

each species possesses a secretion that is characteristic enough to discriminate it from other morphologically recognized species. In *Bombus lucorum* L. two forms have been recognized, each possessing a different and characteristic secretion. It has later been possible to morphologically separate these forms, which have been named "dark" and "blonde", respectively, according to the colour shade.

The secretions have been found to contain acyclic mono-, sesqui- and diterpenes (alcohols and acetates), as well as aliphatic normal chain compounds with 10 to 27 carbon atoms. Among the latter have been found alcohols, aldehydes, acetates, and ethyl esters. Several saturated and mono-unsaturated normal chain hydrocarbons with 21 to 27 carbon atoms, mainly with an odd number of carbon atoms, have been found for all species. Some of the compounds have shown considerable seasonal variation, notably the diterpenes of *B. hortorum* and *B. hypnorum*. There seems to be increased amounts of these components later in the season.

The animals were carefully identified closely following Elfving's classification.<sup>1</sup> Our results to date are summarized in Table 1.

After our first publication in this field,<sup>2</sup> which dealt with the marking secretion of *Bombus terrestris*, Calam<sup>3</sup> has published a short account of a study of marking secretions which includes 4 *Bombus* species also studied by us. His results agree with those given in Table 1 in case of *B. agrorum* and *B. lapidarius*. For *B. lucorum* Calam's results indicate that he has studied the "blonde" form. Our results leave no doubt as to the presence of farnesol in *B. pratorum*. Full details of our work will be published later.

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## The Carbonic Acid Dehydration and its Activation Energy

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Extensive experimental work has been carried out on the kinetics of the CO<sub>2</sub>-H<sub>2</sub>O-system since the work of Faurholt<sup>1</sup> 1924. However, several problems concerning, for example, temperature dependence of the reaction rates and catalysis of the reactions still exist.

By mixing equal volumes of 0.02 M NaHCO<sub>3</sub> and 0.01 M HCl in a Durrum-Gibson stopped-flow spectrophotometer \*\* we have examined the dehydration of H<sub>2</sub>CO<sub>3</sub> in a wide temperature range (2–45°C) and the activation energy is calculated. Bromophenol blue was used as an indicator. The theory of Brinkman *et al.*<sup>3</sup> is used to interpret the plots of pH *versus* time obtained. Using the initial concentrations of the reactants mentioned above, the integrated rate expression \*\*\* approximates:

$$k_{\text{deh}} = 2.303 \times 1.06 \times \frac{\text{pH}_2 - \text{pH}_1}{t_2 - t_1}$$

Fig. 1 shows a trace of percent transmittance *versus* time, directly photographed from the storage oscilloscope screen.

Fig. 2 shows the curve in Fig. 1 transformed to a plot of pH *versus* time. Approximately, this is seen to be a straight line in accordance to first order kinetics.  $k_{\text{deh}}$  is calculated from the slope of the line to 62 sec<sup>-1</sup> (34.8°C). The slight curvature may be due to hydrogen ion catalysis; cf. three last paragraphs.

Fig. 3 shows the Arrhenius plot calculated from Table 1 and compared with the results of other authors.  $E_A$  is cal-

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\*\*\*  $k_{\text{deh}}$  in Table 1 is calculated from the expression shown which, however, has been multiplied by 1.13 due to the spectrophotometric properties of the indicator used.

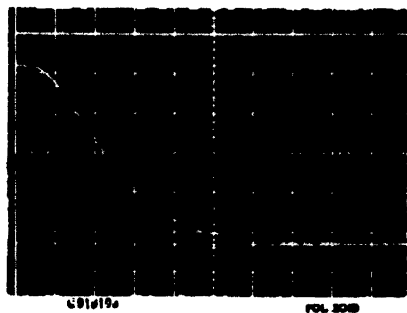


Fig. 1. Transmittance-time plot directly photographed from the oscilloscope screen. Temperature: 34.8°C. 1 unit on the time axis  $\approx$  0.02 sec.

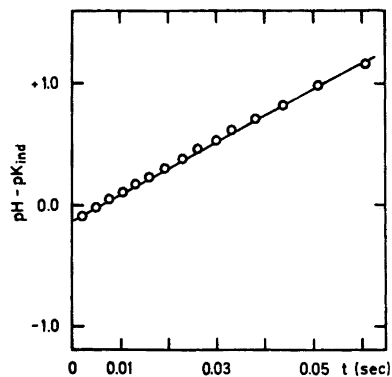


Fig. 2. The curve shown on Fig. 1 transformed to a pH-time plot.

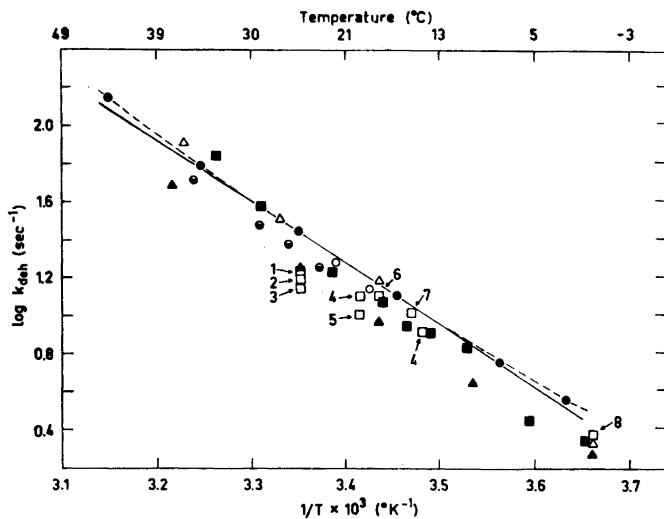


Fig. 3. Arrhenius plot from the results of the present investigation and from those of other authors. ● Present investigation.  $\Delta$  Roughton<sup>3</sup> ( $E_A$  calculated to 16.5 kcal/mol).  $\bullet$  Scheurer *et al.*<sup>4</sup> (Only a few values from this work are included here) ( $E_A$  calculated to 16.1 kcal/mol).  $\blacktriangle$  Magid and Turbeck<sup>5</sup> ( $E_A$  calculated to 14.6 kcal/mol).  $\blacksquare$  Sirs<sup>6</sup> ( $E_A$  calculated to 16.5 kcal/mol). (1) Ho and Sturtevant,<sup>8</sup> (2) Eigen *et al.*<sup>9</sup> (3) Gibbons and Edsall,<sup>10</sup> (4) Saal,<sup>11</sup> (5) Meier and Schwarzenbach,<sup>12</sup> (6) Gibson and Roughton,<sup>13</sup> (7) Brinkman *et al.*,<sup>2</sup> (8) Faurholt.<sup>1</sup>

Table 1. Rate constant of the  $\text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$  reaction. ( $k_{\text{deh}}$  is an average of at least 3 experiments).

|                                       |           |           |            |            |            |            |
|---------------------------------------|-----------|-----------|------------|------------|------------|------------|
| Temp. (°C)                            | 2.1 ± 0.2 | 7.5 ± 0.2 | 16.4 ± 0.1 | 25.3 ± 0.1 | 34.8 ± 0.1 | 44.4 ± 0.2 |
| $k_{\text{deh}}$ (sec <sup>-1</sup> ) | 3.5       | 5.6       | 13         | 27         | 62         | 140        |

culated from our experiments to be 15.1 kcal/mol by a least squares method, but a slight temperature dependence is observed.  $E_A$  changes from 13.1 kcal/mol at the low temperatures, to 16.5 kcal/mol at the high temperatures. This behaviour has not been reported before and could be accounted for by a possible temperature drift at temperatures differing from room temperature. However, since such a drift would cause S-formed Arrhenius plots and since the reproducibility of the measurements of  $k_{\text{deh}}$  is within ± 4 % in the whole temperature range, this source of error can be disregarded. A corresponding change in  $E_A$  of the reverse reaction studied here is found by Pinsent *et al.*<sup>14</sup> ( $E_A = 19.0$  kcal/mol (0°C),  $E_A = 10.8$  kcal/mol (38°C)) and Maren<sup>15</sup> ( $E_A = 14$  kcal/mol (1–8°C),  $E_A = 7$  kcal/mol (25–37°C)). The results of the works of these authors and of the present paper do not agree with those of Magid and Turbeck,<sup>5</sup> who find both  $E_A$ -values independent of temperature. It is very likely that at least one of the  $E_A$ -values in question changes with temperature because of the considerable temperature dependence of  $\Delta H$  of the process. Roughton<sup>3</sup> found that  $\Delta H$  changes from 2.9 kcal/mol at 0°C to 0.5 kcal/mol at 37°C.

Another problem concerning the dehydration process is the disagreement between different authors' determinations of  $k_{\text{deh}}$ , cf. Fig. 3. The fact that the lowest values normally originate from experiments at pH 7–8 and the highest values from experiments at pH 3–5 suggests that  $k_{\text{deh}}$  depends on pH. This as well as the deviation from linearity in Fig. 2 could be due to a slight hydrogen ion catalysis, although this phenomenon, according to our knowledge, has been reported only once before. Koefoed and Engel<sup>16</sup> give data for the catalytic constant and simultaneously treat the possibility of catalysis of the process by means of the assumption of polymeric forms of  $\text{H}_2\text{CO}_3$ , as earlier pointed out by Meier and Schwarzenbach.<sup>12</sup> The mechanisms connected with this postulated phenomenon have not yet been satisfactorily elucidated.

Furthermore, the possibility of the existence of consecutive reactions of the

type  $\text{H}_2\text{CO}_4 \rightarrow \text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$  has not been taken into account. The orthocarbonic acid,  $\text{H}_2\text{CO}_4$ , may be formed to a certain degree under the present experimental conditions, *i.e.*  $\text{HCO}_3^- + \text{H}_2\text{O}^+ \rightarrow \text{H}_2\text{CO}_4$ . Such reactions have not been dealt with before and the experimental data of the present work do not allow definite conclusions to be drawn about this possibility.

Apparently, the dehydration of carbonic acid is not as simple as usually assumed, and the deviation from linearity in the Arrhenius plot could be due to this.

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