lepidoptera on *S. vulgaris* L. and found that the eggs of one of them, *A. caja* L., contained the plant alkaloids.

The persistence of the *S. spathulatus* alkaloids certainly makes them candidates as predator-deterrents. However they are largely present in *N. annulata,* as in *S. spathulatus,* as N-oxides (of intergerrimine and senecionine): compounds which are much more water-soluble than the tertiary bases but correspondingly less toxic to vertebrates[4]. For substances to function as efficient feeding-deterrents a likely requirement is for them to be immediately distasteful to predators. It will be interesting to see which, if any, of the pyrrolizidine alkaloids are effective in this regard. Edgar et al.[9] cite unpublished work by T. Eisner, K. Hicks and D. Aneshasley as demonstrating that pyrrolizidine alkaloids are distasteful to some insect predators.

Impressed by the persistence of the *S. spathulatus* alkaloids in *N. annulata* we were curious to see if they would survive transfer to a natural parasite, a species of *Microplitis* (Hymenoptera: Braconidae)[17]. Accordingly we examined the pupae of this braconid, obtained from larvae emerging from late instar *N. annulata* larvae. The plant alkaloids were present in the parasite. So far as we are aware, this is the first report of the transfer of a plant alkaloid through a herbivorous larva to a carnivorous parasite[18], and further attests to the remarkable metabolic stability of the N-oxides of senecionine and intergerrimine in some insects.

---

[1] Acknowledgments. We thank Dr R. Yamdagni of the Chemistry Department, University of Calgary, Canada, and Dr O. Madsen of the Organic Chemistry Department, The Technical University of Denmark, Lyngby, Denmark, for much help with the MS data collection. We are also very grateful to Dr C.C.J. Culvenor, CSIRO Animal Health Lab., Parkville, Victoria, Australia, who most generously provided us with authentic reference specimens of pyrrolizidine alkaloids.

[2] Visiting Scientist, present address: Chemistry Department, The University, Calgary, Alberta, Canada T2N 1N4.

[3] Author to whom correspondence should be addressed.

[4] L.B. Bull, C.C.J. Culvenor and A.T. Dick, The Pyrrolizidine Alkaloids: Their Chemistry, Pathogenicity, and Other Biological Properties. North Holland Publishing Co., Amsterdam 1968.

[5] R.T. Aplin, M.H. Benn and M. Rothschild, Nature, Lond. *219,* 747 (1968).

[6] M. Rothschild and R.T. Aplin, in: Pesticide Chemistry, vol. 3, p. 177. Ed. A. Tahori. Gordon and Breach, New York 1971.

[7] R.T. Aplin and M. Rothschild, in: Toxins of Animal and Plant Origin, vol. 2, p. 579. Ed. A. de Vries and E. Kochva. Gordon and Breach, New York 1972.

[8] J.A. Edgar and C.C.J. Culvenor, Nature, Lond. *248,* 614 (1974).

[9] J.A. Edgar, P.A. Cockrum and J.L. Frahn, Experientia *32,* 1535 (1976).

[10] T. Reichstein, J. von Euw, J.A. Parsons and M. Rothschild, Science *161,* 861 (1968).

[11] L.P. Brower, Scient. Am. *220,* 22 (1969).

[12] D.E. Gaskins, The Butterflies and Common Moths of New Zealand. Whitcombe and Tombs Ltd, Christchurch 1966. The only bird recorded as feeding on *N. annulata* larvae is the shining cuckoo *Chalcites lucidus* Gmelin, see W.W. Smith, N.Z. J. Sci. Technol. *6,* 61 (1923), and references therein. We thank Dr Ross Galbreath, Entomology Division, DSIR, for drawing our attention to this interesting anomoly.

[13] We are grateful to Miss Eileen Mayo of Christchurch, who designed the stamp, for the identification of this plant. We also thank Mr A.R. Anderson of the New Zealand Post Office H.Q., Wellington, for the information that some 419 million copies of this stamp were distributed, plus several million more surcharged to 4c: thus making the figure probably the most widely circulated illustration of an aposematically coloured insect with a host-plant likely responsible for its chemical defence against predators.

[14] D.G. Drury, N.Z. J. Bot. *12,* 513 (1974).

[15] Our plant identifications were confirmed by Mr Alan Esler and Ms Shirley Bowman, Botany Division, DSIR, Auckland.

[16] The carry over of cardenolides into arthropod eggs is well-established: see for example Reichstein et al.[10] and J. von Euw, T. Reichstein and M. Rothschild, Insect Biochem. *1,* 373 (1971).

[17] Identified by E. Valentine, Entomology Division, DSIR; see also E. Valentine, N. Z. J. Sci. *10,* 1100 (1967).

[18] The similar transfer of carotenoid plant pigments to parasitoids has occasionally been reported: see M. Rothschild, G. Valadon and R. Mummery, J. Zool. *181,* 323 (1977), and references therein.

Studies on hydrogen, halides and thiocyanate ions in dioxane-water mixtures at various temperatures

B. K. Das and Prasanna K. Das

Department of Chemistry, Ravenshaw College, Cuttack 753 003 (India), 3 April 1978

Summary. The free enrgies of transfer (ΔG_t^0) of H^+, Cl^-, Br^-, I^- and SCN^- ions from water to 10, 20, 30 and 40% dioxane-water mixtures have been studied from potentiometric measurements. For anions the ΔG_t^0 values are in the order $Cl^- > Br^- > SCN^- > I^-$.

The study of electrode potentials of individual electrodes have been a subject of interest to electrochemists. Almost exhaustive work[1-3] has been done to determine the electrode potential of various electrodes in aqueous solutions. Very little work[4-6] has been done in the study of such systems in aquo-organic solvents. These studies should bring out not only the characteristic for aqueous component in influencing the electrolyte but also throw light on the basic character of the solvent. In the present communication, the standard free energies of transfer (ΔG_t^0) have been studies from the standard potentials of Ag-AgBr, Ag-AgI and Ag-AgSCN electrodes in 10, 20, 30 and 40% (w/w) dioxane-water mixture at 15, 25, 35 and 45 °C, and an attempt has been made to deal with the basic character of the solvents.

Materials and methods. The free energy changes (ΔG_t^0) accompanying the transfer of H^+X^- (where $X = Br$ or I or SCN) from water to dioxane-water mixtures have been computed by Feakin's method[7] using E_N^0 values of the 3 electrodes reported in our previous communications[8-10]. The ΔG_t^0 values for H^+Cl^- reported by Das et al.[11,12] have also taken into consideration to calculate the ionic ΔG_t^0 values.

Results and discussion. The ΔG_t^0 values for H^+Cl^-, H^+Br^-, H^+I^- and H^+SCN^- in 10, 20, 30 and 40% (w/w) dioxane-water mixtures are given in table 1. The ΔG_t^0 values are found to be positive for H^+Cl^-, H^+Br^- and negative for H^+I^-, H^+SCN^-. So the transfers of I^- and SCN^- are more favoured than Cl^- and Br^-. The ionic ΔG_t^0 values for H^+ i.e. $\Delta G_t^0(H^+)$ were obtained by plotting ΔG_t^0 values for halogen

Table 1. ΔG_t^0 values in $Jmoles^{-1}$

t (°C)	H^+Cl^-	H^+Br^-	H^+I^-	H^+SCN^-
10% dioxane				
15	455	200	− 531	−357
25	420	165	− 560	−338
35	1,770	306	− 511	−357
45	3,110	415	− 724	−386
20% dioxane				
15	928	252	− 878	−347
25	1,009	230	− 897	−270
35	1,103	328	− 965	−299
45	1,205	577	−1,148	−270
30% dioxane				
15	1,543	520	−1,187	−482
25	900	734	−1,023	−492
35	2,490	835	−1,399	−550
45	3,740	1,124	−1,640	−656
40% dioxane				
15	2,518	808	−1,409	−589
25	3,330	1,271	−1,245	−608
35	4,600	1,687	−1,592	−608
45	5,870	2,076	−2,055	−647

Table 2. Ionic ΔG_t^0 values in J

t (°C)	H^+	Cl^-	Br^-	I^-	SCN^-
10% dioxane					
115	− 5,540	7,310	5,846	5,029	5,183
25	− 5,500	5,920	5,665	4,940	5,162
35	−11,800	13,570	12,106	11,289	11,443
45	−19,800	22,910	20,215	19,076	19,414
20% dioxane					
15	−28,800	29,903	29,128	27,835	28,453
25	−10,400	11,409	10,630	9,503	10,130
35	−11,300	12,403	11,628	10,335	11,001
45	−12,900	14,105	13,477	11,752	12,630
30% dioxane					
15	−14,800	17,290	15,635	13,401	14,318
25	−10,600	11,500	11,334	9,577	10,108
35	−20,800	23,290	21,635	19,401	20,250
45	−28,400	32,140	29,524	16,760	27,744
40% dioxane					
15	−21,000	25,600	22,687	19,408	20,411
25	−24,000	27,330	25,271	22,755	23,392
35	−32,400	37,000	34,087	30,808	31,792
45	−41,500	47,370	43,576	39,445	40,853

acids against the anionic radius (r_-) according to the following equation[7]:

$$\Delta G_t^0=\Delta G_t^0(H^+)+Kr_-^{-1}, \qquad (1)$$

where K is a constant.

Since the ΔG_t^0 terms for ions in an electrolyte are additive[13], the ionic ΔG_t^0 values for Cl^-, Br^-, I^- and SCN^- were calculated from the ΔG_t^0 values for H^+Cl^-, H^+Br^-, H^+I^- and H^+SCN^-, respectively. The ionic ΔG_t^0 values are presented in table 2. The $\Delta G_t^0(H^+)$ values are negative at all the temperatures and solvent mixtures studied. So dioxane-water mixtures are more basic than water and the basicity of dioxane-water mixtures is enhanced with the increasing proportion of dioxane in the mixture.

All the 4 anions studied here are found to be in higher free energy state in dioxane-water mixtures and their order is $Cl^- > Br^- > SCN^- > I^-$. Considering the 3 halides, it is seen that the free energy of transfer decreases with increasing ionic diameter. Since the ΔG_t^0 values for SCN^- lies in between Br^- and I^- it can be concluded that the ionic diameter of thiocyanate ion lies in between Br^- and I^-. It is also seen that the ΔG_t^0 values for H^+SCN^- fit well on the straight line graph ΔG_t^0 against r_-^{-1} according to equation (1) if the ionic radius of SCN^- is taken to be equal to 2.08 Å which is in between r_{Br^-} (1.951 Å) and r_{I^-} (2.168 Å)[14].

1 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd ed., p.485. Reinhold Publishing Corporation, New York 1958.
2 G. Sahu and B. Prasad, J. Indian chem. Soc. *46*, 233 (1969).
3 S.C. Lal and B. Prasad, Indian J. Chem. *13*, 372 (1975).
4 H.S. Harned and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd ed., p.462. Reinhold Publishing Corporation, New York 1958.
5 D. Feakins, Physico-chemical Processes in Mixed aqueous Solvents, p.71. Heinmann Educational Books, London 1969.
6 R.N. Roy, W. Vernon and A.L.M. Bothwell, Electrochim. Acta *17*, 5 (1972).
7 D. Feakins and P. Watson, J. chem. Soc. *1963*, 4686.
8 B.K. Das and P.K. Das, J. chem. Soc. Far. I *74*, 22 (1978).
9 U.C. Mishra, B.K. Das and P.K. Das, Thermochim. Acta *28*, 277 (1979).
10 B.K. Das and P.K. Das, J. chem. Soc. Far. I (communicated).
11 U.C. Mishra and P.K. Das, Electrochim. Acta *22*, 59 (1977).
12 B.K. Das, U.C. Mishra and P.K. Das, Acta cient. indica (communicated).
13 D. Feakins, B.E. Hickey, J.P. Lorimer and P.J. Voice, J. chem. Soc. Far. I *71*, 780 (1975).
14 L. Pauling, The Nature of Chemical Bond, 3rd ed., p.519. Oxford University Press, London.

Development of oxidative metabolism in the non-innervated optic lobe of the chick

S.C. Bondy and C.L. Anderson

Laboratory of Behavioral and Neurological Toxicology, National Institute of Environmental Health Sciences, P.O. Box 12233, Research Triangle Park (North Carolina 27709, USA), and Department of Neurology, University of Colorado Medical Center, Denver (Colorado 80262, USA), 17 July 1978

Summary. Early removal of the optic cup of the chick embryo prevents innervation of the contralateral optic lobe. This reduces the rate of development of citrate synthetase. The posthatch increase of the level of this enzyme related to oxidative metabolism is not impaired by denervation of the chick optic lobe.

During cerebral maturation, there is a major change from predominantly glycolytic metabolism to an intense oxidative metabolism. This shift occurs after the cessation of neurogenesis and prior to the onset of neuronal excitability[1]. Activity of the citric acid cycle may be necessary for several specific features of neuronal metabolism. These include the high energy requirements of the sodium pump and of axoplasmic transport[2]. Furthermore, operation of the citric acid cycle is needed for the production of several amino acids found in high concentration in the mature