## 20. *The Racemisation of Some* d-o-(2-*Dimethylaminophenyl*)*phenyltrimethylammonium Salts.*

By Dorothy E. Cook and E. E. Turner.

Shaw and Turner (J., 1933, 135) found that in aqueous solution at 99·5° *d-o-*(2-dimethyl-aminophenyl)phenyltrimethylammonium *d*-camphorsulphonate racemised, as regards the cation, rather more quickly than did the corresponding *d*-ammonium iodide. This effect appeared to be most readily explicable as due to electrostriction differences between the two salts. Were this so, the corresponding d-*ammonium benzenesulphonate* should have an optical stability nearer to that of the camphorsulphonate than to that of the iodide. In effecting a comparison of the three salts, we employed solutions of equimolecular concentration, which we had not done previously. At 90°, the periods of half-racemisation were : benzenesulphonate 210 minutes, iodide 250 minutes, and *d*-camphorsulphonate 310 minutes. In equivalent aqueous solutions, therefore, the camphorsulphonate is more stable, but the

benzenesulphonate is less stable, than the iodide, and the cause of the different stabilities is not apparent.

A study has also been made of the racemisation of the above *d*-camphorsulphonate in different solvents at 90°. The following results show that there is no simple connexion between the speed of racemisation and the dielectric constant ($\mu$) of the solvent :

| Solvent. | Period of half-racemisation (mins.). | $\mu$. |
|---|---|---|
| Water | 310 | 80·0 |
| Ethyl alcohol | 300 | 23·5 |
| Acetone | 155 | 21·4 |
| Acetonitrile | 140 | 38·8 |
| Chloroform | 100 | 5·05 |

Actually, racemisation was more rapid the higher the solubility of the camphorsulphonate in the solvent.

Determination of the rate of racemisation of the above iodide and *d*-camphorsulphonate in aqueous solutions at 85°, 90° and 95° allowed of the calculation of the activation energy of the process. This was found to be, for the iodide, 11,500 cals., and for the camphorsulphonate, 19,000 cals.

<div align="center">EXPERIMENTAL.</div>

d-o-(*2-Dimethylaminophenyl*)*phenyltrimethylammonium benzenesulphonate* was prepared from the corresponding iodide and the equivalent amount of silver benzenesulphonate in boiling aqueous alcohol (Found : N, 6·7. $C_{23}H_{28}O_3N_2S$ requires N, 6·7%).

*Measurements of the Rates of Racemisation.*—These were made by heating a solution of the salt under examination in a sealed glass tube for definite times and at definite temperatures, all usual controls being made use of. The results are tabulated below :

d-o-(*2-Dimethylaminophenyl*)*phenyltrimethylammonium* d-*camphorsulphonate.* (a) $t = 90°$.
(1) Solvent, water; *c*, 0·5268.

| Time (mins.). | $a_{5791}$. | $a_{5461}$. | $k$. | Time (mins.). | $a_{5791}$. | $a_{5461}$. | $k$. |
|---|---|---|---|---|---|---|---|
| 0 | +0·50° | +0·58° | — | 200 | +0·36° | +0·41° | 0·0009$_9$ |
| 50 | 0·46 | 0·53 | 0·0009$_4$ | 280 | 0·32 | 0·37 | 0·0009$_5$ |
| 90 | 0·43 | 0·50 | 0·0009$_8$ | 370 | 0·28 | 0·31 | 0·0010$_2$ |
| 150 | 0·39 | 0·44 | 0·0009$_7$ | $\infty$ | 0·11 | 0·12 | — |
| | Half-life period 310 mins. | | | | Mean $k$ 0·0009$_6$. | | |

(2) Solvent, ethyl alcohol; *c*, 1·1860. Mean $k$, 0·0010. Limits, 0·0009$_9$ and 0·0012$_9$. Half-life period, 300 mins.

(3) Solvent, acetone; *c*, 1·3310. Mean $k$, 0·0019$_4$. Limits, 0·0018$_9$ and 0·0023. Half-life period, 155 mins.

(4) Solvent, acetonitrile; *c*, 1·2950. Mean $k$, 0·0021$_4$. Limits, 0·0020$_2$ and 0·0024. Half-life period, 140 mins.

(5) Solvent, chloroform; *c*, 1·1370. Mean $k$, 0·003. Half-life period, 100 mins. Solution darkened during measurements.

(b) $t = 85°$. Solvent, water; *c*, 0·5268. Mean $k$, 0·0006$_5$. Limits, 0·0006$_1$ and 0·0007$_0$. Half-life period, 460 mins.

(c) $t = 95°$. Solvent, water; *c*, 0·5268. Mean $k$, 0·0013$_3$. Limits, 0·0012$_6$ and 0·0013$_9$. Half-life period, 230 mins.

d-o-(*2-Dimethylaminophenyl*)*phenyltrimethylammonium* d-*iodide.* Solvent, water; *c*, 0·4140.
(1) $t = 85°$. Mean $k$, 0·0009$_3$. Limits, 0·0009, and 0·0009$_7$. Half-life period, 320 mins.
(2) $t = 90°$. Mean $k$, 0·0011$_9$. Limits, 0·0011$_6$ and 0·0012$_5$. Half-life period, 250 mins.
(3) $t = 95°$. Mean $k$, 0·0014$_5$. Limits, 0·0013$_8$ and 0·0014$_6$. Half-life period, 210 mins.

d-o-(*2-Dimethylaminophenyl*)*phenyltrimethylammonium benzenesulphonate.*
Solvent, water; *c*, 0·4478. Mean $k$, 0·0014$_2$. Limits, 0·0014$_0$ and 0·0014$_8$. Half-life period, 210 mins.

UNIVERSITY OF LONDON (BEDFORD COLLEGE).