THE SODIUM "FLAME" REACTIONS

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The problem of the influence of structure on reactivity is extremely broad and complex, and there exists a vast amount of experimental work in this field. The most interesting and useful contributions have consisted in the systematic examination of various examples of a single type of reaction. An instance of this is the investigation of the reactions of sodium atoms with halogens and various halides which has been carried out by Polanyi and his collaborators. This work, which has extended over the last twenty years, constitutes a very extensive contribution to the field of reaction kinetics. The choice of a bimolecular reaction in which one of the two reactants is a free atom possesses distinct advantages. Atomic reactions are clearly the least complex from the standpoint of bonds broken and formed. Further, in this case, the great reactivity of sodium atoms has enabled the investigations to embrace a wide range of reaction partners without any change in one of the reactants. Another important aspect of this work is that the rates of elementary processes were measured directly. From the first it was thought [1] that such data for simple reactions would be of great value in the elucidation of the mechanisms of more complex reactions and in the development of a more general theory of chemical reactivity.

The results obtained so far have revealed a number of interesting and important trends in reaction velocity and, as will be seen, the field is by no means exhausted. These trends have received considerable theoretical attention, and in some cases the fundamental aspects may be said to be fairly well understood. The theoretical interpretation of these reactions has played an important part in attempts to develop a general theory of reactivity, and in emphasising the rôle of such factors as, for example, bond energies, it has stimulated valuable experimental work in other fields.

An excellent summary of the experimental work carried out up to 1942, with extensive references to original papers, has been given by Bawn.[2] Polanyi [1] has given a very clear account of the principles underlying the theoretical method which has been developed for the calculation of the activation energies of this type of reaction, together with a description of the experimental techniques employed and a discussion of some of the results obtained.

It is not possible, in the space of this Review, to describe all the experimental techniques which have been devised to study these fast reactions of sodium atoms, or to deal with the earlier experiments on the reaction of sodium atoms with free halogens and a number of metallic halides. For

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[1] M. Polanyi, "Atomic Reactions", Williams & Norgate, 1932.

[2] *Ann. Reports*, 1942, **39**, 36.

these aspects the above works [1, 2] and the review by Schay [3] may be consulted. This Review is mainly concerned with later developments—the rates of reaction of sodium atoms with organic halides. The important trends in these rates are outlined and the theoretical methods, by means of which some of these trends may be understood, are discussed. The lines on which present investigations are moving are also briefly summarised.

The Diffusion Flame Method.—Nearly all the investigators of the reactions of sodium atoms with organic halides have used the diffusion flame method which was developed by von Hartel and Polanyi.[4] It consists in the measurement of the extent of penetration of one reactant (sodium) into an excess of the other (organic halide) before it is completely consumed by reaction. Conveniently measurable diffusion paths are achieved by the addition of an inert gas. Wall reactions between sodium and the other reactant or secondary products are eliminated by arranging that the sodium diffuses from a nozzle and is completely consumed before it reaches the walls of the reaction vessel.

A stream of inert gas (carrier gas) at a pressure between 0·5 and 10 mm. is first led through a tube (the sodium boat), the surface of which is coated with a freshly distilled film of sodium kept at a constant temperature T ($\sim 520°$ K.). In this way the carrier gas is saturated with sodium vapour at a pressure P_T ($\sim 10^{-3}$ mm.). This stream then flows through a nozzle of *ca.* 4-mm. diameter into the reaction vessel where it encounters a mixture of halide and carrier gas, in which the partial pressure of the halide may vary from 5×10^{-3} mm. to a few millimetres depending on the reaction rate. The sodium diffuses out in all directions from the nozzle and the spherical zone of reaction can be made visible by illumination with D-line resonance radiation. The diameter can be measured by observing the zone at right angles to the incident light. This diameter corresponds to the distance the sodium diffuses before its pressure falls from the value P_T at the nozzle mouth to a value P_0 which corresponds to the limit of detectability of the sodium vapour and can be determined by other experiments. Application of stationary-state conditions to the flame zone gives the expression

$$k = \frac{\left(\ln \frac{P_T}{P_0} - \ln \frac{R}{r}\right)^2 \delta}{(R - r)^2 C_{\mathrm{Hal}}} \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

in which k is the velocity constant of the bimolecular reaction, R is the radius of the " flame " zone, r is the radius of the nozzle, δ is the diffusion constant of the sodium in the carrier gas, and C_{Hal} is the concentration of the halide in the reaction vessel. The validity of this equation depends on the fulfilment of a number of conditions which are never attained exactly in practice. However, Heller,[5] by a careful investigation of the flame zone, was able to define the experimental conditions which constitute

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[3] *Fortschr. Chem. Physik und physikal. Chem.*, 1931, 21.

[4] *Z. physikal. Chem.*, 1930, *B*, **11**, 97.

[5] *Trans. Faraday Soc.*, 1937, **33**, 1556.

a reasonable compromise and under which equation (1) can be expected to give fairly satisfactory absolute values for velocity constants.

For experimental details and the applications of the so-called life-period method, which is a modification of the diffusion flame method developed by Frommer and Polanyi,[6] other sources may be consulted.[6, 7, 8, 9]

Experimental Results.—The most important results for the rates of reaction of sodium atoms with organic halides are summarised below in the form of series. The data given appertain to the bimolecular process *

$$RX + Na \longrightarrow R\cdot + X^{-}Na^{+}$$

irrespective of the subsequent fate of the radical R•. The chlorides are the most suitable halides by means of which various structural effects may be illustrated, since with them the range of conveniently measurable rate constants is the widest. The numerals given above the formula for each compound represent the collision yield, Z_0/k (*i.e.*, the number of collisions needed for one successful transformation); the numeral below the formula is the activation energy, E, in kcals. mole^{-1}. Z_0 and E are calculated from the well-known equations

$$Z_0 = \left\{8\pi \boldsymbol{R}T\left(\frac{1}{M_1} + \frac{1}{M_2}\right)\right\}^{\frac{1}{2}} \sigma^2 N \quad . \quad . \quad . \quad . \quad (2)$$

$$\approx 5 \times 10^{14} \text{ for all these reactions}$$

and

$$k = Z_0 e^{-E/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which σ is the collision diameter, M_1 and M_2 are the masses of the two reactant molecules, and N is Avogadro's number. The results below, with the exception of a few in parentheses, are those obtained by von Hartel and Polanyi,[4] and von Hartel, Meer, and Polanyi.[10] Although it is recognised that this early work does not represent the most accurate diffusion flame work as regards the absolute values of the velocity constants, yet the results constitute the most extensive, self-consistent set of data which have been obtained. Rarely has more recent work led to any serious revision in *differences* in activation energy in series. The arrows indicate *increase* in reaction velocity. Although in most cases only one series has been given to illustrate a particular structural effect, it should be realised that there are frequently numerous examples available (see ref. 1).

I. Change of the halogen atom:

$$\begin{array}{ccccccc} > 10^6 & & 10{,}000 & & 50 & & 1 \\ CH_3F & \longrightarrow & CH_3Cl & \longrightarrow & CH_3Br & \longrightarrow & CH_3I \\ > 25 & & 10{\cdot}0 & & 4{\cdot}3 & & 0 \end{array}$$

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[6] *Trans. Faraday Soc.*, 1934, **30**, 519.

[7] Fairbrother and Warhurst, *ibid.*, 1935, **31**, 987.

[8] Warhurst, *ibid.*, 1939, **35**, 674.

[9] Haresnape, Stevels, and Warhurst, *ibid.*, 1940, **36**, 465.

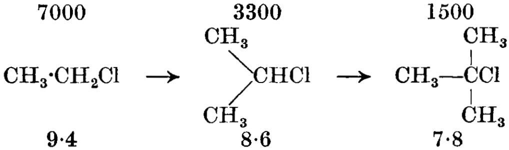
[10] *Z. physikal. Chem.*, 1932, *B*, **19**, 139.

* There are, however, a small group of compounds, not halides, investigated by Bawn and A. G. Evans (*Trans. Faraday Soc.*, 1937, **33**, 1571, 1580), which involve a three-body collision (see also ref. 2).

II. Lengthening of the carbon chain:

$$\underset{10{\cdot}0}{\overset{10,000}{\mathrm{CH_3Cl}}} \longrightarrow \underset{9{\cdot}4}{\overset{7000}{\mathrm{CH_3{\cdot}CH_2Cl}}} \longrightarrow \underset{9{\cdot}2}{\overset{4400}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2Cl}}} \longrightarrow \underset{8{\cdot}6}{\overset{3300}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl}}}$$

III. Primary, secondary, and tertiary halides:



IV. Increase in the number of chlorine atoms on the same carbon atom:

$$\underset{10{\cdot}0}{\overset{10,000}{\mathrm{CH_3Cl}}} \longrightarrow \underset{7{\cdot}4}{\overset{900}{\mathrm{CH_2Cl_2}}} \longrightarrow \underset{5{\cdot}0}{\overset{100}{\mathrm{CHCl_3}}} \longrightarrow \underset{3{\cdot}5}{\overset{25}{\mathrm{CCl_4}}}$$

V. Double bond in α-position to the chlorine atom:

$$\underset{9{\cdot}4}{\overset{7000}{\mathrm{CH_3{\cdot}CH_2Cl}}} \longleftarrow \underset{10{\cdot}4}{\overset{11,000}{\mathrm{CH_2{:}CHCl}}}$$

VI. Double bond in β-position to the chlorine atom:

$$\underset{9{\cdot}2}{\overset{4400}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2Cl}}} \longrightarrow \underset{6{\cdot}0}{\overset{250}{\mathrm{CH_2{:}CH{\cdot}CH_2Cl}}}$$

VII. Presence of oxygen atoms:

$$\underset{10{\cdot}0}{\overset{10,000}{\mathrm{CH_3Cl}}} \longrightarrow \underset{(8{\cdot}5)\ *}{\overset{(2780)}{\mathrm{CH_3{\cdot}O{\cdot}CH_2Cl}}} \longrightarrow \underset{(7{\cdot}6)\ *}{\overset{(1220)}{\mathrm{C_2H_5{\cdot}O{\cdot}COCl}}} \longrightarrow \underset{(3{\cdot}8)\ *}{\overset{(36)}{\mathrm{C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_2Cl}}} \longrightarrow$$

$$\underset{\sim 5(3{\cdot}2)\ *}{\overset{\sim 100(20)}{\mathrm{CH_3{\cdot}COCl}}} \longrightarrow \underset{\sim 2{\cdot}5(1{\cdot}7)\ *}{\overset{\sim 10(5)}{\mathrm{CH_3{\cdot}CO{\cdot}CH_2Cl}}}$$

$$\underset{9{\cdot}4}{\overset{7000}{\mathrm{CH_3{\cdot}CH_2{\cdot}Cl}}} \longrightarrow \underset{(7{\cdot}6)}{\overset{(980)\ \dagger}{\mathrm{HO{\cdot}CH_2{\cdot}CH_2Cl}}}$$

It can be seen that there exist a number of well-marked trends in reaction velocity which result from certain types of structural changes in the radical R. It has been found possible to explain some of these trends by theoretical methods forming part of a more general scheme which has been developed for the calculation of the activation energies of reactions involving three centres.[1, 2] These methods are discussed in the next section.

Theoretical.—The reaction between a sodium atom and an organic monohalide RX can be considered as a transition between a homopolar bond assignment, $(\mathrm{R\cdots X\cdots Na})_h$, and a heteropolar or ionic bond assignment, $(\mathrm{R\cdots X^-\cdots Na^+})_i$. Both correspond to a linear configuration of the three centres, Na, X, and the carbon atom of the radical R,‡ which are thus

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* Walker and Warhurst, unpublished.

† A. G. Evans and Walker, *Trans. Faraday Soc.*, 1944, **40**, 384.

‡ It can be shown for three-centre problems that a linear configuration leads to the least activation energy.

defined completely in terms of two internuclear separations, the R···X and the X···Na distances. The course of the reaction can then be discussed by means of a three-dimensional energy surface. The initial state of the reaction can be represented by $(R—X···Na)_h$ in which the R—X distance is the C—X bond length in the molecule RX, and the X···Na distance is infinite. The final state can be represented by $(R···X^-Na^+)_i$, in which the X^-Na^+ distance is equal to the normal internuclear separation of the gaseous ion pair, and the R···X distance is infinite.

The energy of all possible configurations having the bond assignment $(R···X···Na)_h$ may be evaluated *approximately* by using a semi-empirical method developed by Eyring and Polanyi [11] based on a quantum-mechanical treatment of simple reactions by London [13] (for details, see Polanyi [1] or Glasstone, Laidler, and H. Eyring [14]). This method enables the construction of a completely homopolar energy surface E_h, by means of which the potential-energy changes corresponding to the change in configuration

$$\text{initial state, } (R—X···Na)_h \longrightarrow \text{ final state, } (R···X—Na)_h$$

may be followed. The homopolar final state, however, lies at a much higher energy level than the true final state $(R···X^-Na^+)_i$ owing to the fact that the homopolar binding energy between X and Na is much less than that between X^- and Na^+. The electronic transition, which results in the formation of an ion pair, must take place in a configuration intermediate between those of the initial and of the true final states. The construction of a second potential-energy surface, E_i, which represents the energy of all possible configurations with the bond assignment $(R···X^-···Na^+)_i$, is thus necessary. The energies denoted by E_i may be expressed as :

$$E_i = E(X^-···Na^+) + E(R···X^-)$$

The first term may be calculated fairly accurately by methods similar to those used in the calculation of ionic lattice energies. The energy $E(R···X^-)$ comprises two terms : an attraction term due to the polarisation of the R radical (mainly the carbon atom) by the X^- ion ; and a repulsion term. These may also be evaluated approximately.

Superposition of the two surfaces E_h and E_i in such a manner that the energy level of the final state lies below that of the initial state by an amount equal to the known heat of reaction results in an intersection of the two surfaces in a curve. This curve defines a series of configurations for which E_h and E_i are equal. The point of *lowest* energy on this curve determines the intermediate configuration of least energy and this is called the transition state or activated complex. The difference in energy between the transition state and the initial state is the activation energy of the reaction.

The superposition of two surfaces is illustrated *diagrammatically* in Fig. 1, which shows the equi-energy contours. For simplicity a completely symmetrical surface has been drawn representing a thermoneutral reaction.

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[11] *Z. physikal. Chem.*, 1931, *B*, **12**, 279.

[12] Ogg and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 604, 1375.

[13] *Z. Electrochem.*, 1929, **35**, 552.

[14] " Theory of Rate Processes ", McGraw-Hill, New York, 1941.

The two surfaces intersect in a curve, the projection of which on to the plane defined by the configuration co-ordinates is, in this simple case, a straight line, AB. The transition state is denoted by *T*. The course of the reaction is represented by the dotted line which starts on the surface E_h and crosses to the surface E_i at *T*. This detailed method has been applied to the reactions of sodium atoms with the hydrogen halides[16] and the methyl halides.[15] The trends in the calculated activation energies are in reasonable agreement with experiment.

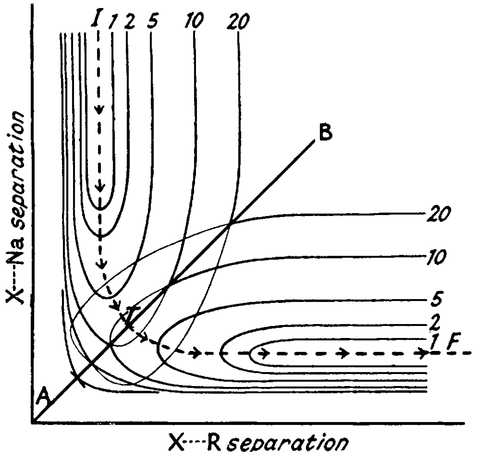

FIG. 1

Fortunately, the method can be further simplified for reactions of sodium atoms, and activation energies calculated without the construction of the two energy surfaces. M. G. Evans and Polanyi[17] have suggested that in these reactions the sodium atom can approach the R—X molecule until the Na···X separation is equal to the ion-pair normal distance corresponding to the final state, without any appreciable change in energy, particularly in the Na···X repulsion energy. There seems to be fairly good evidence in favour of this suggestion (see ref. 16).

This means that the course of the reaction can be represented by a single cross-section of the complete energy surface, the cross-section being parallel to the R···X axis and corresponding to a constant value of the Na···X distance equal to the ion-pair normal distance. Potential-energy changes may then be represented on a two-dimensional diagram.* This is illustrated by curves (*a*) and (*c*) in Fig. 2, the former being the R—X bond extension energy curve, the latter the energy $E(\mathrm{R}\cdots\mathrm{X}^-)$. These are clearly the only two energy terms which vary along the line of the cross-section, depending on the R···X separation. When the relative positions of the two curves (*a*) and (*c*) are adjusted so that the energy difference between the initial state (*I*) and the final state (F_1) is equal to the heat of the reaction (*H*), then the crossing point T_1 represents the transition state. The activation energy is given by E_1.

Actually, on account of resonance between the two bond assignments $(\mathrm{R}\cdots\mathrm{X}\cdots\mathrm{Na})_h$ and $(\mathrm{R}\cdots\mathrm{X}^-\cdots\mathrm{Na}^+)_i$, the two curves (*a*) and (*c*) do not cross

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[15] A. G. Evans and M. G. Evans, *Trans. Faraday Soc.*, 1943, **39,** 19.

[16] M. G. Evans and Warhurst, *ibid.*, 1939, **35,** 593.

[17] *Ibid.*, 1938, **34,** 11.

* This simplification also has the consequence that the activation energy is no longer sensitive to the direction of approach of the sodium atom as is usually the case in a three-centre reaction.

at a point. This resonance is largest at the crossing point, at which the two assignments have equal energies, and decreases rapidly on either side of this point. This results in a " rounding off " of the curves and a separation into an upper and a lower curve, both continuous. This is indicated by the dotted curves. The true transition state lies immediately below T_1, at the top of the curved energy hump. Thus the activation energy obtained by this method from the crossing point T_1 is always greater than the true activation energy of the reaction by an amount w, the resonance energy of the crossing-point configuration. In applying this method it is assumed that w is relatively small or, at least, does not vary greatly from one reaction to another. In the latter event, which does not seem unreasonable particularly if X remains unchanged, the calculated activation energies obtained from crossing-point energies might be expected to show the same gradation as the experimental values for a series of reactions.

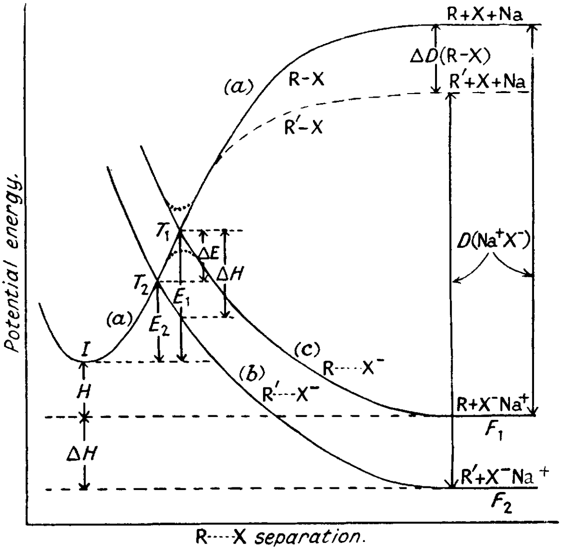

FIG. 2

The following table shows the results obtained by M. G. Evans and Warhurst [16] by this simple method. The main uncertainty in these cal-

Reaction.	$E_{calc.}$, kcals. mole⁻¹.	$E_{obs.}$, kcals. mole⁻¹	Heat of reaction, kcals. mole⁻¹.
$CH_3F + Na$	~ 38 [d]	~ 18·5 [a]	~ 0
$CH_3Cl + Na$	16·2	9·7 [b]	15
$CH_3Br + Na$	8·7	5·1 [c]	19
$CH_3I + Na$	6·1	2·5 [c]	18

[a] Warhurst and Whittle (unpublished). [b] Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633. [c] Haresnape, Stevels, and Warhurst, *ibid.*, 1940, **36**, 465. [d] Recalculation by Quayle and Whittle, using more recent data.

culations probably lies in the evaluation of the repulsion energy term in $E(\mathrm{R}\cdots\mathrm{X}^-)$. Various methods of determining this were explored with the encouraging result that, although the absolute magnitudes of the activation energies were rather sensitive to the type of expression chosen, the gradation in activation energies remained substantially unaltered and in reasonable agreement with experiment.

Discussion of Trends in Reaction Rates.—It is noticeable that the decrease in activation energy along the series $CH_3F \rightarrow CH_3I$ does not run parallel to a monotonous increase in the exothermicity, H, of the reactions. This may be understood by reference to curves (*a*) and (*c*) in Fig. 2.[17] Along the series $CH_3F \rightarrow CH_3I$ the *shapes* of the curves (*a*) and (*c*) change, in particular the C—X bond extension curve (*a*) becomes progressively "softer" (*i.e.*, of decreasing curvature). These curvature changes, which clearly affect the activation energy E_1, are not directly connected with the heat of reaction, and hence a parallelism between activation energy and heat of reaction is not to be expected in such a series.

In contrast to the above, this method of depicting the reactions does lead in certain cases to the expectation of a parallelism between E and H, for series of reactions in which one of the two "end" centres (R or Na) is changed.[12, 17] Consider the reactions of sodium atoms with two organic halides RX and R′X. Suppose the C—X bond dissociation energy in R′X is less than that in RX by an amount $\Delta D(\mathrm{RX})$ and that this difference arises solely from an energy difference in the two radicals R′ and R. This is depicted in Fig. 2.* The energies of the two final states $\mathrm{R} + \mathrm{X}^-\mathrm{Na}^+$ and $\mathrm{R}' + \mathrm{X}^-\mathrm{Na}^+$ both lie at an amount $D(\mathrm{Na}^+\mathrm{X}^-)$ below the corresponding dissociation limits $\mathrm{R} + \mathrm{X}$ and $\mathrm{R}' + \mathrm{X}$, respectively, where $D(\mathrm{Na}^+\mathrm{X}^-)$ is the heat of dissociation into *neutral atoms*. Hence $\Delta H = \Delta D(\mathrm{RX})$. Since the two curves (*b*) and (*c*) are determined principally by the repulsion between the halogen ion X^- and the neighbouring carbon atom of each of the radicals R and R′, their shape will be almost identical, and there will be a constant energy difference, ΔH, between the two. It is evident from the construction shown in Fig. 2 that $E_2 < E_1$ and that $\Delta E < \Delta H$. It can be shown,[17] for a series of RX molecules characterised by decreasing C—X dissociation energies (the decrease being determined by factors which operate chiefly in the radicals), that the relationship

$$\Delta E = \alpha \Delta H \qquad 0 < \alpha < 1 \quad . \quad . \quad . \quad . \quad (4)$$

should hold. The value of α is determined by the slopes of the extension and the repulsion curve in the neighbourhood of the crossing points. The result for the case of $CH_3Cl + Na$ indicates that $\alpha \approx 0{\cdot}27$ should apply for a series of chlorides of the above type.[18]

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[18] Butler and Polanyi, *Trans. Faraday Soc.*, 1943, **39**, 19.

* The influence of changes in bond energy on the activation energy of the sodium flame reaction can be illustrated equally well by setting the dissociation limits for RX and R′X at the same energy level. This results in a common repulsion curve cutting two parallel C—X extension curves between which there is a constant energy difference $\Delta D = \Delta H$ in the neighbourhood of the two crossing points (see, for example, ref. 17).

It is now believed that this effect plays an important part in determining the trend of reaction rate in several of the series listed above. In particular, there is strong evidence that this is the dominant factor for the series II, $CH_3Cl \rightarrow Bu^nCl$, series III, $EtCl \rightarrow Bu^tCl$, and series VI $Pr^nCl \rightarrow CH_2{:}CH{\cdot}CH_2Cl$. The emphasis on bond-energy considerations in the above interpretation led directly to Butler and Polanyi's [18] work on the bond energies of organic iodides in which a pyrolytic method was used. Although some uncertainty attaches to the values obtained for several of the RI bond energies, it seems likely that the trends discovered by Butler and Polanyi are essentially reliable. Iodides, however, are the least suitable compounds for the study of connections between activation energy and heat of reaction, since all iodides react very rapidly with sodium. The slower-reacting chlorides, with a much wider range of reaction velocity, are more suitable, but very few results for C—Cl bond dissociation energies are available. If along series II, III, and VI the *gradations* in C—Cl bond energies are assumed to be the same as those for the C—I bond energies, then equation (4) demands a linear relationship between the R—I bond energy and the activation energy of the RCl + Na reaction, provided that, as emphasised above, the bond energy changes are mainly concerned with radical stability and do not involve serious changes in the shape of the carbon—halogen extension curves near their minima. Fig. 3 shows that such a linear relationship does, indeed, hold very well for the seven halides which constitute series II, III, and VI.[18] The slope of the line, *viz.*, $\approx 0{\cdot}25$, provides an alternative evaluation of α and is in surprisingly good agreement with the value of $\approx 0{\cdot}27$, obtained from the slopes of potential

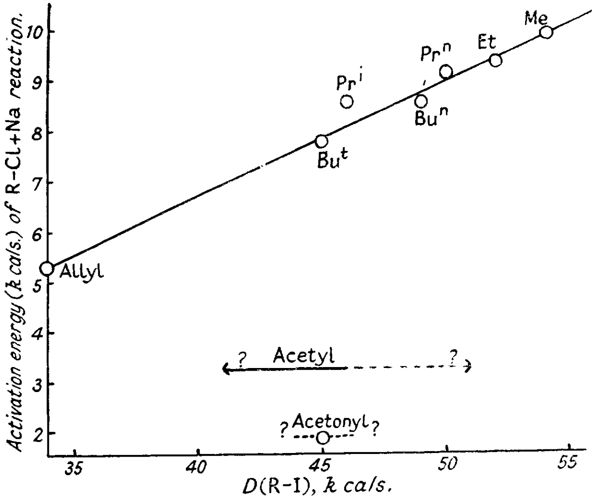

FIG. 3

The data for the activation energies of the RCl + Na reaction are those given in the text with the exception of more recents measurement on allyl chloride by A. G. Evans and Walker (*Trans. Faraday Soc.*, 1944, **40**, 384) and on acetyl and acetonyl chlorides by Walker and Warhurst (unpublished). The R—I bond energies have been taken from the recent review by Szwarc (*Chem. Reviews*, 1950, **47**, 75).

curves. This constitutes strong evidence that in these examples the trend in activation energies is primarily determined by carbon—halogen bond energy changes of the kind outlined above. Fig. 3 contains two striking exceptions. Although the bond energies of acetyl and acetonyl iodide are not very certain, the activation energies of the reactions of sodium atoms with acetyl and acetonyl chloride are much lower than could be accounted for by probable bond-energy values. These, and other instances, are discussed later.

The interest centring round carbon—halogen bond energies arising from this theoretical treatment of sodium " flame " reactions also led to the work of Baughan, M. G. Evans, and M. Polanyi,[19] who put forward an explanation of the decrease in carbon—halogen bond energy along series II and III. In the case of C—I bond energies, the decrease was also correlated, in a very interesting way, with changes in dipole moments. Details of this work are, however, outside the scope of this Review, but this and the work of Butler and Polanyi [18] form noteworthy examples of the way in which the sodium " flame " results have stimulated interest in other fields.

Series V demonstrates another well-marked feature in the reactivity of organic halides towards sodium atoms. It has been observed for chlorides, bromides, and iodides, and has been discussed fully by A. G Evans and Walker.[20] These authors attribute the increased activation energy of vinyl compounds, relative to the corresponding ethyl derivatives, to a strengthening of the carbon—halogen bond, owing to resonance in the halide molecules between the two structures $CH_2{=}CH{-}Hal$ and $\overset{-}{C}H_2{-}CH{=}\overset{+}{Hal}$. The resonance, which is sometimes referred to as " back co-ordination ", confers partial double-bond character on the carbon—halogen bond. This effect, for which there is considerable evidence provided by bond-length, dipole-moment, and force-constant data, clearly cannot occur in the vinyl radical, $CH_2{=}CH\cdot$; hence an increase in bond-dissociation energy occurs. The increase in bond energy, ΔD(vinyl − ethyl) causes a decrease in the heat of the reaction, H. However, the change in H does not necessarily take place with a constant shape of the carbon—halogen extension curve. As the bond is extended, the contribution of the $\overset{-}{C}H_2{-}CH{=}\overset{+}{Hal}$ may decrease rapidly. For this case, Evans and Walker point out that the relationship $\Delta E = \alpha\Delta H$, $\alpha \approx 0{\cdot}25$, should not hold. Indeed, for the extreme case, in which the partial double-bond character of the extended carbon—halogen bond in the transition state has become negligible, Evans and Walker have shown that ΔE would be equal to the full value of ΔH, *i.e.*, $\alpha = 1$ in equation (4). Unfortunately, there are insufficient bond-energy data available for chlorides and bromides to decide this point. For iodides the bond-energy data [18] indicate a value of α much nearer to unity than to 0·25. Evans and Walker also point out that ΔE(vinyl − ethyl) should depend on the halogen atom and should be larger the greater the back co-ordinating power of the halogen. The values of ΔE(vinyl − ethyl) were found to be

[19] *Trans. Faraday Soc.*, 1941, **37**, 377.

[20] *Ibid.*, 1944, **40**, 384.

0·5, 0·9, and 2·2 kcals. for chlorides, bromides, and iodides, respectively, thus indicating, on this theory, an increase in back co-ordinating power from chlorine to iodine.

The trends in the rates of reaction of sodium atoms with organic monohalides which have been discussed so far have been interpreted in terms of various types of bond-energy changes. A few examples have already been noted in which the rate of reaction is much faster than would be expected on bond-energy grounds. It was the consideration of these cases which led to a further development in the theory of these reactions. In the reaction between sodium atoms and a monohalide which contains no negative groups other than the one halogen atom, the resonance in the transition state between the two structures of equal energy, $(R\cdots X\cdots Na)_h$ and $(R\cdots X^-\cdots Na^+)_i$, has been assumed to be relatively small and more or less constant for different reactions. M. G. Evans and Polanyi [21] suggested that whenever the organic halide contained a negative group (or groups) in addition to the halogen atom a new factor influencing the activation energy should appear. It was pointed out that the negative group, by virtue of its relatively high electron affinity, can confer additional stability on the transition state owing to the contribution of a third electronic structure in which the group has assumed a full negative charge by accepting the electron from the sodium. For example, when the reactions of CH_3X and CH_2YX are compared, Y being the additional negative group, there are in the latter case the three transition-state structures

$$H_2YC\cdots X\cdots Na,\ HYC\cdots X^-\cdots Na^+,\ \text{and}\ H_2\overset{-}{Y}C\cdots X\cdots Na^+,$$

whereas in the former only the structures corresponding to the first two participate. The increased stability of the transition state, with its resultant lowering of the activation energy, is clearly not connected with, and exerts its influence independently of, any possible C—X bond-energy difference between the two compounds. Further, the activation energy is reduced by the full amount of the additional resonance energy in the transition state, and the effect is not subject to an " α factor " [equation (4)] as are certain types of bond-energy effects which have been discussed above. Thus, relatively small changes in the transition-state resonance energy can have a significant influence on the reaction rates. A. G. Evans and Walker [20] have discussed this effect in detail for the cases of ClCN, $CN{\cdot}CH_2Cl$, and $CN{\cdot}CH_2{\cdot}CH_2Cl$ and have shown that the very low activation energy for the reaction of ClCN with sodium atoms must be due to the extra resonance structure $\overset{+}{Na}ClC\overset{-}{N}$ in the transition state.

More detailed consideration of this effect of negative groups indicates that the nuclear configuration (the " geometry ") of the transition state is important. In the above examples CH_2XY, it is clear that the stability of the third structure, and hence its contribution, increases with decrease in the $Na^+\cdots Y^-$ separation. The same, of course, applies to the principal ionic structure with regard to the Na^+X^- separation. It has already been

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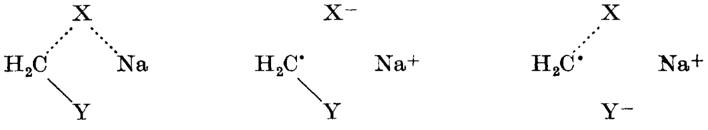
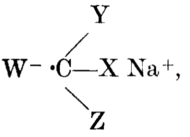
[21] *Nature*, 1941, **148**, 436.

pointed out that there is good evidence that a sodium atom can approach the halogen atom of a carbon—halogen bond up to the normal ion-pair distance of Na^+Hal^- without appreciable increase in energy. This should apply to both X and Y in the compound CH_2YX. Thus the most stable transition state, with the most effective contribution from the third structure, is one in which the sodium atom has approached *both* X and Y up to the respective ion-pair distances Na^+X^- and Na^+Y^-. The three structures may then be indicated thus :



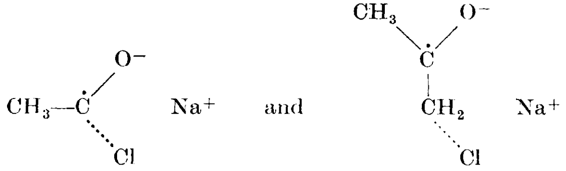
Homopolar Principal ionic Additional ionic

As with the case of CH_3X we have an extended C···X bond in the transition state, but the C—Y retains the normal internuclear separation of the initial state.

This treatment brings out the following features with regard to the influence of negative groups. The effect should always increase the reaction rate and should clearly increase with the number of negative groups, since for each group, up to which the sodium atom can approach to the ion-pair distance in the transition state, there is an additional ionic structure. There are, however, certain limitations to this numerical factor. When the reacting halogen atom and the negative groups are on the same carbon atom it is clear that the effect will increase with the number of groups up to a total of *three*, including the halogen atom. The sodium atom cannot approach four groups (X, Y, Z, W) up to the respective ion-pair distances. Thus one of the four ionic structures in the transition state, *e.g.*,  $W^- \cdot\overset{Y}{\underset{Z}{C}}\text{—}X\ Na^+$, must involve a very large charge separation and hence makes a negligible contribution to the resonance energy.

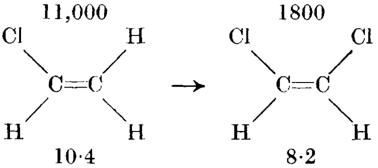
A comparison of the accelerating effect of different negative groups is a much more complicated problem, since the contribution of an additional ionic structure depends, not only on the energy of that structure, but also on the magnitude of the so-called resonance integrals which determine the interaction of the structure with the others. However, a significant feature of the stability of an additional ionic structure, due to a group Y, relative to the homopolar structure is the change $C - Y + e \rightarrow C\cdot\ Y^-$, at constant C···Y separation. Thus the electron affinity, E_Y, of Y and $D(C - Y)$ should be quantities of importance, as pointed out by A. G. Evans and Walker ;[20] and, *other things being equal*, the relative effects of different groups might be expected to follow the sequence of E_Y–$D(C - Y)$ values.

This negative-group effect is considered to be of great importance in the reactions of many halides with sodium atoms. For example, in the cases of the two " anomalies " shown in Fig. 3, the additional ionic structures



are responsible for the high rates of reaction of acetyl and acetonyl chloride compared with what would be expected from bond-energy considerations. Other instances, in which this factor is certainly important, in addition to bond-energy effects, are series IV and the reactions of the mixed bromochloromethanes, the rates of which were measured by Haresnape, Stevels, and Warhurst.[9]

In addition to the examples mentioned above there are a number of other cases of interest. In the following pairs of halides[10]



and

$$\underset{9\cdot4}{\overset{7000}{CH_3\cdot CH_2Cl}} \longrightarrow \underset{7\cdot3}{\overset{800}{ClCH_2\cdot CH_2Cl}}$$

the increased rate of the faster-reacting compound of the pair is mainly caused by the ability of the sodium to approach *two* chlorine atoms up to the ion-pair distance. It is very unlikely in these instances that there are bond-energy differences of sufficient magnitude to account for the trends in rates. A comparison of the rates of reaction of C_6F_{12} (perfluoro*cyclo*hexane)[22] and CH_2F_2,[23] which have recently been measured, provides a striking illustration of this aspect. The results are

$$\underset{\approx 14\cdot0}{\overset{\approx 7 \times 10^5}{CH_2F_2}} \longrightarrow \underset{7\cdot1}{\overset{980}{C_6F_{12}}}$$

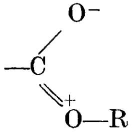
A model of the C_6F_{12} molecule reveals that there are a number of directions along which a sodium atom can approach as many as *four* fluorine atoms up to the ion-pair distance. It is difficult to account for this very large increase in reaction rate in any other way.

Series VII shows that the effect of oxygen atoms in the radical R is rather complicated. The following effects appear to be of importance in the understanding of the relative order of the rates. First, the halides which contain the grouping $O{=}\overset{|}{C}{-}CH_2Cl$ are subject to a bond-weakening factor caused by the allyl type of resonance in the radical, *viz.*, resonance between $O{=}\overset{|}{C}{-}\dot{C}H_2$ and $\dot{O}{-}\overset{|}{C}{=}CH_2$. The approximate C—I bond energy obtained by Butler and Polanyi[18] for acetonyl iodide supports this view.

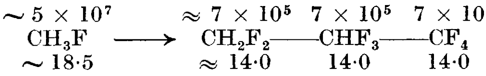
[22] Quayle and Warhurst, unpublished.

[23] Warhurst and Whittle, unpublished.

Secondly, the accelerating influence of the carbonyl group is much more marked than the ether type of grouping, C—O—. As yet only a tentative explanation on theoretical grounds can be put forward for this difference. Lastly, the effect of the carbonyl group is much suppressed when it is present in an ester group. This could be ascribed to a reduction in electron affinity of the oxygen atom owing to the participation of the structure



When the negative groups are the same as the reacting halogen atom, then the structures in the transition state become degenerate, *i.e.*, all have the same energy.* In these relatively simple circumstances it is possible to establish,[24] by a crude valency-bond treatment, an approximate relation between the resonance energy of the transition state and the number of ionic structures, *i.e.*, the number of halogen atoms " in contact with " the sodium atom. The resonance energy of the transition state should be approximately proportional to the *square root* of the number of structures. Preliminary considerations, on these lines, of the series IV, $CH_3Cl \rightarrow CCl_4$, indicate that the decrease in activation energy along the series is due to the negative group effect and to the effect of a decrease in carbon—halogen bond energy, both of which act in the same direction, *i.e.*, increase the reaction rate, and are of about equal magnitude. On the other hand, similar considerations applied to the series



$$\begin{array}{cccccc} \sim 5\times10^{7} & & \approx 7\times10^{5} & 7\times10^{5} & 7\times10^{5} \\ CH_3F & \longrightarrow & CH_2F_2 \text{——} & CHF_3 \text{——} & CF_4 \\ \sim 18{\cdot}5 & & \approx 14{\cdot}0 & 14{\cdot}0 & 14{\cdot}0 \end{array}$$

which has recently been investigated by Warhurst and Whittle,[23] indicate that the above factors may act in opposite directions, an increase in bond energy along the series tending to increase the activation energy, this being more than offset by the negative-group effect. Unfortunately, there are no C—F bond dissociation energy data available. Another factor which may be of significance in this series compared with series of chlorides is the change in shape of the C—F extension curve. There is some evidence of a marked increase in force constant of the C—F bond along the series. The resulting increase in " steepness " of the C—F extension curve will, of course, act in the opposite direction to the negative-group effect.

There is a further interesting aspect of sodium-flame work which should be mentioned. Considerable attention has centred round the comparison of well-marked trends in the sodium-flame reactions with those which are

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[24] Warhurst, unpublished.

* Actually, this is not quite rigorous. The principal ionic structure (*i.e.*, that in which the negative charge is on the halogen atom which is eventually removed) has a slightly lower energy than the remaining ionic members owing to a smaller repulsion energy for the extended C···X⁻ distance.

characteristic of other reactions; for example, the so-called negative ion or S_N2 mechanism.[1, 10, 12, 25]

Present Work.—A number of fields of sodium-flame work are now being investigated. The results for several fluorides have already been mentioned.[9, 23] The rates of reaction with sodium atoms of a number of disubstituted benzene derivatives have recently been measured in order to determine the effect of non-reacting substituents on the reactivity of an aromatic carbon—halogen bond. The next table shows some of the results obtained.[26] It gives the ratio of the velocity constant of the disubstituted compound to that of the corresponding unsubstituted phenyl halide. In the names given at the heads of the columns the non-reacting (or much slower-reacting) substituent is italicised. All the non-reacting substituents are *ortho-para*-directing and the results show the same general trend in reactivity, *viz.*, *ortho* > *meta* > *para* > unsubstituted. Work is in progress on *meta*-directing substituents.

	Bromo*methoxy*-benzene.	Bromo*hydroxy*-benzene.	Bromo*chloro*-benzene.	Chloro*fluoro*-benzene.
ortho	3·1	6·2	15	14
meta	—	2·5	3·2	4·0
para	1·4	—	1·6	~ 1

A completely satisfactory explanation of the data in the foregoing table may well involve new factors in addition to those discussed above for aliphatic compounds. For example, the possible influence of conjugation of the π-electrons of the substituent groups with those of the benzene nucleus may be important. Whilst it is too early to speculate in detail, there are one or two points worthy of comment. The negative-group effect must play a significant part in the case of *ortho*-derivatives, since sterically a sodium atom can approach both substituent groups up to ion-pair distances in the transition state. It seems unlikely that conjugation effects can play an important rôle in the case of *meta*-derivatives. There is some experimental evidence for this view. Warhurst and Whittle[23] have recently measured the rates of reaction of sodium atoms with the —CF_3 group of *meta*-substituted benzotrifluorides, with the results shown in the accompanying table, which gives the ratio of the velocity constant for the *meta*-derivative to that of benzotrifluoride. The effect is clearly of the same order of magnitude as that for the *meta*-derivatives of the previous

Substituent	Cl	F	NH_2
Ratio, $k_{meta} : k_{unsub.}$ . . .	6·9	3·0	2·5

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[25] A. G. Evans, *Trans. Faraday Soc.*, 1946, **42**, 719; " Reactions of Organic Halides in Solution ", Manchester Univ. Press, 1946.

[26] Scanlan, Warhurst, and (in part) Whittle, unpublished.

table. In the substituted benzotrifluorides, since the reacting halogen atoms are on a side chain, there can be no direct " coupling ", by through-conjugation, of the CF_3 and the substituent groups. A few results have also been obtained in a field closely connected with the aromatic compounds, *viz.*, the reactions of aromatic heterocyclic halides. Quayle and Warhurst [22] have found that both 2-chloro- and 2-bromo-pyridine react much more rapidly with sodium atoms than do the corresponding 3-chloro- and 3-bromo-compounds. The relative rates are 340 : 1 and 25 : 1 for chlorides and bromides, respectively. This greater reactivity of halogen atoms in position 2 is well known in other reactions of these compounds.

It has not been possible to refer to all the different fields of sodium-flame work. In some cases the results cannot be said to be understood completely. However, the theoretical method outlined above, which is admittedly not complete and will no doubt be revised and expanded from time to time, particularly as new types of compound are investigated, provides an understanding of a considerable part of the experimental observations.