mechanism of these reactions or the details of the particular simplified model chosen as a basis for the physical interpretation of the results. However, the general implications of the *type* of theory proposed by Bird, Hughes, and Ingold are so wide that a brief discussion of some of its consequences seems warranted.

Their proposed rate expression for a border-line reaction (1) is equivalent to

$$-\mathrm{d}[\mathrm{RX}]/\mathrm{d}t = \left\{k + K(1 - \mathrm{e}^{-\beta[\mathrm{Y}]})\right\}[\mathrm{RX}] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k, K, and β are constants of the reaction. When $\beta[\mathrm{Y}]$ is small the expression becomes

$$-\mathrm{d}[\mathrm{RX}]/\mathrm{d}t = \left\{k + K\beta[\mathrm{Y}]\right\}[\mathrm{RX}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and is of the form corresponding to concurrent first- and second-order reactions with rate constants k and $K\beta$ respectively. For large values of $\beta[\mathrm{Y}]$, eqn. (3) can be simplified to

$$-\mathrm{d}[\mathrm{RX}]/\mathrm{d}t = (k + K)[\mathrm{RX}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

i.e., the reaction is of first order with a rate constant $(k + K)$. For intermediate values of $\beta[\mathrm{Y}]$ the kinetics do not follow a simple order.

If we accept the general form, eqn. 3, of the rate law then, because of the interrelation of kinetic equations and equilibrium expressions, we must be prepared to make a similar modification of the laws of chemical equilibrium. This would involve the development of more general systems of chemical and statistical thermodynamics in which chemical potentials and translational partition functions involve functions of the form $(1 - \mathrm{e}^{-\beta c})$ in place of the first power of the concentration. A further difficulty in setting up such theories is the requirement that β must be characteristic not only of the chemical species concerned but also of the reaction in which it is involved. (It is assumed that—for the simple S_N reactions—it is not necessary to consider that the reaction mechanism during the early stages of the reaction may fundamentally differ from that at equilibrium. The correctness of this assumption—which would be open to challenge in the case of less thoroughly investigated reactions, more especially when surface catalysis or chain reactions are involved—has been verified in a number of specific cases of exchange reactions in which different isotopes of a halogen constitute the nucleophilic reagents X^- and Y^-.) In fact, the incompatibility of the laws of thermodynamics with the formulation of fractional

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[7] Ingold, *op. cit.*, p. 358.

[8] Baker, *Trans. Faraday Soc.*, 1941, **37**, 632.

[9] Baker and Nathan, *J.*, 1935, 1840.

reaction orders according to eqn. (3) seems insuperable. These difficulties cannot be overcome by refinement of the kinetic model and must occur with any formulation of rate laws in the general form

$$v = \left\{k + K\mathrm{f}([\mathrm{Y}])\right\}[\mathrm{RX}]$$

where the function f([Y]) has the properties that it tends to become proportional to [Y] as [Y] ⟶ 0, and independent of [Y] as [Y] ⟶ ∞.

An alternative formulation of intermediate reaction orders would be by means of a simple power law

$$v = k[\mathrm{RX}][\mathrm{Y}]^{\alpha} \text{ where } 0 < \alpha < 1$$

This equation could be reconciled with the laws of chemical equilibrium but would not help to explain the results given by Bird, Hughes, and Ingold. The difficulty with this type of equation is that it implies the participation of a fractional number of molecules in a collision or a transition state and, as has been stated above, such a model is incompatible with the quantisation of matter.

It is therefore concluded that the formulation of border-line mechanisms as the concurrent operation of bimolecular and unimolecular processes is the only representation of such reactions which fits into the general body of physicochemical theory. This conclusion appears to re-open the problem of the chemical interpretation of the rate laws observed by Bird, Hughes, and Ingold.[3]

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