at 253 and 294 mμ were consistent with the presence of the expected 2-acetylthiazolium salt. The band near 300 mμ, which is characteristic of the 2-acetyl substituted thiazole chromophore, was absent when the spectra were run in water or methanol. Furthermore, solution of the mixture for ten minutes in methanol at room temperature, then ether precipitation, led to a 50% decrease in the intensity of the carbonyl band at 5.85 μ, accompanied by the appearance of a new band at 10.7 μ; repeated methanol treatment led to further decrease in the carbonyl band and increase in the 10.7 μ absorption. Since this latter is the C–H bending vibration characteristic of thiazolium salts unsubstituted at C-2[2], it is apparent that the process being observed is a deacylation at C–2.

The leaving group in the deacylation reaction is the same thiazolium zwitterion which has been detected previously,[2] but the lability of the 2-acetylthiazolium salts is much greater than would be expected solely from the stability of this thiazolium zwitterion, and it seems likely that dipole-dipole repulsion in the ketone is also an important factor. At any rate, these results furnish additional support for the mechanism of thiamine action already proposed.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, NEW YORK

RONALD BRESLOW
EDWARD MCNELIS

RECEIVED MARCH 17, 1960

---

## VERIFICATION OF THE ONSAGER LIMITING LAW FOR TRACE-ION DIFFUSION IN ELECTROLYTE SOLUTIONS

*Sir:*

In 1945, Onsager[1] formulated a theoretical expression for the concentration-dependence of trace-ion diffusion and his equations later were translated into a more practical form and also adapted to the self-diffusion case by Gosting and Harned[2] in 1951. The resulting equation for 1:1 electrolytes at 25° is of the form

$$D_j = D_j^\circ\,[1 - 0.7816(1 - \sqrt{d(w)_j})\sqrt{c}] \qquad (1)$$

$d(w_j)$ being a function of the mobilities and valencies of the ions. This is the only limiting equation stemming from the Debye–Hückel theory of interionic attraction that has not been tested experimentally. The usual experimental diffusion methods are inadequate; the diaphragm cell gives inaccurate data in the dilute concentrations due to adsorption effects and the normal open-ended capillary method has, at best, a precision of *ca.* ±1%.

However, the continual monitoring capillary method, developed by Mills and Godbole,[3,4] can provide data with precision better than ±0.2% and should therefore be capable of testing the law. We wish to report self-diffusion coefficients of $Na^+$ ion in dilute sodium chloride solutions as determined with this method. Table I shows the results obtained to date, of an average precision of ± 0.18%, together with values calculated from the limiting law.

TABLE I

| *c*, mole/l. | *D*(obs.) cm.²/sec. | *D*(calcd.) cm.²/sec. |
|---|---|---|
| 0.000225 | 1.335 | 1.330 |
| .00076 | 1.332 | 1.326 |
| .00102 | 1.327 | 1.325 |
| .00500 | 1.319 | 1.315 |
| .0101 | 1.312 | 1.307 |
| .0252 | 1.297 | 1.291 |
| .0286 | 1.298 | 1.288 |
| .0495 | 1.294 | 1.274 |
| .0575 | 1.289 | 1.269 |
| .097 | 1.280 | 1.250 |

Extrapolation of the last four points gives a $D^\circ$ of 1.337 compared with the Nernst limiting value of 1.334.

The results also are illustrated in Fig. 1. It will be observed that for concentrations <0.002*M*, the limiting equation appears to be valid. Further, by replacing the factor $\sqrt{c}$ in equation (1) by $\sqrt{c}/(1 + \kappa a)$, the experimental points can be described to *ca.* 0.04*M*, using an "*a*" value of 4Å.

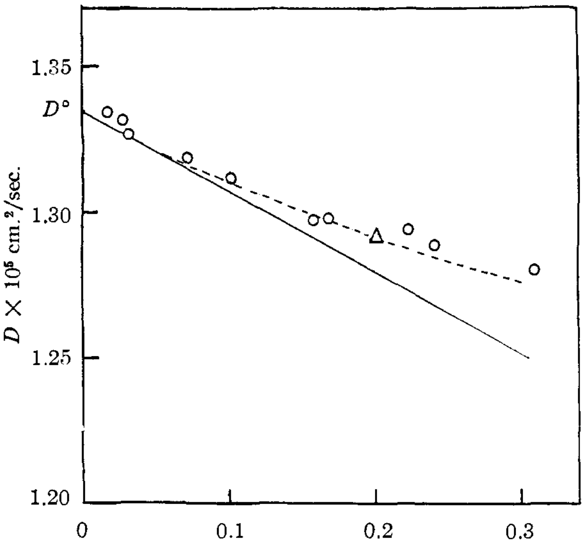


Fig. 1.—Self-diffusion coefficients of $Na^+$ in aqueous sodium chloride at 25°: ○, this work; △, Mills and Adamson; ———, Onsager limiting slope; – – – –, ion size extension (å = 4).

A feature of the experimental method that is not entirely satisfactory and needs further investigation, is the question of the correct flow rate to be maintained across the mouth of the capillary. We have attempted to overcome this difficulty by calibrating the apparatus for flow conditions against the $Na^+$ self-diffusion data of Mills and Adamson.[5] Agreement for a specified flow is obtained with their data at concentrations of 0.04*M* and 1.44*M*. However, this calibration procedure is an indirect method since the cell has in turn to be calibrated against optical data and, further, the average precision of Mills and Adamson's data is only of the order of ±0.4%.

---

(1) L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

(2) L. J. Gosting and H. S. Harned, THIS JOURNAL, **73**, 159 (1951).

(3) R. Mills and E. W. Godbole, *Aust. J. Chem.*, **11**, 1 (1958).

(4) R. Mills and E. W. Godbole, *ibid.*, **12**, 102 (1959).

(5) R. Mills and A. W. Adamson, THIS JOURNAL, **77**, 3454 (1955).

Stokes[6] has suggested that we can use a radiotracer method to measure salt-diffusion coefficients in the case where the ratios of isotopic concentrations are the same inside and outside the capillary. This would allow the continual monitoring apparatus with its high precision to be calibrated directly against other precise data. For instance, Harned and Hildreth's[7] conductiometric NaCl diffusion values, whose smoothed curves ought to be accurate to within ±0.1–0.2%, could be used. In such a determination, we need to have a solution of the diffusion equation for the capillary conditions with a concentration-dependent *D* and this has been formulated recently by Mills and Blackwell.[8] When our flow conditions have been confirmed by this new type of calibration, these investigations will be published in more detail.

(6) R. H. Stokes, private communication.

(7) H. S. Harned and C. L. Hildreth, THIS JOURNAL, **73**, 650 (1951).

(8) R. Mills and J. W. Blackwell, in press.

RESEARCH SCHOOL OF PHYSICAL SCIENCES
AUSTRALIAN NATIONAL UNIVERSITY REGINALD MILLS
CANBERRA, A. C. T., AUSTRALIA E. W. GODBOLE

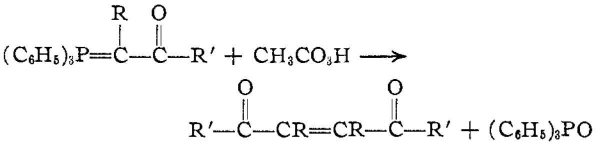
RECEIVED JANUARY 15, 1960

---

## THE FORMATION OF OLEFINS FROM WEAKLY BASIC PHOSPHORANES AND PERACETIC ACID

*Sir:*

In recent years the reactions of phosphoranes have assumed considerable importance. In many cases they provide an easy route to otherwise difficultly obtainable substances.[1] It has now been found that weakly basic phosphoranes react with peracetic acid (40% in acetic acid) to give poor to good yields of the dimeric olefin and the phosphine oxide.



$$(C_6H_5)_3P{=}\overset{\overset{\displaystyle R}{|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + CH_3CO_3H \longrightarrow R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CR{=}CR{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + (C_6H_5)_3PO$$

R = H, $CH_3$; R′ = $CH_3$, $C_6H_5$ $OC_2H_5$

These reactions have been conducted by adding the peracetic acid (slightly more than 1 mole) to a solution of the phosphorane (1 mole) in benzene. The reactions are in general vigorously exothermic. The products have been isolated by basic extraction of the reaction mixture with subsequent removal of the solvent and extraction of the residue with hexane. The olefinic product in these cases is soluble in hexane while the triphenylphosphine oxide is not. Thus, $(C_6H_5)_3P{=}CHCOC_6H_5$ gave triphenylphosphine oxide (I) in 86% yield and *trans*-dibenzoylethylene (73%), m.p. 110–112° (lit.[2] 111°). The *trans*-dibenzoylethylene was converted to 3,6-diphenylpyridazine, m.p. 220–222° (lit.[2] 221–222°). Similarly, $(C_6H_5)_3P{=}CH{-}COCH_3$ gave I and *trans*-diacetylethylene (52%), m.p. 78–79.5° (lit.[3] 78°), di-2,4-dinitrophenylhydrazone, m.p. 290–292° (lit.[3] 291–292°). Reaction of $(C_6H_5)_3P{=}CHCO_2C_2H_5$ afforded I (96%) and diethyl fumarate (41%), b.p. 100° (block) at 10 mm., infrared spectrum identical to that of a known sample. This material was further characterized by conversion to di-*p*-nitrobenzyl fumarate, m.p. 152–153° (lit.[4] 151°). The phosphorane, $(C_6H_5)_3P{=}C(CH_3){-}CO_2C_2H_5$, gave I (89%) and diethyl dimethylfumarate, b.p. 105° at 9 mm. (lit.[5] 111° at 12 mm.), yield 7%. Saponification yielded the acid, m.p. 247–248° (lit.[6] 240°). The infrared spectra were in agreement with the assigned structures of all of the compounds listed above.

Treatment of phenylmethylenetriphenylphosphorane, $(C_6H_5)_3P{=}CH{-}C_6H_5$, in ethanol with peracetic acid gave no stilbene. Triphenylphosphine oxide was formed in 66% yield. It is felt that the greater base strength of this phosphorane caused formation of the phosphonium salt which subsequently decomposed to triphenylphosphine oxide and presumably toluene. This reaction could also contribute to a lowering of the yields from the other phosphoranes.

Recently Bestmann[7] has shown that oxygen sensitive phosphoranes can be converted to dimeric olefins and phosphine oxides by treatment with oxygen. His method and that now being reported complement each other and therefore provide routes to a wide variety of unsaturated materials. The mechanism of the peracetic acid reaction is under study as is its application to synthesis.

(1) U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

(2) C. Paal and H. Schulze, *Ber.*, **33**, 3798 (1900).

(3) K. F. Armstrong and R. Robinson, *J. Chem. Soc.*, 1650 (1934).

(4) J. A. Lyman and E. E. Reid, THIS JOURNAL, **39**, 708 (1917).

(5) K. v. Auwers and L. Harres, *Ber.*, **62**, 1685 (1929).

(6) C. K. Ingold, *J. Chem. Soc.*, 397 (1923).

(7) H. J. Bestmann, *Angew. Chem.*, **72**, 34 (1960).

(8) National Science Foundation Coöperative Graduate Fellow, 1959–1960.

SCHOOL OF CHEMISTRY DONALD B. DENNEY
RUTGERS, THE STATE UNIVERSITY
NEW BRUNSWICK, NEW JERSEY LOIS CRISBACHER SMITH[8]

RECEIVED MARCH 29, 1960

---

## STEREOCHEMISTRY OF DISPLACEMENT REACTIONS AT AN ASYMMETRIC PHOSPHONIUM CATION

*Sir:*

Methylethylphenylbenzylphosphonium iodide (I), in which the phosphorus atom is the sole center of asymmetry, has been resolved recently.[1] Reaction of optically pure dextrorotatory I with sodium hydroxide gave optically pure levorotatory methylethylphenylphosphine oxide (II), $[\alpha]^{25}_D$ −22.8 ± 1.0° (*c*, 2.168 in water). In like manner, levorotatory I formed optically pure dextrorotatory II, $[\alpha]^{25}_D$ 22.4 ± 1.0°.[2] A kinetic study revealed that the reaction is third order, showing a first-order dependence on the concentration of I and a second-order dependence on the concentration of sodium hydroxide.[3]

It now has been determined that the Wittig reaction as applied to I is both product specific and stereospecific. Treatment of 0.02 mole of dextrorotatory I with 0.025 mole of phenyllithium in ether solution, and addition of 0.024 mole of

(1) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, THIS JOURNAL, **81**, 248 (1959).

(2) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).

(3) M. Zanger, C. A. VanderWerf and W. E. McEwen, *ibid.*, **81**, 3806 (1959).