# KINETICS OF THE REACTION BETWEEN BENZYL CHLORIDE AND FORMIC ACID.

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GAVANKAR, HEBLE AND WHEELER[1] have shown that $\omega$-halogenated toluenes react with formic acid to give hydrogen halide, carbon monoxide and the corresponding $\omega$-hydroxylated toluenes or the derivatives formed by loss of water. Thus benzal chloride and benzotrichloride give, respectively benzaldehyde and benzoic acid. Benzyl chloride and bromide also react though more slowly with evolution of hydrogen halide and carbon monoxide; here benzyl alcohol has not been isolated, possibly because it reacts with the formic acid. The last reaction can be written:

$$C_6H_5CH_2Cl + HCOOH = C_6H_5CH_2OH + HCl + CO.$$

Based on this work, a method has been evolved for the estimation of side-chain halogen in simple aromatic compounds (Gavankar *et al., loc. cit.*).

The present paper describes a study of the kinetics of the reaction between formic acid and benzyl chloride. The conditions differ from those of the majority of reactions previously investigated in that there is no solvent or diluent in the system. Not much is known regarding the kinetics of such highly condensed systems* so that the interpretation of the results is difficult. However, as is shown below, the application of a theory of reactions in liquids discussed by one of us[2] indicates the presence in formic acid of a small proportion of a reactive form of the acid such as has been postulated previously by Seshadri.[3]

## *Experimental.*

An accurately measured quantity of anhydrous formic acid (Kahlbaum) was introduced into a glass-stoppered reaction vessel of the gas wash-bottle type fitted with two delivery tubes, one cut short and the other extending to the bottom of the vessel. The longer tube served to admit nitrogen,

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[1] *J. Univ. Bombay*, 1937, 6(2), 112.

* For previous work on the subject from this laboratory see *J. Phys. Chem.*, 1935, 39, 727, 901, 907; *Proc. Ind. Acad. Sci.*, 1935, 2, 265, 483, 605; 1936, 4, 91.

[2] *Proc. Ind. Acad. Sci.*, 1936, 4, 291.

[3] *Curr. Sci.*, 1936, 4, 650.

while the shorter tube could be connected by means of a T-tap to either of two wash-bottles containing aqueous silver nitrate solution. The reaction vessel was heated in a water thermostat, controlled to within 0·5°, and when it had attained the required temperature, the requisite quantity of benzyl chloride (Kahlbaum's " Purest ") was introduced, and a current of nitrogen (two bubbles per second) freed from oxygen (alkaline pyrogallol) and dried (sulphuric acid) was led through the liquid. Initial experiments showed that this rate removed all of the hydrogen chloride, and that there was no appreciable loss of formic acid from the reaction vessel. The hydrogen chloride evolved was absorbed by the aqueous silver nitrate; at the end of a stated time the gas current was switched by means of the T-tap into the other wash-bottle, and the first replaced by one containing a fresh solution of silver nitrate. The alternate use of two wash-bottles was continued until the run was complete. The precipitated silver halide was collected and weighed in a gooch crucible.

## *Experimental Results.*

Experiments were made at 80°, 90° and 100° with various concentrations of the halide in formic acid. The quantity of the reacting liquid used was also varied to eliminate the possibility of systematic errors; for example, if an appreciable quantity of hydrogen chloride was retained on the sides of the vessel above the liquid then the effect of this error would be reduced with increase in the volume of reacting liquid, and the results obtained with say 5 c.c. of formic acid and 0·1 c.c. benzyl chloride would not agree with those obtained with double the quantitites.

Actually no such disagreement was obtained. As the acid was always in large excess, the reaction would be expected to be unimolecular, and as will be seen from Table I a moderately good constant was obtained. In illustration of the type of experimental results the following figures may be quoted:—

*Temp.* 80°. 0·5 *c.c. of benzyl chloride in* 5 *c.c. of formic acid.*

(See Table I, serial No. 5.)

| Times in minutes .. | 30 | 40 | 60 | 80 | 90 | 120 | 180 |
|---|---|---|---|---|---|---|---|
| % Conversion of benzyl chloride .. | 8·9 | 12·7 | 18·0 | 23·0 | 24·7 | 32·5 | 41·4 |
| K (reciprocal mins.; logs to base 10) × $10^4$ .. | 14 | 15 | 14 | 14 | 14 | 14 | 13 |

*Temp.* 90°. 2·0 *c.c. of benzyl chloride in* 10 *c.c. of formic acid.*
(See Table I, serial No. 13.)

| Time in minutes .. | 20 | 40 | 60 | 80 | 100 |
|---|---|---|---|---|---|
| % Conversion of benzyl chloride .. | 8·0 | 15·5 | 21·8 | 27·1 | 32·8 |
| K (reciprocal mins. ; logs to base 10) $\times 10^4$ | 18 | 18 | 18 | 17 | 17 |

Table I summarises all the values of K obtained. These values fall as the concentration of benzyl chloride increases, and it is found that plot of the concentration against the values of K gives approximately a straight line for each temperature.

Reactions are known in which the velocity increases with dilution; for example, the velocity of decarboxylation of trichloro-acetic acid in water.[4] Many suggestions have been made to account for this phenomena, but the cause is as yet not definitely known. A possible explanation for the reaction under examination will be discussed below.

Values for the Arrhenius critical increment (E) have been calculated in the usual manner by plotting log K against $\frac{1}{T}$, and measuring the slope of the approximately straight line thus obtained. The values of E increase with increase in concentration; this is to some extent a corollary to the fall in the reaction velocity.

*Calculation of the value of K from the observed value of E.*—In a paper on the theoretical aspect of reactions in liquids[5] it has been shown that K for a unimolecular reaction undergone by a solute in the liquid phase is given by

$$K = 2 \cdot 80 \times 10^{12} \frac{P^4}{V^{\frac{11}{3}} M^{\frac{1}{2}} T^{\frac{1}{2}}} e^{\frac{-E_1}{RT}} \left(\frac{E_1}{RT}\right)^{f-1} \frac{1}{\lfloor\underline{f-1}}, \tag{1}$$

where $$E_1 = E + \frac{22\,T^2 a}{3} + (2f-1)\,T \tag{2}$$

P is the parachor,
V is the molecular volume,
M is the molecular weight,
$a$ is the coefficient of cubical expansion of the solute, and
$2f$ is the number of square terms defining $E_1$.

In the application of equation (1) it is necessary to see if a small integral value of $f$ can be found which will enable a value of K to be calculated in

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[4] Kappanna, *Z. phys. Chem.*, (A), 1932, **158**, 355.

[5] Wheeler, *Proc. Ind. Acad. Sci.*, 1936, **4**, 291.

TABLE I.

*Summary of K Values.*

| S. No. | Benzyl chloride initially c. c. | Formic acid initially c. c. | K (reciprocal mins.; logs to the base) 10 × $10^4$ | | | Mean values of K (recip. mins.; $\log_{10}$) × $10^4$ | | | Corresponding values of E cals./g. mol. |
|---|---|---|---|---|---|---|---|---|---|
| | | | 80° | 90° | 100° | 80° | 90° | 100° | |
| 1 | 0·1 | 5 | 17 | .. | 48 | .. | .. | .. | .. |
| 2 | ,, | ,, | 18 | 33 | 47 | .. | .. | .. | .. |
| 3 | 0·2 | 10 | 17 | .. | 48 | .. | .. | .. | .. |
| 4 | ,, | ,, | 18 | 36 | 48 | 18 | 35 | 48 | 14,200 |
| 5 | 0·5 | 5 | 14 | 26 | 38 | .. | .. | .. | .. |
| 6 | ,, | ,, | ,, | 25 | 39 | .. | .. | .. | .. |
| 7 | 1 | 10 | 11 | 24 | 37 | .. | .. | .. | .. |
| 8 | ,, | ,, | 12 | 26 | 36 | .. | .. | .. | .. |
| 9 | 2 | 20 | 13 | 22 | 42 | .. | .. | .. | .. |
| 10 | 3 | 30 | 14 | 25 | .. | 13 | 25 | 38 | 14,600 |
| 11 | 1 | 5 | 7 | 18 | 26 | .. | .. | .. | .. |
| 12 | ,, | ,, | ,, | ,, | 25 | .. | .. | .. | .. |
| 13 | 2 | 10 | 8 | ,, | 26 | .. | .. | .. | .. |
| 14 | ,, | ,, | 7 | 16 | 27 | 7 | 18 | 26 | 17,800 |

agreement with the experimental value. It is found however, that even when *f* is put equal to one so that the calculated value of K is as small as possible, it is still many powers of 10 greater than the observed value. To illustrate the calculation :

we have for benzyl chloride at 80° :—

$P = 283{\cdot}4\,;\ P^4 = 6{\cdot}41 \times 10^9$

$V = 120\,;\ V^{11/3} = 4{\cdot}20 \times 10^7$

$M = 126{\cdot}5\,;\ M^{\frac{1}{2}} = 1{\cdot}12 \times 10$

$T = 353\,;\ T^{\frac{1}{2}} = 1{\cdot}88 \times 10$

$a = 10^{-8}.$

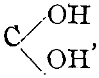
Putting $f = 1$ equation (2) gives for $E_1$,

$$E_1 = 14{,}200 + \frac{22 \times 353^2 \times 10^{-3}}{3} + T = 15{,}500,$$ which on being inserted in (1) with $f$ put equal to 1, gives,

$$K = \frac{2 \cdot 80 \times 10^{12} \times 6 \cdot 41 \times 10^{9}}{4 \cdot 20 \times 10^{7} \times 1 \cdot 12 \times 10 \times 1 \cdot 88 \times 10} e^{\frac{-15{,}500}{2 \times 353}}$$

$$= 5 \cdot 97 \times 10^{2}.$$

K (observed ; reciprocal seconds ; natural logs.) $= 6 \cdot 91 \times 10^{-5}$.

Hence the calculated value of K is nearly $10^7$ times greater than the observed value ; for the highest concentration examined, the ratio is of the order of $10^5$. Moelwyn-Hughes[6] discusses the subject of " Slow Reactions " and cites a number of such reactions where the ratio between the calculated and observed values of K amounts to many powers of 10. He points out that any assignment of reasons for the tardiness of these reactions must be speculative, but that if one of the reagents reacts in the ionised or in a specially activated condition, then a ready explanation can be found for the results. Thus to take the reaction under discussion, if anhydrous formic acid can only react in the form :  $C\begin{matrix}OH\\OH\end{matrix}$, assumed to be present only in traces, then the results can be satisfactorily explained. Further, if we assume that the activation of formic acid is depressed by the presence of benzyl chloride and its reaction product, then we have an explanation of the fact as the concentration of the initial benzyl chloride is increased, the velocity constant decreases.

It will be seen, therefore, that the results given above can be explained by the assumption made by Seshadri (*loc. cit.*) which was based solely on the chemical behaviour of formic acid.

### *Summary.*

The kinetics of the reaction between benzyl chloride and anhydrous formic acid have been examined at 80, 90 and 100°. The velocity of the reaction decreases with increase in concentration of benzyl chloride in formic acid. The observed rate of the reaction is much slower than that calculated from the observed heat of activation ; a possible explanation of the tardiness of the reaction is provided by the assumption that formic acid reacts in an activated form present only in traces.

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[6] *The Kinetics of Reaction in Solution*, 1933, 106.