

[CONTRIBUTION FROM THE CLARKSON COLLEGE OF TECHNOLOGY]

**Transference Number of Phosphoric Acid by the E.m.f. Method**

BY MILTON KERKER AND WILTON F. ESPENSCHIED

RECEIVED AUGUST 7, 1957

The limiting conductance of  $\text{H}_2\text{PO}_4^-$  obtained from the transference number of phosphoric acid by the e.m.f. method does not agree with that obtained from conductance data and is anomalously low. Agreement between the two methods can be obtained by postulating the presence of the ionic species,  $\text{H}_4\text{PO}_4^+$ . Errors made by other workers in interpreting the e.m.f. data are pointed out.

The limiting conductance of the dihydrogen phosphate ion,  $\lambda^0_{\text{H}_2\text{PO}_4}$ , was determined by Mason and Culvern<sup>1</sup> to be 33.0 on the basis of the conductance of  $\text{NaH}_2\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$ . In order to check this surprisingly low value, they also made e.m.f. measurements with suitable concentration cells using the lead amalgam-lead hydrogen phosphate electrode.

Their interpretation of the e.m.f. data led Mason and Culvern to a value for  $\lambda^0_{\text{H}_2\text{PO}_4}$  in agreement with that based on conductance. We find that their interpretation is incorrect and that when their data are recalculated,  $\lambda^0_{\text{H}_2\text{PO}_4}$  becomes anomalously low.

We have studied a similar pair of concentration cells using mercury-di-mercury hydrogen phosphate electrodes and have obtained the same value for  $\lambda^0_{\text{H}_2\text{PO}_4}$  as Mason and Culvern. In order to reconcile these results with those based on conductance, we suggest the possibility of the presence of the ionic species  $\text{H}_4\text{PO}_4^+$ , even in dilute solutions.

**Theoretical**

We have studied the cell with transference  $\text{Hg}, \text{Hg}_2\text{HPO}_4, \text{H}_3\text{PO}_4(m_1) | \text{H}_3\text{PO}_4(m_2), \text{Hg}_2\text{HPO}_4, \text{Hg}$  (I) and by comparison with the corresponding cell without transference studied by Larson<sup>2</sup>  $\text{Hg}, \text{Hg}_2\text{HPO}_4, \text{H}_3\text{PO}_4(m_1), \text{H}_2, \text{Pt}, \text{H}_2, \text{H}_3\text{PO}_4(m_2), \text{Hg}_2\text{HPO}_4, \text{Hg}$  (II)

have calculated the transference number of phosphoric acid.

There are very few studies of concentration cells with transference involving polybasic acids. In addition to the cell used by Mason and Culvern, Ferguson and France<sup>3</sup> and Hamer<sup>4</sup> worked with an aqueous sulfuric acid cell and Kanning and Waltz<sup>5</sup> have studied the same cell with methanol solutions of sulfuric acid. The interpretation of the data in all of this work was limited by the fact that none of these authors appreciated that the transference number in the e.m.f. expression was that of an ion constituent rather than of an individual ionic species.<sup>6</sup>

The treatment of the standard treatises on electrochemistry<sup>7</sup> of the determination of transference

(1) C. M. Mason and J. B. Culvern, *THIS JOURNAL*, **71**, 2387 (1949).

(2) W. D. Larson, *J. Phys. Colloid Chem.*, **54**, 310 (1950).

(3) A. L. Ferguson and W. F. France, *THIS JOURNAL*, **43**, 2150 (1921).

(4) W. J. Hamer, *ibid.*, **57**, 662 (1935).

(5) E. W. Kanning and J. E. Waltz, *ibid.*, **63**, 2676 (1941).

(6) M. Kerker, *ibid.*, **79**, 3664 (1957).

(7) S. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand, Inc., New York, N. Y., 1948, p. 205. D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 222. H. S. Harned and B. B. Owen, "The

numbers by comparison of the e.m.f.'s of cells with and without transference is restricted to 1-1 electrolytes. For this case

$$\frac{dE_t}{dE} = \pm t_{\pm} \quad (1)$$

where  $E_t$  and  $E$  represent the e.m.f.'s of cells with and without transference. Whether the above equation gives the cation or anion transference number depends upon the ion to which the electrodes in the cell with transference are reversible.

For the e.m.f. method, just as for the Hittorf and moving boundary methods, the situation is somewhat complicated for partially ionized electrolytes containing more than two ionic species. Spiro<sup>8</sup> has discussed this matter critically with reference to the latter two methods and has pointed out that experimentally both lead to the same result, namely, the transference number of the ion constituent. However, although the e.m.f. method also gives the transference number of the ion constituent, this quantity, in general, is not obtained directly from equation 1.

For a polybasic acid,  $\text{H}_n\text{A}$ , consisting of ionic species  $\text{H}^+$ ,  $\text{H}_{n-1}\text{A}^-$ ,  $\text{H}_{n-2}\text{A}^{2-}$ , . . . . .  $\text{A}^{n-}$ , the e.m.f. of a cell with transference is given by

$$E_t = \frac{n+1}{n} \times \frac{RT}{F} \int_{m_2}^{m_1} t \, d \ln a_{\pm} \quad (2)$$

where  $m_1$  and  $m_2$  are the stoichiometric concentrations of the acid in the anode and cathode compartments, respectively. The mean ionic activity is related to the ionic activities by

$$a_{\pm} = (a_{\text{H}^+} a_{\text{A}^{n-}})^{1/n+1} \quad (3)$$

The activities of the other ionic species can be related to the above with the appropriate equilibrium constants. The transference number,  $t$ , is

$$t = t_{\text{H}} - \sum_{i=1}^n \frac{n-i}{i} t_{\text{H}_{n-1}\text{A}^-} - Q \quad (4)$$

The ionic transference numbers,  $t_{\text{H}}$ ,  $t_{\text{H}_{n-1}\text{A}^-}$ , are the fraction of current carried by the ion denoted in the subscript and are related to the equivalent conductance,  $\lambda_i$ , and the normality,  $(c_i)$ , of the ions by

$$t_i = \frac{\lambda_i c_i}{\sum \lambda_i c_i} \quad (5)$$

The quantity  $Q$  is determined by the ion to which the electrodes are reversible. For hydrogen electrodes,  $Q = 1$ . For electrodes reversible to the various anionic species  $Q = (n+z)/z$  where  $z$  is the signed charge of the anion.

Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, pp. 309, 352.

(8) M. Spiro, *J. Chem. Educ.*, **33**, 464 (1956).

Operationally,  $t$  is the number of equivalents of acid transferred from anode to cathode compartment per faraday passed. Since the concentration of both the hydrogen and A ion constituent are identical with the stoichiometric normality of the acid,  $H_nA$ , there is no distinction between the transference number of the anion constituent and that for the cation. Although it is still meaningful to talk about individual ion transference numbers, the quantity which is physically transferred is the acid,  $H_nA$ .

The cell without transference consists of two pairs of electrodes, one of which is identical to the electrodes in the cell with transference. If this pair is chosen for the outer electrodes, the e.m.f. of the cell is given by

$$E = \frac{n+1}{z} \times \frac{RT}{F} \int_{m_2}^{m_1} d \ln a_{\pm} \quad (6)$$

where again  $z$  is the signed charge of the anion to which one pair of the electrodes will be reversible. Interchange of the inner and outer electrodes changes the sign of the above.

The transference number is given by

$$\left(\frac{dE_t}{dE}\right)_m = \mp \frac{z}{n} t \quad (7)$$

For cells I and II, this reduces to (see Appendix)

$$\left(\frac{dE_t}{dE}\right)_m = \frac{2}{3} [t_H - 2t_{H_2PO_4} - 0.5t_{HPO_4} + 0.5] \quad (8)$$

The second ionization of phosphoric acid is not appreciable so that equation 8 can be approximated by

$$\left(\frac{dE_t}{dE}\right)_m = \frac{2}{3} [t_H - 2t_{H_2PO_4} + 0.5] \quad (8')$$

### Experimental

**A. Materials.**—Di-mercurous hydrogen phosphate,  $Hg_2HPO_4$ , was prepared by the same procedure used by Larson.<sup>2</sup> The salt was washed four or five times with distilled water. For analysis, the samples were dried at 110°, and the mercury was deposited electrolytically by the method given by Treadwell-Hall.<sup>9</sup> The compound  $Hg_3PO_4$  contains 86.4% mercury, whereas  $Hg_2HPO_4$  contains 80.6% mercury. The compound we prepared contained 80.4 ± 0.2% mercury.

Fisher certified phosphoric acid was used without further purification. A stock solution was analyzed by precipitation of the phosphate as  $MgNH_4PO_4$  and subsequent ignition to the pyrophosphate according to the method described by Kolthoff and Sandell.<sup>10</sup> The working solutions were then made up from this gravimetrically.

**B. Cells.**—A modified calomel type electrode vessel was used.<sup>11</sup> The side arm which normally dips into a solution was constructed with a double bend to slow down diffusion. Electrical contact was through a platinum wire fused into the side arm for mercury contact. The tips of each electrode vessel which would normally dip into a solution were joined to the arms of a three way stopcock. After filling, the entire apparatus was lowered into a constant temperature bath maintained at 25.00 ± 0.05° and, upon reaching equilibrium, the liquid junction was formed by turning the three way stopcock.

**C. Procedure.**—The cells were prepared by first washing the  $Hg_2HPO_4$  several times with phosphoric acid of the same concentration with which it was to be used. The salt was then ground into a paste with some mercury and per-

mitted to stand at least overnight in contact with the phosphoric acid solution to be studied. Mercury was placed in the vessel which was then filled with phosphoric acid and finally a small amount of the paste was added, settling down as a fine layer on the mercury. The stopcock connecting the two electrodes was kept closed except while readings were taken.

The e.m.f. was determined with a Leeds and Northrup type K potentiometer using a Leeds and Northrup lamp and scale galvanometer of sensitivity 0.04 microampere per scale division. The standard cell was of the Eppley unsaturated cadmium type, guaranteed by the manufacturer to be within 0.01% of the certified 1.01923 volts at 23° with a negligible temperature coefficient.

### Results

The results of our e.m.f. measurements,  $E_t$ , at rounded concentrations are given in column 2 of Table I. Those of Larson,  $E$ , are shown in column 3. These data are for a reference electrode of 0.02  $M$   $H_3PO_4$ .

TABLE I

ELECTROMOTIVE FORCE AND CALCULATED TRANSFERENCE NUMBERS FROM PHOSPHORIC ACID CONCENTRATION CELLS						
$m$	$E_t$	$E$	$dE_t/dE$	$dE_t/dE^a$	$t_H$	$t_H^a$
0.00			0.920	0.914	0.960	0.957
.02	0.0000	0.0000	.903	.89	.952	.945
.05	.0124	.0139	.881	.86	.941	.93
.10	.0213	.0239	.865	.84	.933	.92
.20	.0297	.0340	.849	.82	.925	.91
.30	.0341	.0397	.839	.81	.920	.905
.50	.0403	.0471	.827	.80	.914	.90
.80	.0458	.0539	.816	.79	.908	.895
2.00	.0575	.0678	.794	.76	.897	.88
4.00	.0667	.0776	.778	.73	.889	.865

<sup>a</sup> From Mason and Culvern (ref. 1).

In order to reduce the e.m.f.'s obtained from the experimental concentrations to the tabulated rounded values, the following procedure was used. Consider two experimental concentrations  $m$  and  $n$  which are close to the rounded concentrations  $M$  and  $N$ . Then the e.m.f. of the cell with transference is

$$E_{MN} = E_{mn} + \frac{4RT}{3F} \int_M^N t d \ln a_{\pm} - \frac{4RT}{3F} \int_m^n t d \ln a_{\pm} \quad (9)$$

Over this range of concentration,  $t$  is practically constant and can be estimated closely enough by direct comparison of  $E_{(mn)}$  with the data for the cells without transference. Furthermore

$$a_{\pm} = (a_H^3 a_{PO_4})^{1/4} = a_{H_3PO_4} K \quad (10)$$

where  $K$  is an equilibrium constant. This leads to

$$E_{MN} = E_{mn} + \frac{4RT}{3F} t \ln \frac{a_N a_m}{a_M a_n} \quad (11)$$

where  $a_N$  is the activity of undissociated  $H_3PO_4$  in a solution of concentration  $N$ . The activities of the  $H_3PO_4$  have been obtained from the vapor pressure data of Mason and Blum.<sup>12</sup>

Overlapping concentrations were selected so that every determination could be checked for consistency. For example, the cell with concentrations 0.0981 and 0.7865  $m$  gave  $E_t = 0.0240$  v. and that with 0.7865 and 3.941  $m$  gave 0.0211 v. The cell with concentrations 0.0981 and 3.941  $m$  which

(9) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948.

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Book Co., New York, N. Y., 1952.

(11) Wilson Type, Fisher Co. Catalogue number 11-506-40.

(12) C. M. Mason and W. M. Blum, THIS JOURNAL, 69, 1246 (1947).

should have given the sum of the above voltages, 0.0451 v., actually gave 0.0450 v. In nearly all cases the agreement was within 0.1 millivolt. The data in Table I are a summary of 22 cells.

By using the method of least squares we obtain

$$E_t = 0.903E - 0.802E^2 \quad (12)$$

Upon differentiating this

$$\frac{dE_t}{dE} = 0.903 - 1.604E \quad (13)$$

The derivative  $dE_t/dE$  is listed in column 4 of Table I. In column 5 we have compiled the same quantity obtained by Mason and Culvern for their cells with lead amalgam-lead hydrogen phosphate electrodes. The values extrapolated to zero concentration are for the hypothetical state where the phosphoric acid would be completely dissociated into  $H^+$  and  $H_2PO_4^-$  since at none of the experimental concentrations are there significant quantities of  $HPO_4^{2-}$  or  $PO_4^{3-}$ .

Mason and Culvern interpret the quantity  $dE_t/dE$  as giving the hydrogen ion transference number directly. This is incorrect as we have shown above. In order to calculate  $t_H$ , it is necessary to use equation 8' as well as

$$t_H + t_{H_2PO_4} \cong 1 \quad (14)$$

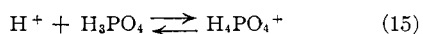
In columns 6 and 7 of Table I are listed  $t_H$  calculated from both our results and those of Mason and Culvern.

We obtained the value of  $t_H$  at infinite dilution by extrapolation of the curve of  $t_H$  against the square root of the concentration. Mason and Culvern did not use their results at less than 0.1 *m* in their extrapolation. Although the agreement between the extrapolated values of  $t_H$  is quite striking, this is probably fortuitous. If Mason and Culvern had given any weight to their data at 0.05 and 0.02 *m*, their  $t_H$  would have been somewhat higher. We are unable to account for the divergence of the results at the higher concentrations. The differences are considerably beyond that expected from the experimental error of 0.1 mv. Of course, the results we report are subject to any possible errors in Larson's work as well as our own.

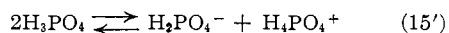
Using a limiting conductance for phosphoric acid of 383 as did Mason and Culvern, we obtain a value for  $\lambda^0_{H_2PO_4}$  of 16. This is obviously out of line with the value of 33 obtained from conductance and much lower than what would normally be expected.

Apparently,  $t$ , the number of equivalents of phosphoric acid transferred is greater than what would be expected on the basis of the mechanism of ionic conduction which we have assumed. If we could account for the transference of additional phosphoric acid to the cathode, these results could be explained.

It is conceivable that such phosphoric acid could be carried by the species  $H_4PO_4^+$ , present due to the reaction



or alternatively



If this were the case, the expression for the trans-

ference number would be

$$t = t_H + 4t_{H_4PO_4} - 2t_{H_2PO_4} - 0.5t_{HPO_4} - Q \quad (16)$$

and the quantity actually determined in columns 6 and 7 of Table I would be

$$t'_H = t_H + 4t_{H_4PO_4} \quad (17)$$

It is possible to calculate an equivalent conductance and concentration for this species. Consider in addition to equation 17 the relations

$$\Lambda_{H_4PO_4} = c_H \lambda_H + c_{H_2PO_4} \lambda_{H_2PO_4} + c_{H_4PO_4} \lambda_{H_4PO_4} \quad (18)$$

$$K_1 = \frac{c_H c_{H_2PO_4}}{c_{H_3PO_4}} \times \frac{\gamma_{\pm}}{\gamma} \quad (19)$$

where

$$c_H = \alpha(1 - \beta)c$$

$$c_{H_4PO_4} = (1 - \alpha - \alpha\beta)c$$

$$c_{H_2PO_4} = \alpha c$$

$$\alpha = \text{fraction of } H_3PO_4 \text{ ionized}$$

$$\beta = \text{fraction of } H^+ \text{ associated to } H_4PO_4^+$$

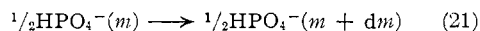
For 0.001 *M*  $H_3PO_4$ , the ionic strength can be estimated to be 0.0009. Using the Debye-Hückel limiting law  $\gamma_{\pm} = 0.965$ . From Mason and Culvern's work  $\gamma = 0.998$  and  $\Lambda_{H_3PO_4} = 336.4$ . Using the limiting conductances given by Mason and Culvern and the Onsager conductance equation,  $\lambda_H = 346.5$  and  $\lambda_{H_2PO_4} = 31.9$ . The value for  $K_1$  given by Nims<sup>13</sup> is  $7.537 \times 10^{-3}$ . Averaging the two sets of data, we find  $t'_H = 0.952$  at this concentration. This leads to  $\alpha = 0.89$ ,  $\beta = 0.015$  and  $\lambda_{H_4PO_4} = 250$ .

We have attempted to obtain independent data for the transference number of phosphoric acid by the Hittorf method but were unsuccessful in preparing non-gassing electrodes. We plan to try the moving boundary method to see whether it will also lead to these unexpectedly high values.

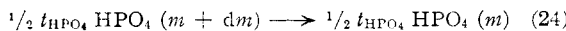
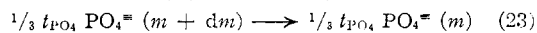
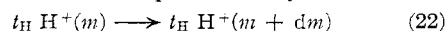
**Acknowledgment.**—We wish to acknowledge the financial assistance obtained from the Atomic Energy Commission which made this work possible.

## Appendix

**Transference Number Expression for Phosphoric Acid.**—When  $m_2$  is only infinitesimally greater than  $m_1$ , for each faraday of electricity passed through Cell I, the reaction at the electrodes is



and the transfer of material by migration across the liquid junction can be represented by



The net cell reaction is obtained by addition of equations 21 to 25, and from this the e.m.f. of the cell is

$$\frac{dE_t}{dE} = \frac{RT}{F} \ln \left[ a_{H^+}^{t_H} \times a_{H_2PO_4^-}^{-1} \times a_{HPO_4^{2-}}^{-1/2} (t_{HPO_4} - 1) \times a_{PO_4^{3-}}^{-1/3} t_{PO_4} \right] \quad (26)$$

In the above,  $a$  with the appropriate subscript represents the activity of an ionic species. By

(13) L. F. NIMS, THIS JOURNAL, 56, 1110 (1934).

utilizing the equilibrium relations

$$K_2 = \frac{a_{\text{H}} a_{\text{HPO}_4}}{a_{\text{H}_2\text{PO}_4}} \quad (27)$$

$$K_3 = \frac{a_{\text{H}} a_{\text{PO}_4}}{a_{\text{HPO}_4}} \quad (28)$$

and

$$t_{\text{H}} + t_{\text{H}_2\text{PO}_4} + t_{\text{HPO}_4} + t_{\text{PO}_4} = 1 \quad (29)$$

we can obtain

$$dE_t = (t_{\text{H}} - 2t_{\text{H}_2\text{PO}_4} - 0.5t_{\text{HPO}_4} + 0.5) \frac{4RT}{3F} d \ln a_{\pm} \quad (30)$$

where the mean ionic activity is defined by

$$a_{\pm} = (a_{\text{H}} a_{\text{PO}_4})^{1/4} \quad (31)$$

A similar analysis of Cell II leads to

$$dE = \frac{2RT}{F} d \ln a_{\pm} \quad (32)$$

so that

$$\frac{dE_t}{dE} = \frac{2}{3} (t_{\text{H}} - 2t_{\text{H}_2\text{PO}_4} - 0.5t_{\text{HPO}_4} + 0.5) \quad (7)$$

POTSDAM, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

## The Thermal Decomposition of 2,2'-Azo-bis-isobutyronitrile

BY J. P. VAN HOOK<sup>1</sup> AND A. V. TOBOLSKY

RECEIVED APRIL 30, 1957

The thermal decomposition of 2,2'-azo-bis-isobutyronitrile has been studied at five temperatures between 100 and 37° by applying the ultraviolet absorption technique. The kinetics of the decomposition have also been investigated at 30.5° by a manometric method. A composite Arrhenius plot using all the available data for the decomposition is given. The over-all rate expression for decomposition of the azo compound in solution is:  $k_d = 1.58 \times 10^{16} \exp(-30.8 \text{ kcal./RT})$ .

### Introduction

Although the compound 2,2'-azo-bis-isobutyronitrile (Azo I) has been quite extensively studied it was felt that further work at temperatures below 60° was necessary in order to arrive at a more complete and satisfactory expression for the rate of thermal decomposition. This is important for an accurate evaluation of the initiator efficiency. The application of Azo I to polymerization kinetics and particularly to initiator efficiency is discussed in a subsequent paper.

Since the elimination of nitrogen from Azo I is quantitative, several investigators<sup>2-5</sup> have utilized the volumetric technique to establish the over-all rate of decomposition. Roy, *et al.*,<sup>9</sup> have measured the nitrogen evolution manometrically. From these studies it was shown that the rate of decomposition is independent of the nature of the solvent and the reaction has the advantage of not being complicated by induced decomposition. The work of Lewis and Matheson,<sup>1</sup> Ziegler, *et al.*,<sup>5</sup> and Roy, *et al.*,<sup>9</sup> includes rate constants for the azo cleavage obtained both in the presence and absence of radical scavengers such as tetrachloroquinone, chloranil and iodine, respectively. The presence of these strong inhibitors has no apparent effect on the rate

of nitrogen evolution. Some investigators have reported a slight induction period in the reaction when the volumetric method is employed but Hyson and Beasley<sup>10</sup> state that this induction period disappears if vigorous agitation is employed.

Another technique which lends itself particularly applicable to rate studies on Azo I involves following the change in optical density in the near ultraviolet. Azo I has a symmetrical absorption band in this region with a peak at 345 mμ. This technique eliminates many difficulties associated with the gas evolution method. The results obtained by Talat-Erben and Bywater<sup>11</sup> for the Azo I decomposition from 70 to 105° seem superior to the gas evolution data in many respects, particularly in regard to the minimum of scatter in experimental points. Their results included work over a ten-fold concentration range with no variation in the order of the reaction or specific rate constant, yielding a straight-forward first-order decomposition in agreement with other methods.

The polarographic technique also has been applied to the kinetic study of the Azo I decomposition.<sup>8</sup> The data in methanol solution are quite comparable with the spectrophotometric and gas evolution data but the results when using dioxane as the solvent show a deviation from the composite Arrhenius plot.

2,2-Diphenyl-1-picrylhydrazyl (DPPH) has also been used to study the rate of production of radicals<sup>12-14</sup> and in polymerization inhibition work.<sup>15</sup>

(1) This paper is based upon a dissertation submitted by James P. Van Hook in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

(2) F. M. Lewis and M. S. Matheson, *THIS JOURNAL*, **71**, 747 (1949).

(3) (a) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949); (b) L. M. Arnett, *ibid.*, **74**, 2027 (1952).

(4) Hunt, U. S. Patent 2,471,959 (May 31, 1949).

(5) K. Ziegler, W. Deparade and W. Meye, *Ann.*, **567**, 141 (1950).

(6) J. W. Breitenbach and A. Schindler, *Monatsh.*, **83**, 724 (1952).

(7) G. S. Hammond, J. N. Sen and C. E. Boozer, *THIS JOURNAL*, **77**, 3244 (1955).

(8) J. Ukida, G. Takajama and T. Kominanu, *Chem. High Poly. Japan*, **11**, 233 (1954).

(9) J. C. Roy, R. R. Williams, Jr., J. R. Nash and W. H. Hamill, *THIS JOURNAL*, **78**, 519 (1956).

(10) A. M. Hyson and J. K. Beasley, Polychemicals Dept., E. I. du Pont de Nemours and Co., Wilmington, Del.; oral presentation at the February 1955 Delaware Chemical Symposium.

(11) M. Talat-Erben and S. Bywater, *THIS JOURNAL*, **77**, 3712 (1955).

(12) K. E. Russell and A. V. Tobolsky, *ibid.*, **76**, 395 (1954).

(13) A. Chapiro, *J. chim. phys.*, **51**, 165 (1954).

(14) A. Chapiro, *ibid.*, **52**, 645 (1955).

(15) P. D. Bartlett and H. Kwart, *THIS JOURNAL*, **72**, 1051 (1950).