# **288.** *Medium Effects in the Prototropy of Ketones. Kinetics of the Bromination of Acetone and Acetophenone in Aqueous Acetic Acid.*

By Trevor G. Bonner, David P. Evans, and H. B. Watson.

A kinetic study of the bromination of acetone and of acetophenone in different mixtures of water and acetic acid (ranging from pure water to 90% acetic acid) has shown that the changes in velocity are to be ascribed to simultaneous variations in the energy of activation and the *PZ* term of the equation $k = PZe^{-E/RT}$. A similar phenomenon has been observed in a number of other reactions by Hinshelwood and his co-workers. For the base-catalysed change the relationship between *E* and log *PZ* is approximately linear. In both base- and acid-catalysed prototropy the values of the parameters fall and finally rise again as the acetic acid content of the medium is increased.

Earlier measurements of the speeds of prototropy of acetone, acetophenone, and nuclear-substituted acetophenones in aqueous acetic acids (Watson *et al.*, J., 1931, 3318; 1932, 1207; 1933, 217) indicated that the acid-catalysed change becomes more rapid as the proportion of acetic acid in the solvent increases; *e.g.*, for acetone in presence of M-hydrochloric acid, the relative velocities of bromination in water, 50% acetic acid, and 75% acetic acid were 1 : 2·1 : 4·8. Since the catalytic influence of the acetic acid was almost negligible in comparison with that of the added mineral acid, the observed variations in speed were clearly due to a medium effect, and they appeared sufficiently interesting to merit further investigation.

It has recently been observed (Fairclough and Hinshelwood, J., 1937, 538, 1573; 1938, 236; compare Hinshelwood, *Trans. Faraday Soc.*, 1938, **34**, 138) that changes in the medium frequently lead to simultaneous variations in the energy of activation and the non-exponential term of the Arrhenius equation, and this gave added interest to a fuller kinetic study of prototropic changes in a continuously varying solvent.

We have therefore determined the velocities of bromination of acetone and of acetophenone (0·1M) catalysed by 0·5M-hydrochloric acid and also by 0·147M-sodium

*Acetophenone.*

| $CH_3{\cdot}CO_2H$, %, in medium. | Base-catalysed. *E*(cals.). | log *PZ*. | Acid-catalysed. *E*(cals.). | log *PZ*. |
|---|---|---|---|---|
| 25 | — | — | 19,400 | 9·4 |
| 50 | 20,300 | 9·4 | 19,200 | 9·4 |
| 75 | 18,400 | 8·0 | 20,100 | 10·4 |
| 90 | 19,300 | 8·7 | 19,800 | 10·9 |

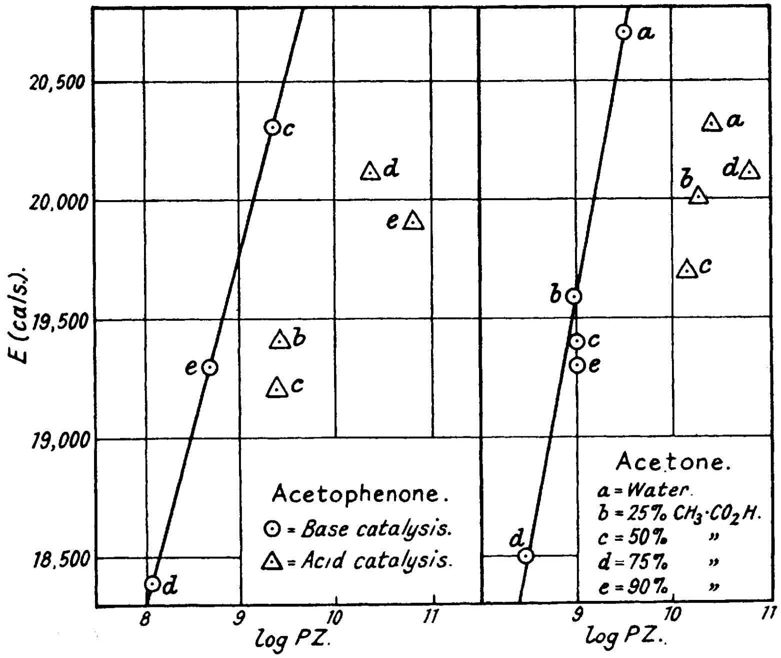
*Acetone.*

| $CH_3{\cdot}CO_2H$, %, in medium, | Base-catalysed. *E*(cals.). | log *PZ*. | Acid-catalysed. *E*(cals.). | log *PZ*. |
|---|---|---|---|---|
| 0 | 20,700 | 9·5 | 20,300 | 10·4 |
| 25 | 19,600 | 8·9 | 20,000 | 10·3 |
| 50 | 19,400 | 9·0 | 19,700 | 10·2 |
| 75 | 18,500 | 8·4 | 20,100 | 10·8 |
| 90 | 19,300 | 9·0 | — | — |

acetate, at different temperatures, in aqueous mixtures having an acetic acid content varying over a range from zero to 90%. In each case the plot of log $k$ against $1/T$ gave a good straight line, and the values of $E$ and log $PZ$ in the equation $k = PZe^{-E/RT}$ are recorded on the previous page.

The following generalisations can be made with regard to the base-catalysed changes. (1) The variations in the medium lead to appreciable changes in both $E$ and $PZ$; the values of the former cover a range of 2000 cals., and those of the latter vary over more than a ten-fold range. (2) $E$ and $PZ$ rise or fall together, the plot of $E$ against log $PZ$ being roughly linear (see figure). (3) Increase in the acetic acid content of the medium from zero to 75% results in a more or less steady fall of both $E$ and $PZ$, but further increase causes both to rise again.

For the acid-catalysed reactions the differences are on the whole small, and it is not possible to attach very great significance to them, but here also there appears to be a tendency for $E$ and $PZ$ to fall and then rise again. The increase in the values of both parameters when the medium changes from 50% to 75% acetic acid must certainly be regarded as real, particularly in the case of acetophenone.



We do not yet attempt any interpretation of the observations, but reference may be made to the following points. First, the results provide a further instance of the simultaneous variation of $E$ and $PZ$ which has been noted for other reactions by Hinshelwood and his collaborators. Secondly, they differ somewhat from observations which have been made upon the hydrolysis of benzoic esters, where a consistent variation of the Arrhenius parameters is found as the proportion of alcohol in alcohol–acetone–water media increases (Fairclough and Hinshelwood, *loc. cit.*), and where also changes in the medium have opposite effects upon alkaline and acid hydrolysis (Timm and Hinshelwood, J., 1938, 862). Hegan and Wolfenden's results for the alkaline hydrolysis of valerolactone (this vol., p. 508) resemble ours, however, in that the value of $E$ falls somewhat from water to 21% alcohol and then rises as the alcohol content of the medium increases further.

## EXPERIMENTAL.

Acetophenone was purified by distillation in a vacuum and freezing; m. p. 19·6°. Acetone was treated by the sodium iodide method and distilled, b. p. 56·9°; identical results were obtained with a specimen of "AnalaR" acetone, kindly provided by Dr. Dippy, which had been dried and distilled through a 4-ft. column filled with glass beads. Acetic acid, water, and bromine were as used in earlier work. Aqueous acetic acids were made up by volume.

The measurements were carried out as described previously (Evans, Morgan, and Watson, J., 1935, 1167; Evans and Gordon, J., 1938, 1434), 10 c.c. N.P.L.-standardised burettes graduated in 0·02 c.c. being used. For temperatures of 25° and higher, the thermostats were electrically controlled by a toluene regulator in conjunction with a Sun Vic vacuum tube switch. Lower temperatures (0°, 5°, 15°) were obtained by means of a refrigerating system coupled with a number of heating lamps similarly controlled and all contained in a well-lagged copper bath filled with a mixture of water and glycol (compare Smith, J., 1936, 1827; we are indebted to Dr. Smith for the details). Temperatures were constant within 0·02°.

The acid-catalysed reactions were of zero order, and a typical example is given below; this gives an indication of the degree of accuracy in the determinations of the energy of activation.

*Bromination of acetophenone in 50% acetic acid.*

[HCl] = 0·5M. [Ph·COMe] = 0·1M. Titres and values of *k* are in terms of c.c. of N/50-thiosulphate for 20 c.c. of reaction mixture; time is in mins.

| Temp. | Time. | Titre. | Fall. | *k*. | | *E*. |
|---|---|---|---|---|---|---|
| 25° | 0 | 10·50 | — | | | |
| | 20 | 8·31 | 2·19 | 0·110 | | |
| | 40 | 6·11 | 4·39 | 0·110 | 0·110 | |
| | 60·5 | 3·83 | 6·67 | 0·110 | | |
| 35° | 0 | 9·81 | — | | | 19,300 |
| | 7 | 7·55 | 2·26 | 0·323 | | |
| | 14 | 5·27 | 4·54 | 0·324 | 0·323 | |
| | 21 | 3·06 | 6·75 | 0·321 | | |
| 45° | 0 | 9·48 | — | | | 19,100 |
| | 2·5 | 7·30 | 2·18 | 0·872 | | |
| | 5 | 5·07 | 4·41 | 0·882 | 0·876 | |
| | 7·5 | 2·93 | 6·55 | 0·873 | | |

Accepted value of $E$ = 19,200 cals.; $\log_{10} PZ$, from equation $k = PZe^{-E/RT}$, is 9·36.

In the base-catalysed changes, however, the velocity coefficients increased as the reaction proceeded, by a factor which varied in different media and was always greater for acetone than for acetophenone. This increase was doubtless due to further bromination. The velocity coefficient at zero time was computed by extrapolation of the straight line obtained by plotting the values of *k* against time; "zero time" was the moment of mixing the reagents. The following examples are typical; they refer to the bromination of acetone in 75% acetic acid in presence of 0·147M-sodium acetate.

| | Temperature 35°. | | | | Temperature 55°. | | | |
|---|---|---|---|---|---|---|---|---|
| Time (mins.) | 0 | 59 | 119 | 164 | 2 | 9 | 17 | 26 |
| Titre (N/50-$Na_2S_2O_3$) | 10·45 | 8·30 | 5·93 | 3·99 | 9·77 | 8·07 | 5·93 | 3·35 |
| Fall in titre | — | 2·15 | 4·52 | 6·46 | — | 1·70 | 3·84 | 6·42 |
| $k \times 100$ | (3·48) | 3·64 | 3·80 | 3·95 | (22·7) | 24·2 | 25·6 | 26·8 |

The velocity coefficients obtained by this method were reproducible within 1—1·5%, and are more accurate than those recorded by Morgan and Watson (J., 1935, 1173).

The velocity coefficients for the acid- and base-catalysed reactions are summarised below, as fall of N/50-thiosulphate titre per minute for 20 c.c. of reaction mixture. Each is the mean of three concordant determinations. The values of $E$ and log $PZ$, determined in the usual way, have been recorded in the text.

*Bromination of acetophenone.*

[Ph·COMe] = 0·1M.

| $CH_3 \cdot CO_2H$, %, in medium. | [HCl] = 0·5M. | | | | [NaOAc] = 0·147M. | | |
|---|---|---|---|---|---|---|---|
| | $10^2k_{15°}$. | $10^2k_{25°}$. | $10^2k_{35°}$. | $10^2k_{45°}$. | $10^2k_{35°}$. | $10^2k_{45°}$. | $10^2k_{55°}$. |
| 25 | — | 8·55 | 25·6 | 69·2 | — | — | — |
| 50 | — | 11·0 | 32·4 | 88·0 | 1·54 | 4·30 | 11·9 |
| 75 | 7·50 | 24·4 | 75·4 | 218·0 | 1·74 | 4·43 | 11·2 |
| 90 | 44·6 | 144·0 | 12·6* | — | 1·57 | 4·23 | 11·1 |

*Bromination of acetone.*

$[Me_2CO] = 0{\cdot}1$M.

| $CH_3{\cdot}CO_2H$, %, in medium. | [HCl] = 0·5M. | | | | [NaOAc] = 0·147M. | | |
|---|---|---|---|---|---|---|---|
| | $10^2k_{0°}$. | $10^2k_{15°}$. | $10^2k_{25°}$. | $10^2k_{35°}$. | $10^2k_{35°}$. | $10^2k_{45°}$. | $10^2k_{55°}$. |
| 0 | 1·53* | 5·54 | 18·4 | 62·0 | 1·07 | 3·09 | 8·45 |
| 25 | — | 6·87 | 22·2 | 69·1 | 1·85 | 5·19 | 13·4 |
| 50 | 1·37 | 9·21 | 29·9 | — | 2·84 | 7·69 | 20·2 |
| 75 | 2·72 | 19·6 | 63·3 | — | 3·50 | 9·20 | 22·6 |
| 90 | — | — | — | — | 3·38 | 9·00 | 23·7 |

* Temperature = 5°.

We thank Messrs. Imperial Chemical Industries for grants.

THE TECHNICAL COLLEGE, CARDIFF.

[*Received, June* 17*th*, 1939.]