influence of the resultant density gradients on the flux of water vapour to be analogous to the well-known influence of density gradients on the flux of heat from a plate surrounded by an externally undisturbed fluid[2], and were able to demonstrate quantitatively (see their Fig. 7) the validity of this analogy. Such a result makes it difficult to appreciate Dr. Kingdon's suggestion.

Examination of the data tabulated by Boelter et al. reveals the considerable influence of density differences in experiments of this type. Thus, other things being equal, the rate of evaporation is more than doubled if the density of air adjacent to the water surface, relative to air at some distance, is decreased from 0·98 to 0·90. Since Dr. Kingdon's experimental arrangement[3] was similar in form to that used by Boelter et al., one may expect similar trends, and the strong influence of gas density upon rate of evaporation[4] is explicable.

The effect of convective flow on vapour flux is not determined by density differences alone; inter alia, the dimensions of the system involved are important. In the experiments of Langstroth, Diehl and Winhold[5] drops of liquid were supported at the centre of spherical flasks, the walls of which were coated with an adsorbent of the vapour. For experiments of this type convective flow is of lesser significance the smaller the value of a modified Grashof number $d^3g/\nu^2\ (1\ -\ \rho_0/\rho a)$, where d is the diameter of the vessel, g is the gravitational acceleration, ν is the mean kinematic viscosity of the gas-vapour mixture, ρa is the gas density at the vessel wall and ρ_0 that at the centre. Thus Langstroth et al. found the influence of convection to be undetectable experimentally in flasks of 31 mm diameter or less, but quite significant in a flask of 43 mm diameter. In my experiments a conical flask of volume 500 ml. was used, and no adsorbent coating was applied. Convective flow induced by density gradients may be expected to have been important, in line with the experimental observations.

Summarizing, the three experiments[3,4,6] designed to examine the influence of gases on the rate of evaporation of water were carried out under conditions allowing considerable free convection for appropriate differences in density.

W. W. MANSFIELD

C.S.I.R.O. Chemical Research Laboratories,
Melbourne,
Australia.

[1] Boelter, L. K. M., Gordon, H. S., and Griffin, J. R., Indust. Eng. Chem., 38, 596 (1946).
[2] Coulson, J. M., and Richardson, J. F., Chemical Engineering, 1, 174 (Pergamon Press 1961).
[3] Kingdon, K. H., J. Phys. Chem., 67, 2732 (1963).
[4] Mansfield, W. W., Nature, 205, 278 (1965).
[5] Langstroth, G. O., Diehl, C. H., and Winhold, E. J., Canad. J. Res., 28 A, 580 (1950).
[6] Sechrist, F., Nature, 199, 899 (1963).

Photolysis of L-Histidine

IT is well known that ultra-violet irradiation of proteins can cause changes of physiological importance but, despite the increasing number of publications on aspects of this problem, little is known of the primary processes which must precede or accompany the destruction of the macromolecule. Our interest is in the mechanism of the photolytic degradation of some of the simple amino-acids as an aid to a better understanding of the primary photolytic processes. This communication gives the results of a detailed, but qualitative, chemical investigation of the products of photolysis of L-histidine as a first step in this broader study.

Irradiations were carried out on 0·032 M aqueous solutions adjusted to pH 7·4 with 2 N ammonia and kept at less than 20° C by a cold finger insert. The incident intensity of the light from a polychromatic mercury lamp with the major line at 336 mμ was about 1 watt/cm^{2}. The products were identified by paper chromatography.

From a 15-h photolysis the following products were identified : (a) aspartic, glutamic and γ-hydroxyglutamic * acids[1], serine, α-alanine, β-alanine, glycine and asparagine; (b) hydroxyproline, citrulline, urea *, histamine, 4-hydroxymethyl *-, 4-methyl *-, 4-formyl *-, 4-hydroxyethyl *-, and 4-ethyl *-imidazole and imidazole * itself, as well as imidazole acetic, imidazole lactic, urocanic and imidazole-4-carboxylic * acids. Oxalic * and glyoxalic * acids were recognized by specific tests[2], likewise CO_2. A positive test[3] for 2-hydroxyimidazole was obtained, but its validity is questionable under the reaction conditions. A 1-h photolysis under the same conditions gave the same pattern of end products. Quantitative variations in yield were apparent between the two parallel experiments, for example, histamine, glutamic, γ-hydroxyglutamic and urocanic acids increased in concentration with the shorter period of irradiation, while imidazole and 4-methylimidazole decreased. The differences became more marked as the irradiation time was shortened to 30- and to 15-min periods. In these last two cases, L-histidine labelled with ^{14}C at position 2 in the ring was photolysed, and detection of end products was limited to those compounds containing the label. All the degradation products in group (b) were again recognized with marked increases in concentration of histamine and urea at 15 min irradiation. Although a quantitative study is necessary and is under way, it is apparent that initial attack occurs at both the heterocyclic ring and the side chain. The side chain, in fact, appears remarkably sensitive to what is essentially oxidative photolysis in marked contrast to our experience in the case of tyrosine[4]. Several workers[5-8] have reported their findings from photolytic degradations of L-histidine under aerobic conditions and without exception their reports appear incomplete. Our results are explicable if in every case of bond rupture, the probability exists that hydrogen and hydroxyl moieties add to the reactive centres. Subsequent oxidative transformations may follow. Such a hypothesis led us to predict and confirm the presence of γ-hydroxyglutamic acid, and most of the other hitherto unobserved end products which are marked *. It is interesting to note that the majority of the imidazole-containing compounds identified are known to possess physiological properties similar to, but less efficient than, histidine itself[9].

R. B. JOHNS
T. JASKEWYCZ

Department of Organic Chemistry,
University of Melbourne,
Parkville, N.2,
Australia.

[1] Benoiton, L., and Bouthillier, L. P., Can. J. Chem., 33, 1473 (1955) ; Adams, E., and Goldestone, A., J. Biol. Chem., 235, 3504 (1960).
[2] Feigl, F., Spot Tests in Organic Analysis, 382 (Elsevier Publishing Co., 1960).
[3] Folin, O., and Ciocalteu, V., J. Biol. Chem., 73, 629 (1927).
[4] Gordon, P. G., and Johns, R. B. (unpublished results).
[5] Tomohiro, Y., Nagasaki Igakki Zassi, 28, 1117 (1953) ; Chem. Abs., 48, 6842g (1954).
[6] Fujiwarra, T., Takano, N., Morokuma, T., and Yamada, M., Nagasaki Igakki Zassi, 24, 726 (1954); Chem. Abs., 49, 2538f (1955).
[7] Luse, R. A., and McLaren, A. D., Photochemistry and Photobiology, 2, 343 (1963), and other references cited.
[8] Pavolini, T., Cultrera, R., and Piffiri, P. G., Gazz Chimica Ital., 91, 706 (1961) ; Chem. Abs., 56, 8204g (1962).
[9] Mosebach, K. O., Klinische Wochenschrift, 39, 80 (1961).

Electrolytically Activated Contractile Polymer

FOR several years it has been known that certain types of polymers, 'chemical muscles', change dimensions depending on their chemical environment[1]. A typical one is that prepared as a co-polymer of polyvinyl alcohol (PVA) and polyacrylic acid (PAA)[2]. This polymer swells or shrinks osmotically depending on the total ionic concentration inside the polymer. This is determined primarily by the