# A MODIFIED FORM OF THE "LIFE PERIOD" METHOD APPLIED TO THE REACTION OF SODIUM VAPOUR WITH BROMO BENZENE.

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The "life period" method was first used by Cremer, Curry and Polanyi[1] to study the reactions between hydrogen atoms and aliphatic halides, and simultaneously by Frommer and Polanyi[2] for the reactions between sodium vapour and organic halides. The method is based on the following principles which we present here for the case of a reaction of sodium vapour and an organic halide.

$$RHl + Na = R + HlNa,$$

where R is an organic radical. The steady flow of an inert gas laden with sodium vapour is introduced into an excess of the halide, and a stationary reaction zone is thus maintained. The number, $n$, of sodium atoms introduced per second, as well as the number, $N$, of sodium atoms, and the concentration, $c$, of the halide in the reaction zone are determined. From these observations the velocity constant, $k$, is obtained :

$$k = \frac{n}{N \cdot c} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$N/n$ is the average life of a sodium atom in the reaction zone.

The method was used by Fairbrother and Warhurst[3] for the measurement of the rate of reaction of sodium vapour with chloro-, bromo-, and iodo-benzene, a suitable alteration being made to introduce these less volatile compounds into the reaction vessel. In this investigation the original method was used to determine $N$. This consisted of a laborious point-to-point photometry of the absorption photographs of the flame

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[1] Cremer, Curry and Polanyi, *Z. physik. Chem.*, *B*, 1933, **23**, 445.
[2] Frommer and Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 519.
[3] Fairbrother and Warhurst, *ibid.*, 1935, **31**, 987.

zone, followed by a lengthy graphical analysis of the photometer readings over the whole zone. A suggestion of Professor Polanyi's to modify the method in order to avoid this laborious procedure is developed in a paper by Fairbrother and Tuck[4] in which an important contribution towards its realisation is made. It was proposed to determine $N$ by a single measurement of the average absorption of sodium light by the "flame." The average density of sodium vapour, and hence $N$, can be found from this value of the absorption. Fairbrother and Tuck constructed a photoelectric photometer of appropriate sensitivity and stability to measure the small absorptions of the flame zones, and this instrument has been used in the present investigation. In order to carry out measurements of reaction velocities on these lines, much lower sodium vapour pressures have to be used than previously, the factor limiting the sodium pressure in the present method being the range of density within which the absorption of sodium vapour is proportional to its density. When using these sodium pressures, which vary from $8 \times 10^{-5}$ to $3 \times 10^{-4}$ mm. it was necessary to readjust some experimental factors. It was also found necessary to establish whether the saturation of the carrier gas with sodium vapour, which was assumed previously without direct experimental evidence, does actually take place. A method was devised to settle this point by absorption measurements.

Apart from aiming at an improved method for measuring reaction rates we also wished to use it on this occasion to establish more exactly the rate of the reaction

$$C_6H_5Br + Na = C_6H_5^- + BrNa$$

and to measure its activation energy from the temperature coefficient of the rate.

## Experimental.

The apparatus was very similar to that used by Fairbrother and Warhurst,[3] and is shown in Fig. 1. The photoelectric photometer is denoted by P, and a new stabilised source of resonance light by S in the diagram. In order to regulate the temperature of the sodium boat independently of that of the reaction zone the boat B was placed in a side arm which projected from the side of the main reaction vessel R. The experimental procedure for the measurement of a velocity constant was as follows. Hydrogen, at a pressure of about 5 mm., was circulated through the apparatus by the pump Z in the direction indicated by the arrows. The liquid air trap $F_4$ was used to remove mercury vapour from the stream. The speed of flow was regulated by the Hauschild valve V and measured by the pressures at the extremities of the calibrated capillary $K_1$. The flow was divided at Y; one part passed through the halide traps $H_1$ and $H_2$, and introduced halide vapour into the reaction vessel; the other part passed over the sodium boat B, and thus introduced sodium vapour into the reaction vessel at the nozzle O. The ratio of the two rates of flow was fixed by the resistances of the two capillaries $K_2$ and $K_3$. These values have been previously determined by calibration experiments. The traps $F_1$, $F_2$ and $F_3$ were used to remove the reaction products and excess halide from the carrier gas flow.

Complete saturation of the carrier gas flow, by which the bromobenzene was introduced into the reaction vessel, was ensured in the following way. In the trap $H_2$ (the evaporator), through which the carrier gas first

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[4] Fairbrother and Tuck, *Trans. Faraday Soc.*, 1936, **32**, 624.

passes, bromo benzene was present at a temperature 10-20° C. higher than corresponded to the intended concentration of the vapour; the latter was adjusted to the right value by the trap $H_1$ which acted as a condenser,

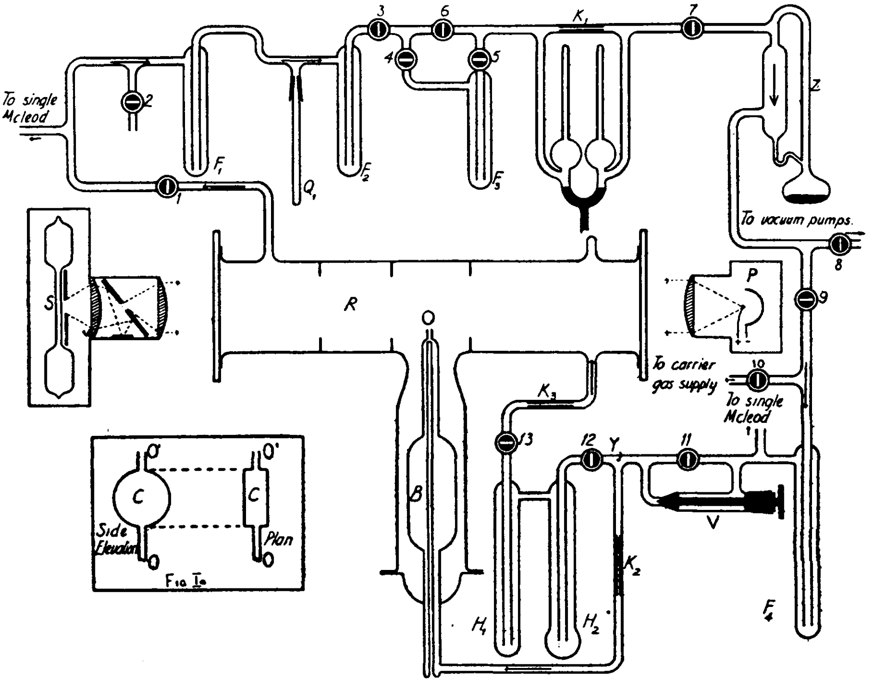

FIG. 1.

reducing the concentration. The amount of bromo-benzene taken up in $H_1$ was determined over a wide range of gas flows. These results enable an estimation of the vapour pressure $p_{\mathrm{HI}}$ of bromo-benzene in $H_1$ to be made. The results are given in Table I.

TABLE I.

| Rate of Flow of Hydrogen in Moles/sec. × $10^4$. | Temp. of Evaporator $H_2$ in °C. | Temp. of Condenser $H_1$ in °C. | $p_{\mathrm{HI}}$ in $H_1$ mm. |
|---|---|---|---|
| 3·44 | 0·0 | − 20·7 | 0·142 |
| 3·57 | − 10·6 | − 20·6 | 0·138 |
| 1·39 | − 7·9 | − 20·6 | 0·149 |
| 1·21 | − 8·4 | − 20·6 | 0·136 |
| 4·31 | − 13·0 | − 29·2 | 0·068 |
| 1·71 | − 18·0 | − 29·1 | 0·063 |

Values of 0·172 and 0·082 mm. at − 20·6 and − 29·2° C. respectively have been obtained by extrapolation of the data of Young (*J.C.S.*, 1889, **55**, 486). A value of 0·155 at − 20·6 has been interpolated from the results of Rolla (*Rend. Linc.* (5), 18 H. [2] 365, 1909). Mundel (*Zeit. f. Phys. Chem.*, 1913, **85**, 451) gives the values of 0·244 at − 20·6° C.

The values of $p_{\mathrm{HI}}$ are independent of the rate of flow of hydrogen through $H_1$ and the temperature of $H_2$, and agree quite well with the first two sets of values given at the foot of the table. The values obtained from the data of Young may be somewhat high due to the extrapolation.

The number of sodium atoms $n$ entering the reaction zone per second was estimated from the pressure $P_{H_2}$ and the flow $F_{H_2}$ of hydrogen passing through the sodium boat, together with the vapour pressure $P_{Na}$ of sodium at the temperature of the boat

$$n = \frac{F_{H_2} . P_{Na}}{P_{H_2}}.$$

The saturation of the carrier gas with sodium vapour was investigated experimentally by estimating $P_{Na}$ from absorption measurements. A small cylindrical cell C with plane ends a measured distance apart (Fig. 1*a*) was fixed on to the nozzle mouth O (Fig. 1), and arranged so that its axis coincided with that of the reaction vessel. Hydrogen from the sodium boat was passed through the cell, and was thus introduced through the nozzle O′ of the cell into the reaction vessel which contained bromobenzene vapour. A diaphragm on one of the cell faces ensured that the only sodium vapour in the path of the beam of resonance light was that in the cell C; the absorption of this sodium was measured. For experimental reasons the absorption was only measurable at temperatures higher than that of the sodium boat. The results are shown in Fig. 2, where it can be seen that the absorption of a constant density of sodium decreases linearly with increase in cell temperature. The value of this constant density was obtained by extrapolating the straight line to lower temperatures and the use of the absorption curve of Fairbrother and Tuck.[4] The density in the cell was found in this way to be (1·80 ± 0·2) × $10^{-12}$ moles/cm.$^2$. This value agrees quite well with the density 1·73 × $10^{-12}$ calculated from the temperature of the sodium boat assuming complete saturation. This latter value gives the point marked ⊕ in Fig. 2.

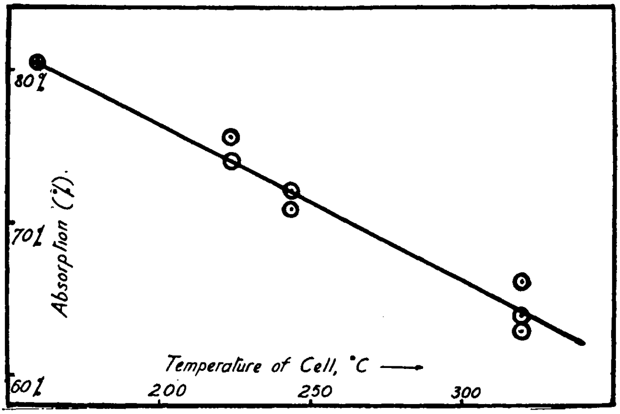

FIG. 2.

The partial pressure of bromo-benzene in the reaction vessel, and thus the concentration, was estimated by the same principles as used for the determination of $n$.

The total number $N$ of sodium atoms in the flame zone was estimated in the following way. The average absorption of a flame was obtained from the ratio of the blank reading on the photometer ($I_0$) and the flame reading ($I_t$). Tuck and Warhurst [5] have measured the change in absorption of a constant density (2·37 × $10^{-13}$ moles/cm.$^2$) of sodium with temperature which they found to be represented by a straight line. Remembering that within our experimental range absorption is proportional to density at any given temperature, we recognise that the point on the straight line of Tuck and Warhurst gives the slope of the absorption

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[5] Tuck and Warhurst, *Trans. Faraday Soc.*, 1936, **32**, 1501.

$\left(1 - \frac{I_t}{I_0}\right)$ against density of sodium vapour for that particular temperature in question. Thus, if $A$ is the absorption of $2{\cdot}37 \times 10^{-13}$ moles/cm.$^2$ at the flame temperature and $A'$ is the average absorption of the flame, then the average density $N'$ of the sodium vapour is

$$N' = \frac{A'}{A} \times 2{\cdot}37 \times 10^{-13}.$$

The total number of sodium atoms $N$ is then obtained by multiplication of $N'$ and the cross-sectional area of the beam of resonance light.

The result obtained for the reaction between sodium vapour and bromobenzene are given in Table II.

TABLE II.

| Expt. No. | Aver. Absn. in Per Cent. | Total No. of Atoms, N $\times 10^{12}$ Moles. | Sodium Temp. °C. | $v/\delta$ c.g.s. $\times 10^2$. | $k \times 10^{-12}$ c.c. mol.$^{-1}$ sec.$^{-1}$. | Deviation from Mean. |
|---|---|---|---|---|---|---|
| **Temperature 255° C.** | | | | | | |
| 11 | 3·1 | 0·393 | 214·5 | 5·4 | 6·00 | + 4·00 |
| 12 | 3·0 | 0·378 | 210·0 | 5·50 | 8·30 | + 6·30 |
| 10 | 10·1 | 1·29 | 213·5 | 8·23 | 2·59 | + 0·59 |
| 16 | 4·5 | 0·565 | 209·0 | 8·36 | 4·35 | + 2·35 |
| 13 | 13·1 | 1·66 | 211·0 | 8·91 | 2·72 | + 0·72 |
| 3 | 8·3 | 1·04 | 207·5 | 10·12 | 2·83 | + 0·83 |
| 1 | 6·5 | 0·805 | 195·5 | 10·25 | 2·00 | 0·00 |
| 4 | 8·6 | 1·09 | 209·0 | 10·8 | 3·36 | + 1·36 |
| 5 | 8·5 | 1·07 | 209·0 | 10·80 | 3·32 | + 1·32 |
| 2 | 7·9 | 0·983 | 195·5 | 11·2 | 1·80 | − 0·20 |
| 9 | 18·8 | 2·38 | 213·0 | 11·75 | 1·94 | − 0·06 |
| 14 | 20·6 | 2·62 | 211·0 | 11·9 | 2·03 | + 0·03 |
| 28 | 11·5 | 1·28 | 197·5 | 11·9 | 2·92 | + 0·92 |
| 29 | 11·1 | 1·24 | 195·5 | 11·9 | 2·68 | + 0·68 |
| 15 | 14·1 | 1·78 | 208·0 | 13·80 | 2·16 | + 0·16 |
| 34 | 14·4 | 1·93 | 194·0 | 14·2 | 1·85 | − 0·15 |
| 35 | 13·7 | 1·84 | 194·0 | 14·2 | 1·90 | − 0·10 |
| 23 | 13·8 | 1·83 | 193·0 | 15·9 | 2·10 | + 0·10 |
| 24 | 13·4 | 1·77 | 193·0 | 15·9 | 2·13 | + 0·13 |
| 6 | 19·0 | 2·40 | 206·5 | 16·90 | 1·69 | − 0·31 |
| 7 | 17·1 | 2·16 | 206·5 | 16·90 | 1·77 | − 0·23 |
| 8 | 15·0 | 1·90 | 206·5 | 16·90 | 2·01 | + 0·01 |
| 30 | 17·7 | 2·36 | 195·0 | 16·9 | 1·96 | − 0·04 |
| 31 | 16·7 | 2·25 | 195·0 | 16·9 | 2·01 | + 0·01 |
| 27 | 23·5 | 3·07 | 195·0 | 18·5 | 1·83 | − 0·17 |
| 26 | 17·8 | 2·33 | 191·5 | 19·3 | 1·67 | − 0·33 |
| 25 | 19·7 | 2·57 | 193·0 | 19·6 | 1·72 | − 0·28 |
| 32 | 26·1 | 3·55 | 194·5 | 20·4 | 1·40 | − 0·60 |
| 33 | 25·6 | 3·44 | 194·0 | 20·4 | 1·39 | − 0·61 |
| **Temperature 330° C.** | | | | | | |
| 21 | 12·4 | 2·33 | 215·5 | 7·6 | 3·82 | + 0·72 |
| 22 | 11·1 | 2·08 | 213·0 | 7·6 | 3·95 | + 0·85 |
| 41 | 16·5 | 3·17 | 216·0 | 9·4 | 2·98 | − 0·12 |
| 40 | 17·6 | 3·39 | 217·2 | 9·4 | 3·04 | − 0·06 |
| 18 | 17·5 | 3·28 | 215·0 | 10·9 | 3·57 | + 0·47 |
| 17 | 16·4 | 3·07 | 213·0 | 10·9 | 3·46 | + 0·36 |
| 37 | 23·2 | 4·47 | 216·0 | 11·4 | 2·64 | − 0·46 |
| 36 | 23·2 | 4·47 | 216·0 | 11·4 | 2·69 | − 0·41 |
| 19 | 22·5 | 4·21 | 215·0 | 11·9 | 3·00 | − 0·10 |
| 20 | 20·4 | 3·82 | 215·0 | 11·9 | 3·26 | + 0·16 |
| 38 | 29·0 | 5·59 | 216·0 | 13·3 | 2·45 | − 0·65 |
| 39 | 28·8 | 5·55 | 216·5 | 13·3 | 2·44 | − 0·66 |

## Discussion.

The results at the lower temperature (255° C.) enable three important conclusions to be drawn concerning the experimental conditions:

(*a*) Within the limits of $v/\delta = 10 \times 10^{-2}$ to $19 \times 10^{-2}$ (where $v$ is the linear speed of the carrier gas at the nozzle mouth in metres/second and $\delta$ is the diffusion constant of sodium in the carrier gas in c.g.s. units), the values of $k$ show but little variation. There is a deviation amongst seventeen values of only ± 10 per cent. from the mean value of $k = 2{\cdot}0 \times 10^{12}$. Below the limit $v/\delta = 10 \times 10^{-2}$, $k$ rises sharply with a decrease of $v/\delta$. Above the limit $v/\delta = 19 \times 10^{-2}$, $k$ shows a slight decrease with an increase of $v/\delta$.

(*b*) Within the range of $10 \times 10^{-2} < v/\delta < 19 \times 10^{-2}$, for constant values of $v/\delta$, a variation of $N$ over wide limits produces no definite drift in the value of $k$ but, rather, haphazard variations about the mean value. This independence of the value of $k$ from $N$ seems to strongly justify the method used for the estimation of $N$.

(*c*) There is no definite drift of the velocity constant with sodium temperature. If the maximum density at the nozzle mouth were greater than the limit set by the linearity of the absorption curve this would lead to an underestimation of the total number of atoms in the flame zone, and therefore to high values of $k$.

The sharp rise in the value of $k$ below the limit $v/\delta = 10 \times 10^{-2}$ indicates that below this limit back diffusion of the halide down the nozzle occurs to an appreciable extent. Heller [6] in an extensive survey of the diffusion flame method, concludes that back diffusion begins to occur to a serious extent below the limit $5 \times 10^{-2}$. This limit was derived from considerations of a reaction of average speed and with a pressure of the halide ten times as large as the pressure of sodium at the nozzle mouth. In the present work, however, the reaction is rather fast and, what is more important, the ratio of the halide pressure to the sodium pressure is of the order of 200. This may explain the difference between the two lower limits for $v/\delta$.

The slight fall in the value of $k$ within an increase in $v/\delta$ above the limit $19 \times 10^{-2}$ indicates a serious reduction of halide concentration in the reaction zone at these high speeds of flow of carrier gas.

The present method, therefore, gives satisfactory values of the velocity constant so long as $10 \times 10^{-2} < v/\delta < 19 \times 10^{-2}$, and the values of $N$ are within the limits corresponding to 10 per cent.-20 per cent. average absorption, the sodium temperatures not exceeding about 215° C. These limiting conditions have been used in some recent work on the reactions of a number of polyhalogenated methane derivatives with sodium.

The small number of values at the higher temperature (330° C.) cannot be analysed on these lines; it can only be seen that there is some indication of a rise in the value of $k$ below the limit $v/\delta = 9 \times 10^{-2}$. On account of the greater difficulties in maintaining steady conditions experimentally the accuracy is less than at the lower temperature. The mean value of the constants at 330° C. is $3{\cdot}1 \times 10^{12}$.

The two values of $k$ at the temperatures 255° C. and 330° C. give a value of the activation energy of $3{\cdot}8$ $k$ cals./mole. This value corresponds to a collision cross-section of $5{\cdot}1 \times 10^{-16}$ cm.$^2$, which is considerably less

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[6] Heller, *Trans. Faraday Soc.*, 1937, **33**, 1556.

than the value of $3 \cdot 5 \times 10^{-15}$ cm.$^2$ used by Hartel and Polanyi [7] for the reactions of aliphatic halides and sodium vapour. This value of $5 \cdot 1 \times 10^{-16}$ cm.$^2$ corresponds to a collision diameter of 2·6 A., which is approximately the sum of the radii of a sodium and a bromine atom. In view of the fact that a similar value of the collision cross-section can also be derived from the temperature coefficient of the $CH_3Cl + Na$ reaction,[7] we consider that this value of $5 \times 10^{-16}$ cm.$^2$ is the more appropriate one for monohalogenated compounds.

The mean value of $k$ at 255° C. gives a collision yield (number of effective collisions/total number of collisions) of 1/36. Fairbrother and Warhurst [3] have measured the velocity constant of this reaction, the value given is $k = 1 \cdot 62 \times 10^{13}$. Tuck and Warhurst [5] have corrected the value to $k = 6 \cdot 08 \times 10^{12}$ at 244° C. This latter value is about three times greater than that presented here for about the same temperature. The value given by Tuck and Warhurst, however, was admitted to be merely a better approximation to the true constant.

The collision yield for the reaction of methyl bromide with sodium vapour given by Heller and Polanyi [8] is 1/75, when a collision cross-section of $3 \cdot 5 \times 10^{-15}$ cm.$^2$ is assumed. Actually, the velocity constant of the reaction is about 3·5 times greater than the value for the reaction of sodium vapour with bromo-benzene. From a general point of view the significant feature of the comparison is the fact that the two reaction rates are of the same order; a theoretical analysis of this result is contained in the paper of Evans and Warhurst.[9]

## Summary.

(1) The velocity of reaction of sodium atoms with bromo-benzene has been measured by the life period method.

(2) The saturation of the carrier gas with sodium vapour has been verified experimentally.

(3) Reliable values of the velocity constant have been obtained within the limits $10 \times 10^{-2} < v/\delta < 19 \times 10^{-2}$; and $190° \text{ C.} < T_{Na} < 215° \text{ C.}$; and $N$ lies between the limits corresponding to 10 per cent.-20 per cent. absorption.

(4) The activation energy of the reaction has been estimated from the temperature coefficient.

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[7] Hartel and Polanyi, *Z. physik. Chem. B*, 1930, **11**, 97.
[8] Heller and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633.
[9] Evans and Warhurst, *ibid.*, 1939, **35**, 583.