$C_{20}H_{22}O_6N_2$ requires C 62.16; H 5.74; N 7.25) was obtained from 3,3′,4,4′-tetramethoxychalcone oxide (3.44 g) in the same way with the exception that the main part of the epoxide remained undissolved in the initial boiling ethanolic mixture.

5-Phenyl-5-(1-phenylethyl)-hydantoin. The boiling solution of 2.38 g of dypnone oxide [6], (the crude epoxide containing both of the isomers may be used), in ethanol (20 ml) was treated with ethanolic potassium hydroxide and urea as above. The precipitation of a voluminous potassium salt followed close on the addition of the reagents. After refluxing the mixture for 2 h the precipitate was separated by filtration and washed with a small amount of ethanol. It was then dissolved in water (200 ml) by heating and adding a little sodium hydroxide. The solution thus obtained was saturated with carbon dioxide and the precipitated mass collected and recrystallised from ethanol. Yield 1.0 g (36 %), m.p. 305—307°. (Found: C 72.82; H 5.82; N 10.07; $C_{17}H_{16}O_2N_2$ requires C 72.84; H 5.75; N 9.99). The filtrate from the insoluble potassium salt was poured into water (400 ml). The solution was clarified by filtration and was then saturated with carbon dioxide. The obtained precipitate was collected and recrystallised from ethanol. Yield 1.1 g (39 %) of m.p. 265—266°, (Found: C 72.69; H 5.80; N 10.05; $C_{17}H_{16}O_2N_2$ requires C 72.84; H 5.75; N 9.99). The two products of this preparation are presumably the diastereoisomers of 5-phenyl-5-(1-phenylethyl)-hydantoin.

5-(2-Methoxyphenyl)-5-benzylhydantoin. 2′-Methoxychalcone oxide [7] (2.54 g) was treated with ethanolic potassium hydroxide and urea analogously with the model preparation above. After pouring the reaction mixture in water, the solution, however, was extracted with ether instead of being filtered, by reason of the stickiness of the cloudy precipitate. Saturation of the water phase, from which all the ether had been removed, with carbon dioxide, and repeated recrystallisation of the obtained precipitate from dilute ethanol gave 0.3 g (10 %) of m.p. 224°, (Found: C 69.11; H 5.87; N 9.44; $C_{17}H_{16}O_3N_2$ requires C 68.90; H 5.44; N 9.45).

Benzyl-(2-methoxyphenyl)-glycolic acid. The above procedure was repeated but without urea. The filtrate after precipitating α-hydroxy-2′-methoxychalcone with carbon dioxide was acidified with dilute sulphuric acid and the obtained precipitate recrystallised from dilute ethanol, yielding 0.35 g (13 %) of m.p. 183—184°, (Found: C 70.44; H 5.84; $C_{16}H_{16}O_4$ requires C 70.57; H 5.92).

α-Hydroxy-2′,4′,6′-trimethoxychalcone[7] but no hydantoin or hydroxy acid was obtained when 2′,4′,6′-trimethoxychalcone oxide was subjected to the described treatment with or without urea.

Work is in progress to find out suitable conditions for hydrolysis of the present hydantoins.

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A Contribution to the Principles of Electrodiffusion

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Electrodiffusion was suggested by Mysels [1] and Lamm [2] as a method for studying the equilibrium kinetics of certain reactions involving ions. The term refers to the increased diffusion which occurs on the superposition of an electric field in the diffusion direction. The magnitude of this effect is related to the field characteristics and to the kinetics of the system studied. More recently, Giddings [3-5] and Bak and Kauman [6] have contributed to the theory of electrodiffusion.

The theory of Mysels and that of Bak and Kauman refer (although this is not explicitly stated) to the case of selfdiffusion or to the case where a large excess of an electrolyte, which does not partake in the kinetic equilibrium, is added in order to maintain a constant field throughout the diffusion column. In this case the

Joule heat evolved in the cell may render experiments difficult because of the convection danger. It was evidently this fact which led Lamm [2] to study the possibility of obtaining an electrodiffusion effect of a mutual type with the system

$$AB \rightleftharpoons A^+ + B^-$$
$$C(1-a) \quad Ca \quad Ca$$
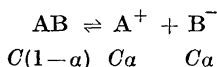
The theory overlooks, however, the fact that, due to the lack of divergence of the electric current, such an effect will not be obtained in a system that contains only those components which are involved in the dynamic equilibrium. In such a case each ion will migrate with a velocity proportional to its mobility and carry a constant proportion (equal to the transfer number) of the electric current. The latter being constant *, the velocities and also the step-lengths of the ions will be inversely proportional to the ionic concentration, C.

Now, ordinary (mutual) diffusion is the result of an assymmetrical initial condition and a random walk which attempts to smooth out the initial condition. It can, however, be shown that in the case mentioned the variation of the step-lengths has the effect of compensating the skewness of the initial condition. This is most easily realized in the case where a is small. In this case the migration rates are proportional to $1/Ca$. But the "lifetime" of the ions, $T^{\pm}$, is also proportional to $1/Ca$. Hence, the step-lengths are proportional to $1/(Ca)^2$:

$$l \sim 1/C^2a^2$$

Now, according to the law of mass action,

$$Ca^2(1-a) = K$$

so that for small a

$$l \sim 1/C^2a^2 \approx 1/KC$$

i. e. the step-lengths are inversely proportional to the total concentration. In cases where the migration rates of the positive and negative ions are equal, we obtain a simple visualization of electrodiffusion by regarding AB as concentrated in thin layers at a mutual distance equal to the step-length. Each layer will then contain an equal quantity of AB. This is essential, since we may now regard electrodiffusion

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* i. e. constant with respect to x but not with respect to t.

simply as a random walk of ions, A^+ or B^-, from layer to layer. Hence the ions will change places with one-another giving rise to self-diffusion but not to "ordinary" diffusion, the number of ions and molecules in the layers being unaffected by the random walk. If a is not small, the simple visualization breaks down and the argument becomes more complicated, but the final conclusion still holds.

It should perhaps be stressed that the lack of divergence which is responsible for the difficulties mentioned is a characteristic property of the electric current. In the chromatographic dispersion case treated by Giddings [4] we do not have this difficulty, which can be eliminated by the addition of KCl or some other electrolyte as will be more closely outlined below.

The formulae derived by Lamm [2] for the electrodiffusion coefficient of the positive and negative ions respectively, i.e. D^+ and D^-, are good approximations to the truth if the relative concentration change in the cell is small (differential diffusion). However, as already mentioned, the small variation of D^+ and D^- is sufficient to prevent any mutual diffusion from taking place. Since we thus have a case of pure self-diffusion it is obviously without meaning to speak of the diffusion of AB as a whole. Now, by adding a second electrolyte component, it is indeed possible to obtain a sort of mutual type diffusion in which, however, the presence of the additional electrolyte allows A^+ and B^- to diffuse more or less independently of one another.

Generally it will be necessary to use two components also from other reasons, e. g. to provide a suitable pH. If the quantity of the second electrolyte component is not too large the Joule heat evolved can be maintained within reasonable limits. It seems possible, in this way, to effect Lamm's original idea of a mutual type electrodiffusion. Another way is, of course, to measure the selfdiffusion of A^+ or B^- in the presence of a mutual gradient between AB and the medium.

Equations valid also for systems of this kind are given below (cf. Ref. [6]).

Symbols

a = degree of dissociation.
n = total number of species.
c_j = concentration of the species j in electrochemical equivalents per ml with the sign of the charge included.

(If the species is uncharged the sign may be chosen at will).

u_j = ionic mobility of j with the sign of the ionic charge included.

D_j = individual diffusion coefficient of j.

$\varkappa$ = specific conductivity (a function of time and position).

t = time.

t_j = transfer number of j.

x = height coordinate in diffusion cell.

$\mathbf{i}$ = current density (vector). ($\mathbf{i} = \mathbf{i}$ (t)).

i = current density in one-dimensional case. ($i = i$ (t)).

$\mathbf{X}$ = strength of superposed electric field (vector).

F = Faraday's constant.

$\mathbf{v}_j$ = velocity of the ion j (vector).

$\mathbf{J}_j$ = (electrophoretical) flow of the ionic species j (vector).

J_j = flow of j in one-dimensional case.

Q_j = net reaction rate.

Equations

The current density equals the product of the conductivity and the field strength:

$$\mathbf{i} = \varkappa \mathbf{X} \qquad (1)$$

The condition of electroneutrality reads

$$\sum_m c_m = 0 \qquad (2)$$

where m denotes summation over ionic species only.

For the conductivity we have

$$\varkappa = F \sum_m c_m u_m \qquad (3)$$

The ionic velocity equals the product of the mobility and the field strength

$$\mathbf{v}_j = u_j \mathbf{X} = u_j \mathbf{i}/\varkappa \qquad (4)$$

Hence we have for the electrophoretical flow

$$\mathbf{J}_j = c_j \mathbf{v}_j = c_j u_j \mathbf{X} = c_j u_j \mathbf{i}/\varkappa = \frac{\mathbf{i}}{F} \frac{c_j u_j}{\sum_m c_m u_m} \qquad (5)$$

Leaving out the terms relating to ordinary diffusion we have

$$(\partial c_j/\partial t) = - \operatorname{div} \mathbf{J}_j + Q_j(c_1, c_2, \cdots, c_n) \qquad (6)$$

where Q_j represents the purely chemical rate law, e. g.

$$Q_j = \sum_p k_{jp}\, c_1^{r_{1p}} c_2^{r_{2p}} \cdots c_n^{r_{np}}$$

In the one-dimensional case we have

$$J_j = i c_j u_j / F \sum_m c_m u_m \qquad (7)$$

and

$$\frac{\partial c_j}{\partial t} = Q_j(c_1, \cdots, c_n) - \frac{i}{F} \frac{\partial}{\partial x} \left(\frac{c_j u_j}{\sum_m c_m u_m} \right) \qquad (8)$$

Including additional terms arising from ordinary diffusion, the equation reads

$$\frac{\partial c_j}{\partial t} = Q_j(c_1, \cdots, c_n) - \frac{i}{F} \frac{\partial}{\partial x} \left(\frac{c_j u_j}{\sum_m c_m u_m} \right) +$$
$$+ D_j \frac{\partial^2 c_j}{\partial x^2} - \frac{\partial}{\partial x} (c_j u_j X') \qquad (9)$$

where

$$X' = \frac{\sum_m D_m (\partial c_m/\partial x)}{\sum_m c_m u_m} \qquad (10)$$

is the Nernst ("internal") potential gradient, which depends exclusively on the concentrations and the concentration gradients but not directly on the superposed field.

The quasilinear system (8) of first order partial differential equations will give a complete description of electrodiffusion in all kinds of systems. It may be regarded as a combination of Kohlrausch's differential equation known from electrophoresis with the well-known chemical rate laws. It should not be overlooked that the mathematical difficulties involved in solving these equations may be considerable.

Finally it should be pointed out that the absence of an effect in the case AB follows in a very easy way from these equations. If no other electrolyte is added we have

$$\frac{\partial}{\partial x} \left(\frac{c_j u_j}{\sum_m c_m u_m} \right) = \frac{\partial t_j}{\partial x} = 0$$

where t_j denotes the transfer number.

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