

the nearest neighbour anion interaction. The anion at  $(2/3, 1/3, -1/6)$  must occupy the ordered calcite-type position, relative to that at the origin, or an aragonite-type position. However, because of the interaction with the next neighbours of this nitrate group, these anions must also occupy ordered calcite-type positions. A similar result applies likewise to the nitrate group at  $(1/3, 2/3, 1/6)$  and its next neighbours, and so forth. As a result the present model yields a positionally ordered equilibrium structure of solid lithium nitrate at any temperature.

It may be noted that a nitrate group is *a priori* expected to occupy either a calcite- or an aragonite-type position, *i.e.* a special position in the unit cell, for symmetry reasons, neglecting the interaction with the remaining lattice. On the other hand, if the system possesses some orientational disorder, the instantaneous equilibrium configuration may deviate from the statistical symmetry ( $R\bar{3}c$ ). To a smaller extent this may be expected to apply to the configuration of the cations too. As a result, the positions of the nitrate groups may deviate instantaneously somewhat from the special positions mentioned above. Such deviations are probably not sufficient to make the unacceptable O—O distances of Table 1 accessible to the system at equilibrium, if the Li—O distances *etc.* are to be of reasonable lengths. This remains valid even if the small uncertainty in the *z*-parameter value used for oxygen in an aragonite-type position is incorporated. Furthermore, only four of the six quoted O—O distances less than 2.8 Å are sufficient to derive the present result. Also, the ordered calcite-type O—O contact distances are actually significantly longer than 2.8 Å, being, however, considerably less than those observed in the ordered phases of sodium and potassium nitrate.

According to the above discussion any orientational disorder in solid lithium nitrate is expected to be small or zero at equilibrium. This should not, however, exclude the possibility that the nitrate groups may reorient about the *c*-axis from one position to the equivalent orientation at higher temperatures. At a given moment the fraction of reorienting molecules is expected to be small<sup>12</sup> (or zero).

1. Newns, D. M. and Staveley, L. A. K. *Chem. Rev.* **66** (1966) 267.
2. Kracek, F. C., Barth, T. F. W. and Ksanda, C. J. *Phys. Rev.* **40** (1932) 1034.
3. Cherin, P., Hamilton, W. C. and Post, B. *Acta Cryst.* **23** (1967) 455.
4. Felty, E. J. *Diss. Abstr.* **24** (1964) 4423.
5. Strømme, K. O. *Acta Chem. Scand.* **23** (1969) 1616.
6. Rhodes, E. and Ubbelohde, A. R. *Proc. Roy. Soc. Ser. A.* **251** (1959) 156.
7. Fermor, J. H. and Kjekshus, A. *Acta Chem. Scand.* **23** (1969) 1581.
8. Fischmeister, H. F. *J. Inorg. Nucl. Chem.* **3** (1956) 182.
9. Riccardi, R. and Sinistri, C. *Ric. Sci. Rend. Sez. A* **8** (1965) 1026.
10. Strømme, K. O. *Acta Chem. Scand.* **23** (1969) 1625.
11. Pauling, L. *Nature of the Chemical Bond*, Cornell 1960.
12. Darmon, I. and Brot, C. *Mol. Cryst.* **2** (1967) 301.

Received April 30, 1970.

## Volatile Components of the Cephalic Marking Secretion of Male Bumble Bees

BERTIL KULLENBERG

*Ecological Station of the University of  
Uppsala, S-380 61, Ölands Skogsby, Sweden*

GUNNAR BERGSTRÖM and  
STINA STÄLLBERG-STENHAGEN

*Institute of Medical Biochemistry,  
University of Göteborg, S-400 33 Göteborg,  
Sweden*

Volatile compounds present in the secretions emanating from glands in the heads of male bumble-bees have been studied in 13 species of the genus *Bombus* and 6 species of the genus *Psithyrus*, the last mentioned being the so-called cuckoo bumble-bees which parasitize the nests of *Bombus*. The secretion is used during the flying season—July to September, depending on species—to mark different objects in the flying territories, a very characteristic behaviour. It has been found that

Table 1. Volatile substances found in the cephalic marking secretion of male bumble bees of the genera *Bombus* and *Psithyrus*.<sup>a</sup>

	Molecular weight	<i>B. hortorum</i> L.	<i>B. subterraneus</i> L.	<i>B. agrorum</i> F.	<i>B. muscorum</i> L.	<i>B. scrocoënsis</i> F.	<i>B. sporadicus</i> Nyl. <sup>b</sup>	<i>B. terrestris</i> L.	<i>B. lucorum</i> L. "dark"	<i>B. lucorum</i> L. "blonde"	<i>B. patagiatus</i> Nyl. <sup>b</sup>	<i>B. cullumanus</i> K.	<i>B. lapidarius</i> L.	<i>B. pratorum</i> L.	<i>B. hygonorum</i> L.	<i>Ps. bohemicus</i> Seidl	<i>Ps. rupestris</i> F.	<i>Ps. campestris</i> Pz.	<i>Ps. barbuletus</i> K.	<i>Ps. silvestris</i> Lep.	<i>Ps. globosus</i> Ev.
Geraniol	154											x		x							
Citronellol	156																x				
Geranyl acetate	196											x		x							
Citronellyl acetate	198																				
all- <i>trans</i> -Farnesol	222	⊕																		⊕	
(-)-2,3-Dihydrofarnesol	224						⊕														
all- <i>trans</i> -Farnesyl acetate	264											x		x					x		
2,3-Dihydrofarnesyl acetate	266						x														
Geranylgeraniol	290	x	⊕					x			x		x								
Geranylcitronellol	292						x								x			⊕			
Geranylgeranyl acetate	332						⊕		x		⊕		x	⊕		x					
Tetradecanol-1	214		x										x							x	
Hexadecanol-1 <sup>c</sup>	240		⊕										⊕		x	⊕				⊕	
Hexadecanol-1	242							x					x	x	x		x				x
Octadecanol-1 <sup>e</sup>	268	x		⊕															x		x
Eicosanol-1	296																	⊕			
Tetradecyl acetate	256						⊕														
Hexadecyl acetate	284						x														
Octadecenyl acetate <sup>d</sup>	310			⊕																	
Octadecyl acetate	312																		x		
Eicosyl acetate	340								x												
Docosyl acetate	368								x												
Ethyl decanoate	200						x	x													
Ethyl dodecanoate	228						x	x	x	⊕											
Ethyl tetradecanoate <sup>f</sup>	254						x		⊕											x	x
Ethyl hexadecanoate	282							x	x						x						
Ethyl hexadecadienoate	280												x								
Ethyl hexadecatrienoate	278							x	x												
Tetradecanal	212						x									x				x	x
Hexadecanal	238		x													x					
Nonadecene <sup>d</sup>	266	⊕																			

<sup>a</sup> Main component is marked by ⊕.<sup>b</sup> Uncompletely known species.<sup>c</sup> Double bond position: *B. agrorum* 7, 8; *B. lapidarius* 9, 10; *Ps. bohemicus* 11, 12.<sup>d</sup> Double bond position 9, 10.<sup>e</sup> Double bond position 9, 10, determined for *B. muscorum* only.<sup>f</sup> Double bond position 9, 10, determined for *B. lucorum* only.

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 I.

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 I 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.

1. Elfving, R. *Die Hummeln und Schmarotzerhummeln Finnlands, Fauna Fennica 10*, Soc. Fauna Flora Fennica, 1960.
2. Bergström, G., Kullenberg, B., Ställberg-Stenhagen, S. and Stenhagen, E. *Arkiv Kemi* **28** (1968) 453.
3. Calam, D. H. *Nature* **221** (1969) 856.

Received May 4, 1970.

## The Carbonic Acid Dehydration and its Activation Energy

POUL ERIK SØRENSEN\* and ARNE JENSEN

*The Royal Danish School of Pharmacy, Chemical Laboratories A and D, DK-2100 Copenhagen Ø, Denmark*

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 I and compared with the results of other authors.  $E_A$  is cal-

\* Present address: Chemistry Department A, The Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark.

\*\* Durrum Instrument Corporation, 3950 Fabian Way, Palo Alto, California 94303, U.S.A.

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